SYNTHESIS AND METAL BINDING PROPERTIES OF SELECTED ORGANOPHOSPHORUS PLANT GROWTH REGULATORS

A thesis submitted to the
UNIVERSITY OF CAPE TOWN
in fulfilment of the requirements for the degree of
DOCTOR OF PHILOSOPHY
by

MOHAMED AFZAL DHANSAY B.Sc (Honours)

Department of Chemistry,
University of Cape Town,
Rondebosch, Cape Town,
South Africa.

February 1992

ABSTRACT

This thesis describes an investigation by computer simulation of the effects of selected organophosphorus plant growth regulators on metal ion speciation in soil solutions. A computer based chemical model of a soil solution has been developed. It consists of 577 complexation equilibria and 65 solubility products for potential solids. Selected redox equilibria and atmospheric equilibria have also been considered.

In the construction of the model, numerous contributing factors influencing the various equilibria in soil solutions were considered. An extensive literature survey was conducted to determine the present state of knowledge of plant growth regulators, plant nutrition, plant root exudates, soils and metal chelate equilibria in soil solutions. This survey assisted in the selection of components constituting the soil solution model.

Four organophosphorus plant growth regulators, **I, II, III** and **IV** have been synthesised and characterised.

$H_2O_3PCH_2NHCH_2CO_2H$ **(I)**

N - (Phosphonomethyl) glycine (Ligand 1)

$HO_2P(CH_2NHCH_2CO_2H)_2$ **(II)**

N,N'[Phosphinicobis(methylene)] bis glycine (Ligand 2)

$(H_2O_3PCH_2)_2NCH_2CO_2H$ **(III)**

N,N - bis(Phosphonomethyl) glycine (Ligand 3)

$H_2O_3PCH_2NH(CH_2CO_2H)_2$ **(IV)**

N - (Phosphonomethyl) iminodiacetic acid (Ligand 4)

The protonation equilibria of compounds **I, II, III** and **IV** have been examined in aqueous solution using ^{1}H, ^{13}C and ^{31}P nuclear magnetic resonance. The protonation equilibria and aqueous equilibria of compounds **I, II, III** and **IV** with Ni^{2+} ions as well as that of **IV** and Mn^{2+}, Fe^{2+}, Co^{2+}, Cu^{2+} and Zn^{2+} ions have been determined using glass electrode potentiometry.

Chemical equilibrium constants and solubility products of the various soil solution complexes, arising out of the chosen component list, were extracted from recent critical compilations in the literature. Together with the equilibrium constants determined for the selected organophosphorus plant growth regulators, a thermodynamic database was constructed. The effects of **I** and **IV** on soil solution speciation (pH = 6.5, I = 0.020 $mol.dm^{-3}$ and T = 25 ^{o}C) was examined using computer modelling.

The results indicate that the plant growth regulators under examination, affect soil solution speciation significantly and could have a profound effect on the bioavailability of metal ions to plants.

DEDICATION

TO MY PARENTS

SULAIMAN ABDULCADER DHANSAY
and AISHA DHANSAY

QUOTATION

"The ultimate goal of all research in general and chemical modelling in particular is additional understanding of processes and events which can, under the proper conditions, facilitate the improvement of human life physically, emotionally and aesthetically." [Jen79]

- Everett A. Jenne

ACKNOWLEDGEMENTS

Sincere **thanks** are expressed to

Professor Peter W. Linder, my supervisor, for his guidance, encouragement and friendship throughout the course of this work.

Professor Tomasz A. Modro for supervising the synthetic work.

Dr Ralph G. Torrington for introducing me to the finer skills of potentiometry.

Members of the former UCT Phosphorus Chemistry Research Group viz., Dr Sunil Vather, Alfie le Roux, Jill Symes and Madeleine Pearce for their friendship and assistance.

Members of the UCT Complex Equilibria Research Group viz., Professor Graham Jackson, Dr Sarah Cocks - Wilson, Dr Ulrike Kramer - Schnabel, Alexander Voyé, Ivo Müller, Julius Pretorius, Adnaan Ederies, Karen van der Meulen, Fran Pocock, Bridgit Davis and Bandile Mzizi for their friendship and many useful discussions.

Noel Hendricks and Zayed Brown for their friendship and skillful determination of NMR spectra.

Anwar Jardine for producing the computer diagrams of the chemical structures.

My Parents, brothers Mansoor and Waheed, sisters Zakira and Farida, brothers-in-law Dr Omar Brey and Afzal Brey, niece Ayesha, and nephews Imran and Muneeb for their support, interest and encouragement.

UCT, the Council for Scientific and Industrial Research (CSIR) and the Foundation for Research and Development, (FRD) for financial assistance.

The staff of the University of Cape Town Library and Computer Centre for their efficiency.

PUBLICATION

Organophosphorus herbicides and plant growth regulators. Part 1. Synthesis and protonation behaviour of glyphosate and related compounds.

M. A. Dhansay, P. W. Linder, R. G. Torrington and T. A. Modro,
Journal of Physical Organic Chemistry, 1990, **3**, p248.

CONFERENCE PROCEEDINGS

A poster entitled "Protonation equilibria of organophosphorus plant growth regulators" was presented at the South African Chemical Institute's 75th anniversry conference held at the Elangeni Hotel, Durban, 1987.

A poster entitled "Nickel complexation of organophosphorus plant growth regulators" was presented at the SACI Physical Chemistry Convention held at the Dikhololo Game Reserve, Pretoria, 1989.

CONTENTS IN BRIEF

TABLE OF CONTENTS

LIST OF SYMBOLS AND ABBREVIATIONS

μ_A : chemical potential of a species A

μ_A^o : chemical potential of a species A in the standard state

ΔG_m^o : standard molar Gibbs free energy

ΔH_m^o : standard molar enthalpy

ΔS_m^o : standard molar entropy

F : Faraday constant

R : gas constant, 8.314 $JK^{-1}.mol^{-1}$

T : temperature in Kelvin

^oC : temperature in degrees Celcius

log : logarithm to the base 10

ln : natural logarithm to the base e (2.303)

μ : ionic strength in $mol.dm^{-3}$

I : ionic strength in $mol.dm^{-3}$

z_i : ionic charge of species i

c_i : concentration of species i in $mol.dm^{-3}$

$\underline{M}$: concentration of a species in $mol.dm^{-3}$

[i] : concentration of species i in $mol.dm^{-3}$

{i} : activity of species i

γ : activity coefficient

a : activity of a species

ϵ : convergence criterion

K : stepwise equilibrium constant

K' : conditional equilibrium constant

β : overall stability constant

E : emf reading

E_o : electrode intercept

E^o : standard electrode potential of a redox couple

E_h : Redox potential of a solution

R_f : crystallographic R - factor

U : objective function

(g) : gaseous species

(aq) : aqueous species

(s) : solid species

δ : NMR chemical shift

NDP : number of dissociable protons

pK_w : negative logarithm of the ionic product of water

pK_a : negative logarithm of an acid dissociation constant

pH : negative logarithm of the free hydrogen ion concentration

pe : negative logarithm of the free electron concentration

pL : negative logarithm of the free ligand concentration

Z_H : average number of protons bound to ligand

Z_M : average number of ligand molecules bound to metal

Q_M : average number of protons displaced per metal ion upon complexation

[H] : free proton concentration

[L] : free ligand concentration

[M] : free metal concentration

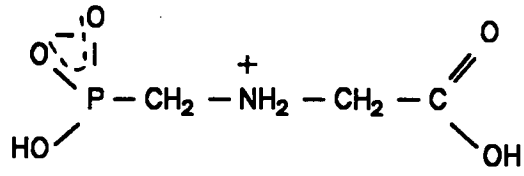
T_H : total proton concentration

T_L : total ligand concentration

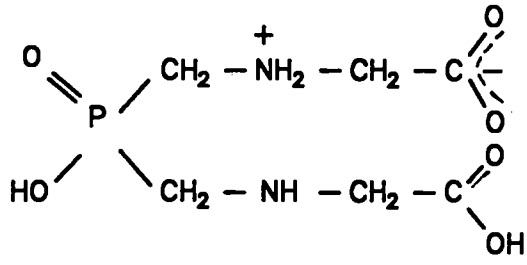
T_M : total metal concentration

LIG1 :	N - (Phosphonomethyl) glycine (Ligand 1)
LIG2 :	N,N' [Phosphinicobis(methylene)] bis glycine (Ligand 2)
LIG3 :	N, N - bis (Phosphonomethyl) glycine (Ligand 3)
LIG4 :	N - (Phosphonomethyl) iminodiacetic acid (Ligand 4)
IDA :	Iminodiacetic acid
IDP :	Iminodi(methylenephosphonic acid)
NTA :	Nitrilotriacetic acid
NTP :	Nitrilotri(methylenephosphonic acid)
Caff :	trans - 3 - (3, 4 - dihydroxyphenyl) propenoic acid (Caffeic acid)
4NC :	4 - Nitro - 1, 2 - dihydroxybenzene (4 - Nitrocatechol)
EDDA :	Ethylenediiminodiacetic acid
EDTA :	Ethylenedinitrilotetraacetic acid
CDTA :	trans - 1, 2 - Cyclohexylenedinitrilotetraacetic acid
DTPA :	Diethylenetrinitrilopentaacetic acid
EGTA :	Ethylenebis (oxyethylenenitrilo) tetraacetic acid
EDDHA :	Ethylenediaminedi (o - hydroxyphenylacetic acid)

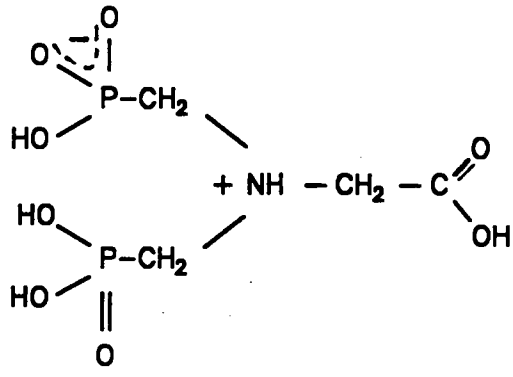
CHEMICAL STRUCTURES OF COMPOUNDS



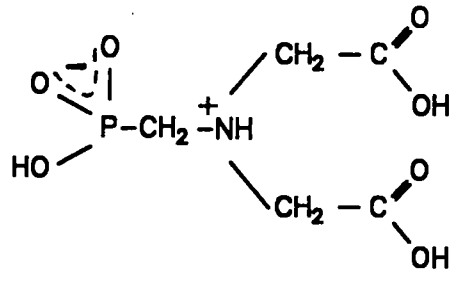
N - (Phosphonomethyl) glycine (Ligand 1) **I**



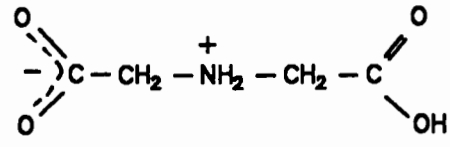
N,N' [Phosphinicobis(methylene)] bis glycine (Ligand 2) **II**



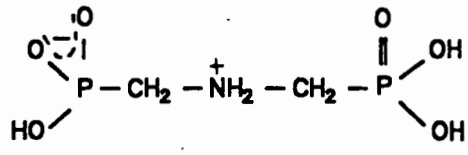
N, N - bis (Phosphonomethyl) glycine (Ligand 3) **III**



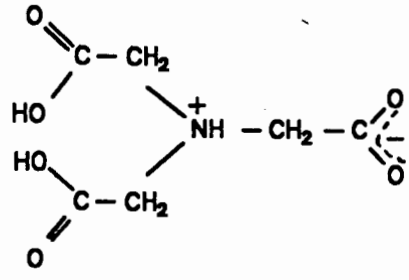
N - (Phosphonomethyl) iminodiacetic acid (Ligand 4) **IV**



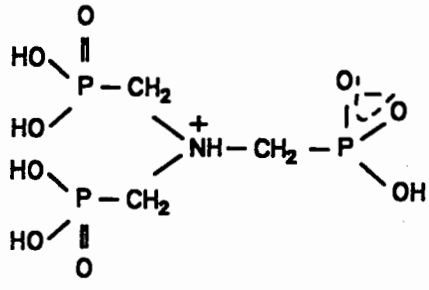
Iminodiacetic acid **V**



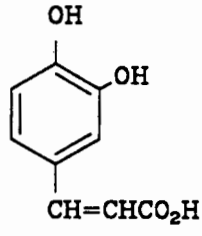
Iminodi(methylenephosphonic acid) **VI**



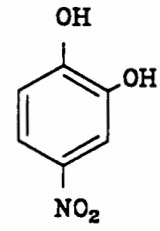
Nitrilotriacetic acid **VII**



Nitrilotri(methylenephosphonic acid) **VIII**



Caffeic acid **IX**



4 - Nitrocatechol **X**

CHAPTER 1

GENERAL INTRODUCTION

CONSISTING OF

PLANT GROWTH REGULATORS

PLANT NUTRITION

PLANT ROOT EXUDATES

SOIL

METAL CHELATE EQUILIBRIA

PLANT NUTRIENT BIOAVAILABILITY

OBJECTIVES OF THIS STUDY

1.1 PLANT GROWTH REGULATORS

The world population in 1986 was 5 billion having increased by 25% from the 4 billion recorded in 1975. Despite the fact that one in every six people is malnourished, the average world population growth rate is 1.7% per annum giving a projected world population in excess of 6 billion by the year 2000 [Sta89].

At present about 11% of the worlds arable land is being cultivated but the spiralling population growth rate requires a more efficient utilization of these resources to maintain per capita food production as the productivity of most of the remaining land is limited by factors such as drought, mineral stress, shallow depth and water excess [Fot84].

The problem of producing sufficient food for the worlds population is at present more a regional than a universal issue but since all animal life is entirely dependent on the plant kingdom for sustenance, the need for more reliable agricultural yields is an ever increasing global challenge.

Efforts to optimize crop yields have largely been directed to improved cultivation techniques, ensuring adequate supplies of water and nutrients, protection from insect pests and weeds, and selective breeding resulting in plant strains which are more resistant to environmental stresses [Wit78], [Hal90]. However, even under the most favourable conditions, crop yields have limitations determined by the natural growth regulatory systems of plants. Plant growth regulators hold the key to exceeding the natural growth limits of plants and ensuring a more efficient utilization of fertile land. The use of plant growth regulators is one of the most important agricultural advances in recent times and its use in future is virtually assured.

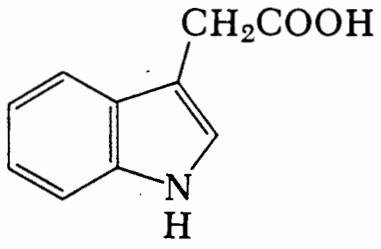
Plant growth regulators are natural or synthetic substances (other than nutrients) which when added in small amounts modify growth, development and the qualitative and quantitative yields of plants [Nic78], [Nic82], [Hal90]. The term "plant hormones" is restricted to naturally occurring growth substances and these have been divided into five categories namely, auxins, gibberellins, cytokinins, abscisins and ethylene. The chemical structures of some naturally occurring plant growth regulators are presented in figure 1.1. Plant growth processes include seed dormancy, germination, leaf growth, flowering, fruit growth, fruit ripening and leaf senescence all of which are controlled by the naturally occurring hormones.

The names and functions of some of the naturally occurring plant hormones can be summarized as follows:- [Nic78], [Nic82], [Jan86], [Jun86] and [Hal90].

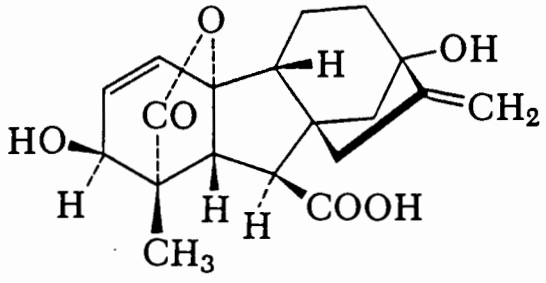
AUXINS are growth promoting hormones responsible for cell elongation. The most common natural auxin is indole acetic acid (IAA). Phenylacetic acid as well as its para - hydroxy derivative are also important auxins.

GIBBERELLINS are terpenoid compounds responsible for cell enlargement and cell division in subapical meristems. They are involved in a wide array of developmental processes such as seed and plant dormancy, germination and fruit growth. More than 50 gibberellins have been identified of which gibberellic acid (GA_3) was the first to be structurally characterized.

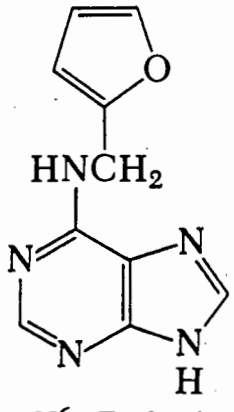
CYTOKININS control cell division in plants and delay senescence. They also initiate the development of chloroplasts thus inducing the greening of leaves. At present more than thirty cytokinins have been isolated from plants, the first being kinetin, N^6 - furfuryl aminopurine. A common feature of most cytokinins is the presence of the N^6 - substituted adenine group.



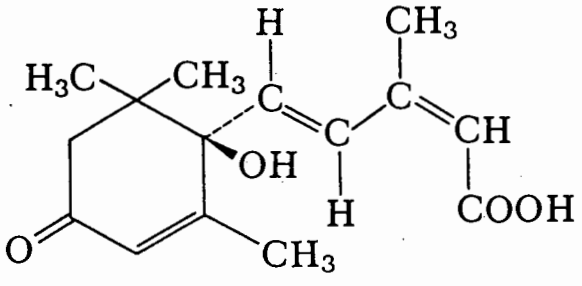
Auxin : Indoleacetic acid



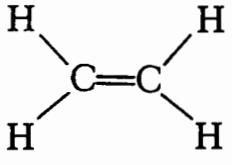
Gibberellin : Gibberellic acid



Cytokinin : N^6 - Furfuryl aminopurine



Abscisin : Abscisic acid



Ethylene

Figure 1.1 Chemical structures of some naturally occurring plant growth regulators.

ABSCISINS accelerate the abscision of leaves and initiate plant responses to environmental stress. The wilting of plants is often accompanied by a rapid increase in abscisic acid (ABA) concentration while a return to a more adequate supply of water results in a decrease in ABA concentration.

ETHYLENE produces a variety of plant responses including the control of fruit ripening and leaf abscision.

Research into the effects of plant growth regulators has undergone considerable growth in the last 50 years. Plant growth is a control system determined by the naturally occurring growth hormones and being able to manipulate the controls of this process would eventually lead to a better understanding of growth limitations. Charles Darwin was one of the earliest workers in the plant hormone field. Despite acknowledging that he was an intruder in the field of botany, it is now accepted that his work on the study of plant growth and movement led to the discovery of auxins [Hes80]. Kenneth V. Thimann has presented good accounts of the historical development of plant hormone research [Thi74], [Thi80].

Synthetic plant growth regulators produce their effects by changing the endogenous levels of the naturally occurring hormones in the desired direction and to the desired extent. They are used to control sprouting in onions and potatoes, to delay fruit ripening thus prolonging shelf life, to reduce stem length in wheat and other cereal crops thus preventing lodging in heavy winds and rain, and to control colour and vitamin content in fruit and vegetables amongst other processes. By delaying or enhancing the growth and maturation of fruit and crops they can be used effectively as "pesticides" having disrupted the normal life cycle of certain insect pests [Nic78].

Plant responses have been found to vary substantially to the application of plant growth regulators depending on environmental conditions, stage of plant growth, soil composition and fertility. Even single varieties of plants grown under similar conditions have been found to differ in response and exceptions are almost always reported to any general plant response [Nic82], [Ban86].

Plant growth regulators are used at virtually every stage of crop development in the sugarcane industry [Hal90]. The organophosphorus compound N,N-bis(Phosphonomethyl) glycine, (**III**), commonly called Glyphosine was registered as the first sugarcane ripener in the United States in 1972. N-(Phosphonomethyl) glycine,(**I**), commonly called Glyphosate was registered as the second sugarcane ripener in 1980 and is today used extensively as a ripener in the sugarcane growing regions of Southern Africa [Nic82]. The activities of Glyphosate and Glyphosine are primarily as herbicides preventing the late growth of the cane thereby causing the major part of the assimilate to be stored as sucrose. Increases in yield of between 10% and 20% have been reported [Nic78]. Glyphosate also acts as a fruit ripener, a desiccant and a growth retardant [Nic82] while two structurally related organophosphorus compounds, N,N'[Phosphinicobis(methylene) bis glycine], (**II**) [Mai80] and N-(Phosphonomethyl) iminodiacetic acid, (**IV**) [Nic82] both exhibit growth retarding properties.

Growth control of grass on golf courses and highway roadbanks is economically feasible. N,N-bis(Phosphonomethyl) glycine, (**III**), and N-(Phosphonomethyl) iminodiacetic acid, (**IV**) amongst many other retardants have shown the most promising results in achieving this on Tall Fescue [Elk74a] and Kentucky Bluegrass [Elk74b]

$H_2O_3PCH_2NHCH_2CO_2H$ **(I)**

N - (Phosphonomethyl) glycine (Ligand 1)

$HO_2P(CH_2NHCH_2CO_2H)_2$ **(II)**

N,N'[Phosphinicobis(methylene)] bis glycine (Ligand 2)

$(H_2O_3PCH_2)_2NCH_2CO_2H$ **(III)**

N,N - bis(Phosphonomethyl) glycine (Ligand 3)

$H_2O_3PCH_2NH(CH_2CO_2H)_2$ **(IV)**

N - (Phosphonomethyl) iminodiacetic acid (Ligand 4)

Of the four organophosphorus plant growth regulators mentioned, the effects on plant growth as well as the possible modes of action of N-(Phosphonomethyl) glycine, Glyphosate (**I**), has been studied most extensively. Quackgrass is a weed which is difficult to control and competes with crops for nutrients, light and moisture. Glyphosate shows excellent control of quackgrass as a pre crop emergence herbicide [Spr75c], [Alc88].

Glyphosate has been reported to reduce aromatic amino acid levels by inducing phenylalanine ammonia lyase (PAL) activity resulting in an inhibition of protein synthesis and an accumulation of growth limiting phenolics [Duk78], [[Fal89]. Amrhein et. al. have found that Glyphosate inhibited the incorporation of isotopically labelled shikimate into the aromatic amino acids phenylalanine, tyrosine and tryptophan. Since chorismate is the common precursor of these three compounds they have postulated that Glyphosate inhibits the conversion of shikimate into chorismate [Amr80], [Hol80]. Similar proposals have been reported

by Jaworski [Jaw72]. This theory of aromatic amino acid inhibition by Glyphosate is supported by the observation that addition of phenylalanine, tyrosine and tryptophan, singly or in combination, reverses the growth inhibiting effects of Glyphosate [Roi74], [Had77], [Gre79], [Bre80] and [Sha87].

There is also strong evidence that Glyphosate acts by promoting the oxidation of indole acetic acid, (IAA), a naturally occurring growth auxin. Lee has reported a positive correlation between IAA oxidation and growth inhibition in the presence of Glyphosate [Lee82] and has also found that Glyphosate was more effective than Glyphosine and aminomethylphosphonic acid in promoting IAA oxidation [Lee83]. Further evidence found by Lee was that plants with a high natural rate of IAA metabolism such as pea, were less susceptible to the effects of Glyphosate than plants with a low IAA metabolism such as buckwheat, soybean and mungbean [Lee85]. Apical dominance in plants is a phenomenon controlled by auxins and cytokinins and an auxin decrease or cytokinin increase results in its inhibition. Glyphosate by virtue of promoting IAA metabolism has been shown to encourage the release of lateral buds in soybean seedlings [Lee84].

Inactivation of Glyphosate in certain soils is by adsorption [Tor77]. Sprankle et. al. have postulated that Glyphosate is reversibly bound to clays and organic matter through the phosphonic end as an increase in soil phosphate concentration decreases adsorption [Spr75a]. Glyphosate in a quartz sand was readily absorbed as shown by the decrease in fresh weight of wheat plants [Spr75b]. Sprankle et. al. also reported that a sandy loam soil adsorbed less Glyphosate than a clay loam soil. The absorption of Glyphosate by plants is thus affected by pH, soil type and composition, and phosphate level.

Rueppel et. al. have reported that soil microorganisms are responsible for the degradation of Glyphosate in soil. In soils containing microorganisms, up to 50% of ^{14}C labelled Glyphosate was evolved as $^{14}CO_2$ in a 28 day period whereas the studies conducted under sterile conditions showed minimal $^{14}CO_2$ evolution. Their studies were conducted in four different types of soils [Rue77].

From the preceding discussion on the adsorption, absorption, mobility and availability of Glyphosate to plants in soils, it is clear that numerous factors control its eventual effect on plants. Much of the inconsistency of plant responses to plant growth regulators is as a result of a lack of understanding of these controlling processes. The organophosphorus compounds under discussion, **(I)**, **(II)**, **(III)** and **(IV)** all possess metal-binding functional groups and an examination of their chemical equilibria in soils in the presence of nutrients, plant root exudates and soil constituents could assist in explaining plant responses to the application of plant growth regulators.

1.2 PLANT NUTRITION

Through the history of plant nutrition, many experiments were conducted providing evidence for the importance of certain elements but it was Arnon and Stout [Arn39] and later Epstein [Eps65] who formulated the criteria of essentiality of elements for plants.

Solution cultures played an important role in establishing element essentiality as they provided well defined growth media for plants. By subjecting plants to a deficiency or absence of certain elements in these hydroponic solutions, thirteen elements have been established as essential nutrients for plant growth [Ben82]. Omission of these elements from growth media resulted in abnormal growth, failure

to complete the life cycle or premature death of plants. These elements were specific and their functions were not replaceable by other elements.

Six of these elements are required in relatively large amounts and are considered macronutrients, viz; calcium, magnesium, potassium, nitrogen, phosphorus and sulphur, while the remaining seven elements, manganese, iron, copper, zinc, molybdenum, boron and chlorine are required in trace amounts and are classed as micronutrients [Eps72], [Cla80], [Jan86], [Mar86] and [Sta89].

The thirteen essential elements of plant growth usually comprise 5 to 8% of the dry weight of plants. The elements carbon, oxygen and hydrogen, constitute the bulk, 92 to 95%, of plant matter and although these elements are also essential for plant growth, they are not classified as nutrients [Jan86].

The elements, sodium, cobalt, nickel and silicon are also found in soils and in some cases, have been shown to be beneficial to plants. Aluminium and cadmium which are available to plants can be tolerated in low concentrations but are regarded as toxins owing to their adverse effects at higher concentrations.

Table 1.1 lists the essential and beneficial elements of plant growth as well as their bioavailable forms to plants. Metal ions are found in solution as the aqua ion but by convention are represented as the free ion. The toxins, aluminium and cadmium have also been tabulated.

Plants obtain all their essential elements from the aqueous phase of soil. Gross imbalances of certain elements lead to changes of the speciation of the bioavailable forms of other elements and very often, an apparent deficiency of one element arises from the presence of toxic levels of another element.

Natural causes such as flooding, which lead to anaerobic conditions, as well as manufacturing, mining and waste disposal practices all alter the bioavailable concentrations of metal ions in soils. Pesticides and fertilizers as well as the organic component thereof can also cause imbalances of mineral elements in a productive soil. Sulphur dioxide (SO_2) and nitrogen oxide (NO_2) generated by coal burners in industry are converted to dilute sulphuric acid and dilute nitric acid in the atmosphere resulting in acid rain. This causes serious damage to plant and aquatic life since acidic conditions cause the rapid release of metal ions such as aluminium.

Following is a summary of the functions of the essential and beneficial elements in plants as well as the deficiency and toxicity symptoms [Eps72], [Rus73], [Foy78], [Cla80], [Bon82], [Bar84], [Kab84], [Fot84], [Mar86], [Jan86] and [Sta89].

The elements **carbon**, **hydrogen** and **oxygen**, form the building blocks of carbohydrates, proteins, lipids and nucleic acids and account for the bulk of the dry mass of all plants. As previously reported, these elements are not classified as nutrients but are nevertheless essential for plant growth.

Magnesium is a component of chlorophyll and activates many enzymes used in photosynthesis, respiration and protein synthesis. A deficiency of this ion results in interveinal chlorosis whereas an excess causes a deficiency of calcium and potassium.

Table 1.1

THE ELEMENTS OF PLANT NUTRITION :-
Essential elements, beneficial elements and toxins

Element	Chemical Symbol	Bioavailable Forms	References
Carbon	C	CO_2	[Sta89]
Oxygen	O	O_2, CO_2, H_2O	[Sta89]
Hydrogen	H	H_2O	[Sta89]
Magnesium	Mg	Mg^{2+}	[Cla80], [Sta89]
Potassium	K	K^+	[Cla80], [Sta89]
Calcium	Ca	Ca^{2+}	[Cla80], [Sta89]
Nitrogen	N	NH_4^+, NO_3^-	[Cla80], [Sta89]
Phosphorus	P	$H_2PO_4^-$, HPO_4^{2-}	[Cla80], [Sta89]
Sulphur	S	SO_4^{2-}	[Cla80], [Sta89]
Manganese	Mn	Mn^{2+}	[Cla80], [Sta89]
Iron	Fe	Fe^{2+}	[Cla80], [Sta89]
Copper	Cu	Cu^{2+}	[Cla80], [Sta89]
Zinc	Zn	Zn^{2+}	[Cla80], [Sta89]
Molybdenum	Mo	MoO_4^{2-}	[Cla80], [Sta89]
Boron	B	H_3BO_3	[Cla80], [Sta89]
Chlorine	Cl	Cl^-	[Cla80], [Sta89]
Sodium	Na	Na^+	[Cla80]
Cobalt	Co	Co^{2+}	[Shu83]
Nickel	Ni	Ni^{2+}	[Bro87]
Silicon	Si	H_4SiO_4	[Cla80]
Aluminium	Al	Al^{3+}	[Foy78]
Cadmium	Cd	Cd^{2+}	[Bin86]

Potassium is the most abundant metallic element in the cytoplasm and serves in regulating water movement thus maintaining turgor pressure. It is also involved in the inactivation of enzymes that regulate photosynthesis and respiration rates. Deficiency symptoms include chlorosis and scorching in older leaves as well as poorly developed root systems resulting in low crop yields. Toxicity seldom occurs but high concentrations reduce manganese, magnesium and zinc uptake in certain plant species.

A high proportion of **calcium** is found in the cell walls. This is as a result of the abundance of binding sites for Ca^{2+} in the cell walls as well as the restricted transport across the plasma membrane into the cytoplasm. Calcium is also found as calcium pectate in the middle lamella, the cementing layers between cells. A calcium deficiency results in deformed terminal leaves and reduced root growth whereas excessively high concentrations reduce soil acidity and may decrease manganese and iron availability at high pH.

Nitrogen is an inert gas that is unavailable to plants unless it is fixed in the soil in soluble inorganic forms or as part of organic matter. The transformation of nitrogen gas to its main bioavailable forms NO_3^- and NH_4^+ by certain species of bacteria is known as nitrogen fixation. Nitrogen forms an integral part of many cell constituents including amino acids, nucleic acids and the chlorophyll molecule. Symptoms of deficiency include reduced growth, the yellowing of leaves and a loss of fruit colour and flavour. An excessive supply of nitrogen results in abnormally dark leaves.

Phosphorus is a component of nucleoproteins, phospholipids and compounds such as adenosine triphosphate (ATP) and adenosine diphosphate (ADP). The conversion of ATP to ADP is an important source of energy in living cells. Inorganic phosphate has been shown to control the ripening of fruit and a control of its supply

to plants can thus delay the ripening process. A deficiency of phosphorus results in a reduction of most metabolic processes in plants causing a reduction of yields, stunted growth and impairment of colour in leaves. Symptoms of excess phosphorus are hard to diagnose because they are associated with deficiencies of metal ions such as zinc, copper, iron and manganese.

Sulphur is a component of several amino acids including methionine and cysteine which are both essential to human nutrition. It is also a component of the vitamins thiamine and biotin. A deficiency results in pale or yellow leaves since sulphur is necessary for chlorophyll synthesis, although not a part of this molecule. Plants absorb most of their required sulphur from soils as the sulphate ion (SO_4^{2-}). Sulphate ions are reduced to hydrogen sulphide (H_2S) and elemental sulphur in water - logged soils thus inducing a deficiency of this ion in plants.

Manganese is involved in chlorophyll synthesis, respiration and photosynthesis. It also serves as an enzyme activator for oxidation - reduction processes in plants. A deficiency leads to chlorosis between the main veins of leaves while toxic levels of a manganese supply causes leaf crinkling. Most plant requirements of manganese are met in acidic soils while deficiencies are most likely to occur in alkaline soils owing to the poor solubility of manganese oxides and hydroxides.

Iron is a component of various enzymes and it functions as a catalyst in the synthesis of chlorophyll. The total iron content of most soils is high but it is often unavailable, particularly at high pH, where the soluble iron content is low. An iron deficiency in soils of high pH is referred to as lime - induced chlorosis. At low pH values, the bioavailable form of iron, Fe^{2+}, is generally higher and sufficient to meet the needs of most plants.

Copper is a component of many enzymes and affects chlorophyll synthesis as well as carbohydrate and protein metabolism. The copper(II) ion is often tightly bound in organic matter complexes and plants grown in soils with a high organic matter content are often deficient in copper. A copper deficiency results in chlorotic or dead spots on leaves as well as stunted growth and death of terminal leaves.

Zinc plays an important role in protein synthesis and is also involved in the synthesis of indoleacetic acid, IAA, a natural auxin. Since it is associated with growth hormones, a zinc deficiency results in growth suppression, reduced internode length and abnormal root growth.

Molybdenum is a component of the enzyme system that reduces nitrates to ammonia. When absent or in very low concentrations, the synthesis of proteins is blocked and plant growth is reduced. Early symptoms of deficiency are pale green leaves which later become curled and wrinkled. Because of the low soil molybdenum concentrations, toxicity rarely occurs.

The precise role of **boron** in plants is still obscure although it is known to function in flowering, fruiting, cell division, nitrogen metabolism and hormone movement. A deficiency leads to stunting, discolouration and death of shoot tips. Leaves become thick, curled and brittle. An excess of boron is toxic and results in enlarged nodes and premature dropping of fruit.

Chlorine is involved in photosynthesis and is closely linked to plant metabolic activity. Because of its abundance in soils, there is more concern about chloride toxicity than deficiency. Experimentally induced deficiency results in wilting , stubby roots and bronzing. Toxicity symptoms include leaf chlorosis, growth suspension and reduced yields.

Plant species are characterized as natrophilic or natrophobic depending on their growth response to **sodium**. The role of sodium ions is considered from two viewpoints; its essentiality and/or extent to which it can replace potassium ion functions in plants. Sodium ions stimulate growth by their effects on cell expansion and the water balance in plants. In some plants, replacement of potassium ions by sodium ions actually increases plant growth which cannot be achieved by increasing the potassium ion content.

Cobalt is present in the coenzyme cobalamin, vitamin B_{12}. It is an important element for grazing animals as its compounds play a vital role in haemoglobin formation. Sheep and cattle for example may become anaemic by eating vegetation from cobalt deficient soils. The requirement of cobalt(II) ions for nitrogen fixation in legumes has been established.

Nickel is the metal component of the enzyme urease and is readily absorbed by plants. Nickel competes with other metals such as calcium, magnesium, iron and zinc, and high levels of nickel could induce an iron or zinc deficiency.

Silicon is present in soil solutions as monosilicic acid, $Si(OH)_4$, and is generally abundant in most soils. Its importance has been shown in certain higher plants, for example, Wetland rice showed a reduced growth and grain production followed by wilting in soils with a low silicon content. Larger requirements of silicon appear to be confined to the reproductive stages of certain plants.

Aluminium is an important structural component of clay minerals and is very abundant in soil solutions. Growth stimulation has been reported for low concentrations of aluminium in aluminium tolerant crop species although its

physiological function in plants is not clear. Reduced yields of crops grown in acidic soils are often attributed to increased availability of Al^{3+} ions rather than the high H^+ ion concentration. The accumulation of aluminium, and other toxins such as lead and cadmium, in plants is of major concern since it is the medium through which it enters the diet of man.

Cadmium is a cumulative poison in man and animal nutrition. Although cadmium is considered non - essential for plant growth, it is nevertheless effectively absorbed by plants. Cadmium mobility in soils is reduced above pH values of 7.5 where it is adsorbed onto solid surfaces. Correlations between cadmium in plant material and in growth media have been reported with soil pH as a major controlling factor.

1.3 PLANT ROOT EXUDATES

Plant roots are known to release low molecular weight compounds into the rhizosphere which serve the microorganisms as a source of nutrition [Van64]. Early studies were directed to the isolation and identification of these compounds mainly to help in understanding the mutual metabolic interaction between plants and microorganisms.

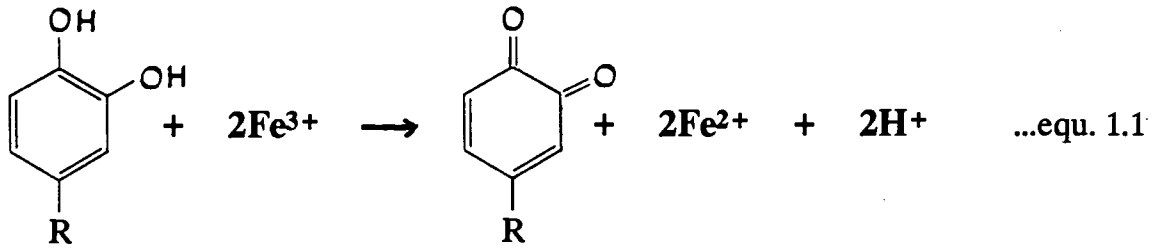
The components in root exudates of the crop cereals, barley and wheat were identified as sugars such as maltose, glucose, galactose, etc., amino acids such as glycine, cystine, alanine, etc. and organic acids such as oxalic acid, lactic acid,malic acid and succinic acid [Van64] The components of the exudates released by cucumber, cabbage, tomato, pepper [Van65], maize [Van67] and beans [Van72] were also reported as sugars, amino acids, organic acids and some unidentifiable "phenolic acids" and "phenolic substances". Early research was also more qualitative than quantitative but amounts of 0.5 mg of exudate per plant collected over a ten day period have been reported [Van64], [Van65].

One of the pioneers in the field of iron nutrition in plants, John C. Brown, had previously shown that certain "inefficient" soybean genotypes were unable to grow satisfactorily under conditions of low iron whereas other "efficient" soybean genotypes were able to extract sufficient iron from the same soil [Bro56]. Brown and Ambler later reported the presence of up to fifteen phenolic type compounds with reducing properties in the exudate of an "efficient" soybean genotype [Bro73]. This observation was then linked to the iron nutrition of plants and plants were classed "iron - efficient" if they responded to iron - deficiency stress and "iron - inefficient" if they did not. The stress induced processes, termed "the iron stress response mechanism" were summarized as follows, (a) release of hydrogen ions from plant roots, (b) release of reducing compounds from plant roots, (c) reduction of Fe^{3+} to Fe^{2+} at the roots and (d) an increase in the organic acid concentration (especially citric acid) in the root for iron transport [Bro78].

Olsen and Brown temporarily identified these reductants as organic acids with oxidizable phenolic groups and proposed a general reaction (eq. 1.1) to account for observed changes in solutions of iron - efficient dicotyledonous plants growing under conditions of iron stress [Ols80a]. This to some extent explained the lowering of pH in solutions in which these reductants were released as well as the "disappearance" of reductant within a day as it reduces Fe^{3+} to Fe^{2+} and is oxidized to its corresponding substituted benzoquinone.

Iron - efficient plant species usually recover from iron chlorosis, whether naturally or experimentally induced, within a very short period of time. The symptoms of iron stress in plants are the yellowing of terminal leaves. Once the response mechanism has been triggered the initial drop in pH reverts to its original value within a day or

two. Stressed leaves also regain their green colour quickly and it is this sequence of events which forms the basis of Olsen and Brown's proposals [Ols80a].



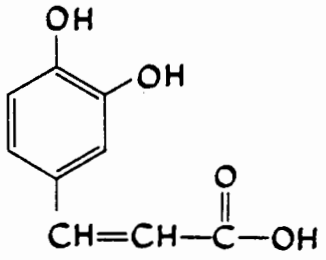
...equ. 1.1

R = Alkyl Group

The composition and quantity of root exudates released by plants vary under different conditions as well as during the various stages of plant growth. Maize and cucumber seeds have shown an increase in exudation proportional to an increase in temperature while seedlings of the aforementioned plant types showed a marked increase in exudation when subjected to low temperatures temporarily [Van67]. Seedlings of barley, wheat, cucumber and bean exude to a considerably greater extent than seeds and the spectrum of compounds identified differed appreciably for beans [Van72]. Dower, Davis and Byers reported that 2,3 dihydroxybenzoate was exuded by an iron efficient species at rates inversely proportional to the soluble iron content thus confirming that the iron response mechanism is only operational under conditions of iron stress and that it may be regulated depending on the severity of the deficiency [Dow70].

The major components of the exudate released by tomatoes have been identified as caffeic acid (**IX**) and p-coumaric acid [Ols81], [Kan87]. p-Coumaric acid is not a reductant for iron(III) but hydroxylase enzymes for the conversion of p-coumaric acid to caffeic acid have been identified.

Chlorogenic acid, which upon hydrolysis results in caffeic acid has also been reported as a component of the exudate released by tomatoes as well as being a primary component of the exudate released by sunflower [Het84]. Mugeneic acid has been isolated as a component of barley and oats exudates but it has not been found among any of the dicotyledonous plant species [Bro86].



Caffeic Acid (**IX**)

Ortho-dihydroxy phenols such as caffeic acid play an important role in complexing ferrous and/or ferric iron and moving these metal species to the root. Caffeic acid has been shown to increase the solubility of both ferrous and ferric iron by means of chelation and to increase the uptake of iron in barley roots grown in nutrient solutions of high calcium content [Jul83].

In solutions in which the nitrate ion is the only form of nitrogen present, dicotyledonous plants such as peas, beans and sugar beet respond differently to monocotyledonous plants such as barley oats and millet under conditions of iron stress in that certain monocots show iron - efficiency without a corresponding decrease in the pH of the nutrient solution. This has been explained in terms of the release of hydroxyl ions in the root as the nitrate ion is reduced to ammonia. The drop in pH observed with dicotyledonous plants could be attributed to the pronounced increase in the release of organic compounds particularly citrate and

malate [Lan81].

It is reasonable to assume that the presence of organic compounds in the rhizosphere with the potential to chelate metal ions will affect metal ion speciation and consequently the uptake of metal ions by plants. Hydroxyl ions as well as Cu^{2+}, Ni^{2+} and to a lesser extent Zn^{2+} and Mn^{2+} ions inhibit the reduction of Fe^{3+} [Ols80b]. Romheld et. al. have reported the enhanced uptake of Zn^{2+} and Mn^{2+} ions of iron efficient plants during iron deficiency [Rom82].

It is apparent that there are many schemes controlling the availability of iron to plants of the iron-efficient type with the reduction of Fe^{3+} to Fe^{2+} being the most important factor. Wallace predicts that there may be as many as fifteen different mechanisms of plant response to iron deficiency [Wal86]. This is based on the number of possible combinations of the four processes involved in the iron response stress mechanism as reported previously by Olsen et al [Ols80a]. In contrast to the proposals of Olsen et. al., Bienfait et. al. [Bie82] contend that the reduction of iron takes place enzymatically at the root surface. Uren [Ure84] also supports this hypothesis of contact reduction since Olsen's theory is based on observations of chlorotic plants. In essence, Uren differs from Olsen's view that the responces of iron deficient plants are the same as that of healthy plants.

1.4 SOIL

Weathering is the basic soil forming process. It deals with the complex interactions of the lithosphere with the atmosphere and hydrosphere and is driven by solar energy [Kab84].

The composition of the soil parent materials is determined by its parent rocks and the composition of the soil solution is thus determined following pedogenesis by the parent material [Dav80]. Soils and their compositions are constantly changing with time. They vary laterally in composition and vertically they exhibit various layers termed a soil profile. Fitzpatrick [Fit83] very appropriately views soil as a four dimensional space - time continuum.

Major soil groups are based on climatic differences. The National Co-operative Soil Survey has initiated a system, the United States Comprehensive System of Soil, for the systematic classification of soils. This classification contains 8 000 soil series and 80 000 soil types and phases [Jan86]. Among the many factors considered for the classification of soils are colour, chemical composition, texture, acidity, alkalinity and particle size.

The components of soil are mineral matter, soil organic matter, soil air and the soil solution. Figure 1.2 graphically represents the composition of a typically productive soil. Soil organisms, although not part of the soil, do form part of the interacting systems of soil which are : - **Inorganic minerals, organic matter, soil organisms, soil atmosphere** and the **soil solution.**

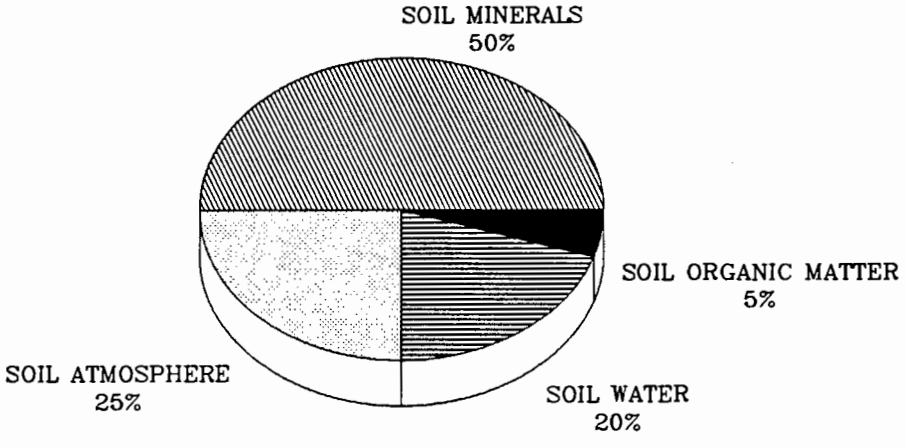


Figure 1.2 Soil Components

1.4.1 INORGANIC MINERALS

The inorganic component of soil varies in size, composition and its physical and chemical properties. Soil texture describes the individual mineral particles ie. sand, silt and clays. Sand and silt consist almost entirely of the resistant residues of rock minerals and are predominantly silicates, $(SiO_4^{4-})_n$, with a crystalline structure. An electrically neutral crystal is formed when cations such as Al^{3+}, Fe^{3+}, Fe^{2+}, Ca^{2+}, Mg^{2+}, K^+ and Na^+ are covalently bonded to the oxygen atoms. These silicates could form chain (pyroxenes), sheet type (micas, chlorites) or three dimensional (feldspars) complexes.

Clays have the simplest structures and consist primarily of Kaolinite, $Al_4Si_4O_{10}(OH)_8$, a layered structure of silicate tetrahedra and hydrated alumina octahedra and Montmorillonite, $Al_6(Si_4O_{10})_3(OH)_6.nH_2O$, an alumina layer sandwiched between two silicate layers. Illite, $K(Al)_2Si_4O_{10}(OH)_2.H_2O$, is the least abundant of the three clay minerals.

Clays form the finest soil particles while silt consists of small sand particles coated with clays and their properties are thus intermediate between sand and clays. Loamy soils are rich in organic material and consist of various proportions of sand, silt and clays. Clay surfaces readily adsorb water and metal ions and have a higher exchange capacity - a measure of their reactivity - than the surfaces of silts and sandy soils. Figure 1.3 represents a soil triangle used to classify soils on the basis of their proportions of sand, silt, clay and organic matter content [Fot84].

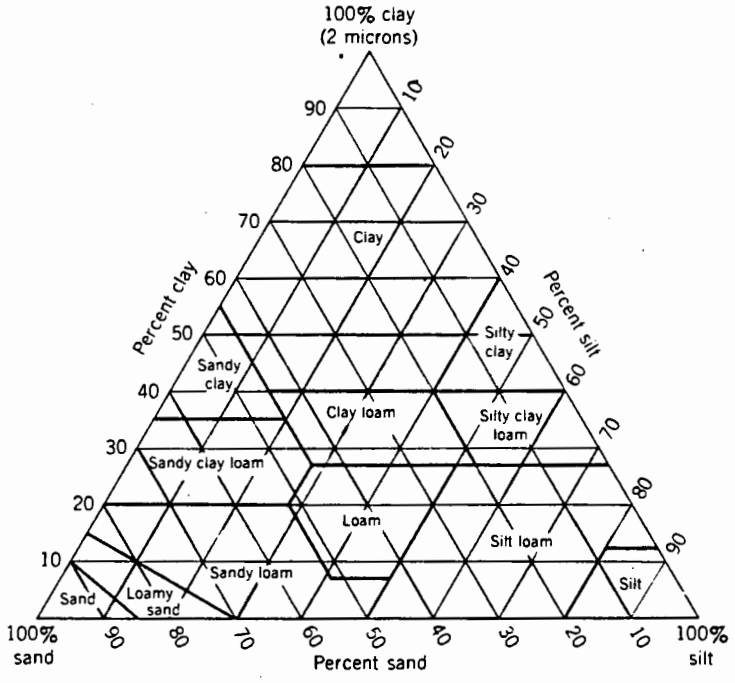


Figure 1.3 A soil triangle used to classify soils [Fot84].

All soils contain crystalline and amorphous minerals. The oxides and hydroxides of aluminium, iron and manganese are the most common although silicates, carbonates and sulphates may be present in appreciable amounts depending on soil pH and anion concentration. Soil solution concentrations of specific metal ions are often controlled by the solubilities of one or more of the soil minerals under specific conditions of pH and soil redox. Minerals dissolve and replenish the soil solution with free metal ions following leaching or the absorption of nutrients by plant roots. Some common soil minerals for selected metal ions are listed in Table 1.2 [Lin79a].

Table 1.2

Soil minerals for selected metal ions

Metal ion	Formula	Mineral
Mg^{2+}	$MgCO_3$	Magnesite
Mg^{2+}	$Mg(OH)_2$	Brucite
Ca^{2+}	$CaCO_3$	Calcite
Ca^{2+}	$Ca(OH)_2$	Portlandite
Ca^{2+}	$CaSO_4$	Anhydrite
Ca^{2+}	$CaSO_4.2H_2O$	Gypsum
Ca^{2+}, Mg^{2+}	$CaMg(CO_3)_2$	Dolomite
Ca^{2+}	$Ca_5(PO_4)_3OH$	Calcium - hydroxyapetite
Mn^{2+}	$MnCO_3$	Rhodocrosite
Fe^{3+}	$Fe(OH)_3$	Amorphous iron
Fe^{2+}	$FeCO_3$	Siderite
Fe^{2+}, Fe^{3+}	$Fe_3(OH)_8$	Ferrosic hydroxide
Zn^{2+}	$ZnCO_3$	Smithsonite
Cd^{2+}	$CdCO_3$	Octavite
Al^{3+}	$Al(OH)_3$	Amorphous aluminium
Al^{3+}	γ-$Al(OH)_3$	Gibbsite
SiO_4^{4-}, Mg^{2+}	Mg_2SiO_4	Forsterite
SiO_4^{4-}, Ca^{2+}	ß - Ca_2SiO_4	Larnite
SiO_4^{4-}, Mn^{2+}	Mn_2SiO_4	Tephroite
SiO_4^{4-}, Zn^{2+}	Zn_2SiO_4	Willemite

1.4.2 SOIL ORGANIC MATTER

Soil organic matter consists of humic and non - humic substances [Fle80]. Humic substances consist of fulvic acids, humic acids and humins. Of these, only fulvic acids are soluble under both acidic and basic conditions. Humic acids are soluble under

basic conditions only whereas humins are only sparingly soluble in basic solutions. Non - humic substances are proteins, fats, carbohydrates and low molecular weight substances of microbial, animal or plant origin and are easily broken down by soil microorganisms.

Humic substances form the bulk of soil organic matter and are chemically complex organic compounds with molecular weights ranging from a few hundred to several thousand grams per mole. The main functional groups are carboxyl, phenolic, hydroxyl, amino and carbonyl. Soil organic matter is derived from living organisms. Plant leaves decay on the surface and in the soil. Roots and dead organisms decompose by enzymatic digestion carried out by soil microorganisms. The presence of soil organic matter significantly enhances the water holding capacity of soil and may account for as much as 90% of the adsorptive and absorptive capacities of sandy soils [Jan86].

Functional groups of the insoluble organic component of soil provide exchange sites for cations; the exchange capacity being strongly pH dependent. In addition to adsorption, coordination complexes are formed with Mn^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+} and other cations [Bar84].

Soil solution organic matter increases the soluble metal ion concentrations, particularly that of zinc and copper which form thermodynamically stable complexes with most organic compounds. Simple organic compounds such as amino acids, carboxylic acids and phosphoric acids which occur naturally in soils, are effective chelating agents for trace elements in the soil solution and play an important role in nutrient supply to the roots of plants since low molecular weight complexes have a high mobility in soil [Kab84].

1.4.3 SOIL ORGANISMS

It is appropriate to commence this section by quoting J. A. Wallwork from The Distribution and Diversity of Soil Fauna, [Wal75].

"The soil is teeming with life. It is a world of darkness, of caverns, tunnels and crevices, inhabited by a bizarre assortment of living creatures...".

The soil living organisms (biomass) vary in size from the macrofauna, vertebrate animals of the burrowing type, the mesofauna, insects, arthropods and earthworms, and microfauna such as bacteria, algae and fungi. A productive soil under maintenance will have a negligible population of macrofauna but it is literally alive with mesofauna and microfauna.

Nematodes and rotifers, falling into the class of mesofauna, are essentially aquatic animals and those forms active in soils only occur when there is sufficient water available. They usually occur in the top 10 cm of the soil profile in the vicinity higher than the roots. Populations of 10^6 per m^2 for nematodes and 10^5 per m^2 for rotifers are not uncommon [Ric74].

Microorganisms are ecologically very important because they are the producing, consuming and transporting members of the soil ecosystem and are involved in the flow of energy and in the cycling of elements particularly in the vicinity of plant roots (rhizosphere) where they are known to accumulate [Fle80]. Bacteria and fungi decompose organic matter produced by plants and animals releasing minerals into the soil.

A bacterium genus, azobacter, converts molecular nitrogen into nitrogenous compounds available to plants. Organic nitrogen is mineralized during microbial

decomposition to release ammonium ions, NH_4^+, which can subsequently be oxidized to nitrate ions, NO_3^-, under aerobic conditions. Both of these forms of nitrogen are now available to plants. Microorganisms also convert carbon in organic materials to carbon dioxide, CO_2, and thereby complete the biological carbon cycle initiated by photosynthesis. Organic sulphur as well as organic phosphorus are mineralized by microbiota which are also capable of solubilizing the large stores of inorganic phosphorus in soils. It is clear that the soil microorganisms play an important role in the cycling of nutrients, particularly that of nitrogen, carbon, sulphur and phosphorus [Ste86] and [Pau89].

Soil biota has been discussed extensively by Richards [Ric74] and it is obvious from the large population sizes encountered that soil biota could have a major impact on soil nutrient bioavailability.

1.4.4 SOIL ATMOSPHERE

The soil atmosphere constitutes some 25% of the soil volume of a silty soil [Kab84]. This figure is of course variable depending on the nature, particle size, chemical composition and organic matter content of the soil all of which are related to its water holding capacity. The soil atmosphere consists of different proportions of the same gases found in the atmosphere above the soil and is found in the pore spaces of soil.

Gases in the soil atmosphere, which is not necessarily a continuous phase, are in equilibrium with gases in the soil solution. The solubility of oxygen (O_2) in water is low at room temperature and atmospheric pressure. Water saturated with air contains 6 cm^3 oxygen per litre (0.6%) but significantly more carbon dioxide (CO_2) at 22.5 cm^3 per litre (2.25%). The rate of diffusion of oxygen is also 10^4 times slower in water than in air [Fle80].

Oxygen is used in respiration by microorganisms and plant roots and its concentration decreases with soil depth. Carbon dioxide is given off by plants, microorganisms and decomposing organic matter and is an important source of carbon for plants. In contrast to oxygen, the concentration of CO_2 increases with soil depth.

The addition of water to soil by rainfall or otherwise, expels some of the air and plants may be deprived of oxygen in flooded or wet soils. It has been reported that the growth of peas and tomatoes was reduced when subjected to an oxygen deficiency [Fot84]. For tomatoes, a deficiency early in growth was most detrimental and for peas, a deficiency near blossom was most damaging. Nobel and Palta [Nob89] demonstrated that certain species of cacti when subjected to an atmosphere of 0% oxygen for three hours, resumed respiration optimally at 5% oxygen as the O_2 concentration was increased to 21%. Exposure of the roots to 2% carbon dioxide lead to a stoppage of respiration and death of the cortical cells after six hours. They concluded that although the need for well drained and highly aerated soils by cacti has been attributed to its high oxygen requirements, their results showed a greater susceptibility of plant roots to elevated CO_2 levels than for decreased O_2 levels.

Soils which are high in clay minerals and organic matter will have a higher water holding capacity than sandy or silt soils which drain easily. Consequently, the percentage of air and level of oxygen will be lower in a clay or loamy soil. Soil atmosphere and the oxygen and carbon dioxide concentrations in soil are affected by soil type, temperature, organic matter content, microorganism populations and the season.

The respiratory quotient, RQ, of a soil is the ratio of the volume of carbon dioxide released to the volume of oxygen consumed. For well aerated soils, RQ tends to unity [Rus73].

The main function of oxygen, related to plant growth, is as an electron acceptor in the transformation of organic substrates to carbon dioxide and water as represented in equation 1.2 [Fle80].

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \qquad \text{...eq. 1.2}$$

When soils are flooded, the rate of oxygen uptake exceeds the rate of oxygen replenishment and a reduced atmosphere is created. In the absence of adequate oxygen, other electron accepters such as nitrates, manganic compounds, iron(III) compounds, sulphates and sulphites begin to function depending on their concentrations and tendency to accept electrons [Fot84].

The formation of carbonic acid, equation 1.3, from carbon dioxide and water results in the release of H^+ ions upon dissociation.

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow 2H^+ + CO_3^{2-} \qquad \text{...eq. 1.3}$$

Hydrogen ions tend to release other cations adsorbed to insoluble organic matter and inorganic minerals. Metal ion toxicities of aluminium(III) and manganese(II) for example are therefore most likely to occur under acidic conditions. On the other hand, metal ion deficiencies in plants are commonly associated with alkali soils where most minerals are present in their sparingly soluble oxide and hydroxide forms.

1.4.5 SOIL SOLUTION

The soil solution is the only continuous phase in soils and through the action of mass flow, carries nutrients to the plant root surface. The soil solution is thus the interface and vital link between plant and soil and it is this component of soil and the various equilibria established within it that is of interest in this study.

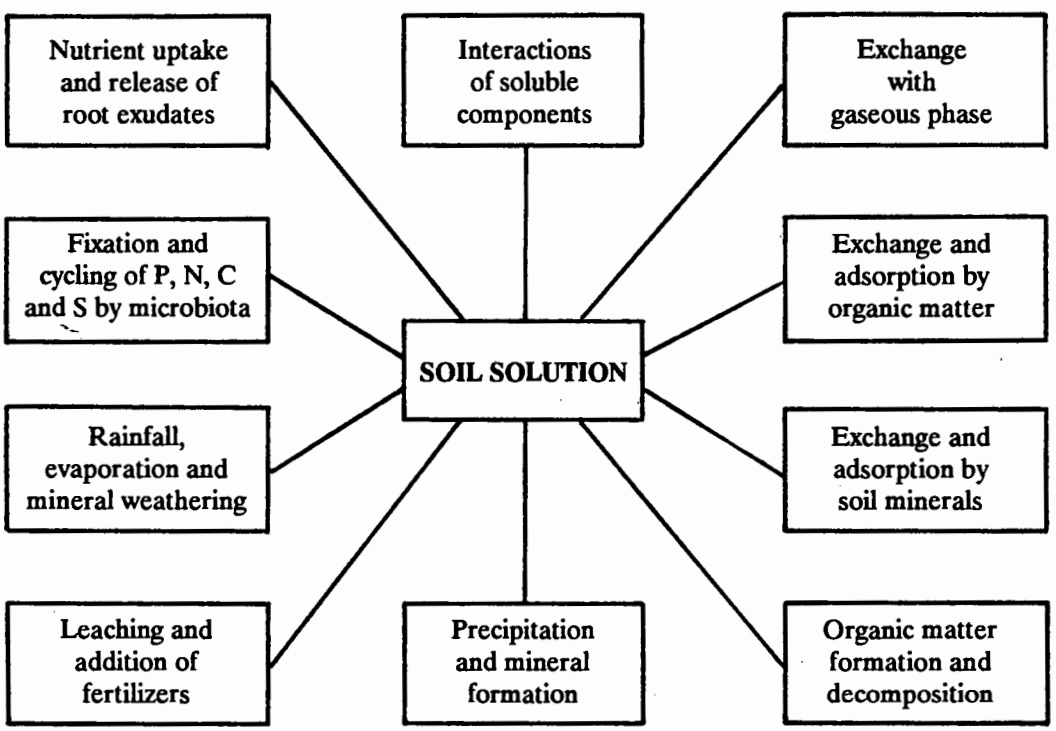


Figure 1.3 Soil solution equilibria

The chemical composition of a soil solution is in a constant state of flux as a result of many interacting factors. Nutrients absorbed by plants may be replenished in the soil solution following dissolution of soil minerals provided that conditions of pH are favourable. Ions adsorbed onto the solid soil phase or insoluble organic matter may also dissolve to reestablish soil solution equilibria. Changes in pH and soil

water content may cause precipitation and mineral formation while the addition of fertilizers as well as the leaching of ions from the soil profile in the vicinity of the rhizosphere all change soil solution speciation. As reported previously, the cycling of nutrients by soil microbiota could also have a profound effect on the speciation of some nutrients. Figure 1.3 diagrammatically represents the major interactions of a soil solution.

1.5 METAL CHELATE EQUILIBRIA

The availability of essential, beneficial, and toxic metal ions to plants is governed by solubility which is dependent on many physical and chemical properties such as pH, temperature, redox, soil composition, soluble organic matter etc. [Hod69], [Nor72a], [Sim78], [Som79], [Lin79a], [Wal83b].

One of the most common metal ion deficiencies is that of iron, particularly in alkaline and calcareous soils. Synthetic chelating agents have been used since the early 1950's for correcting iron as well as other essential metal ion deficiencies in soils [Wei54], [Wal55], [Dek57], [Tif60b]. Chelating agents increase the soluble concentrations of metal ions and also facilitate the movement of micronutrients towards plant roots [Lin78c], [Wal83b]. Application of chelating agents could lead to toxicity if high concentrations of toxic metals become available to plants. Absorption of phytotoxic amounts of essential metals could also result in the inhibition of several enzymes as well as increased activity of others in plants [Ass90].

Plants are either grown in hydroponic nutrient solutions or in soils in which case the soil solution is the phase suppplying it with nutrients. Plants growing in stirred aerated hydroponic solutions have a constant supply of nutrients uniformly distributed in solution whereas plants growing in soils are subjected to lower concentrations at the root surface owing to absorption by plants and competition

from microorganisms. As plants absorb nutrients a concentration gradient is set up perpendicularly to the root surface. Diffusion of nutrients from regions of high concentration to low concentration and mass flow, the movement of nutrients in the aqueous phase, are the two processes which maintain nutrient supply at the root surface [Bar84]. A gross imbalance between the nutrient uptake of plant roots and the nutrient supply characteristics of soils could have an adverse effect on plant growth. The fundamental purpose of synthetic chelate application to soils is thus to act as carriers of essential metals towards plant roots and to maintain a satisfactory level of these ions in the soil solution.

Chelating agents have been found to respond differently when applied to plants growing in hydroponic nutrient solutions as opposed to those growing in soils [Dek57], [Wal80a], [Wal80b]. Metal chelates at the root surface are in equilibrium with free metal and free chelate. As the aqua ion is absorbed by plants, a shift in the equilibrium occurs and the complex dissociates, releasing free metal ions which are now available for plant absorption. This results in an increase in the free ligand concentration which causes desorption of metals bound to insoluble organic minerals and insoluble organic matter in soils which will eventually become available for plant nutrition. In hydroponic solutions, adsorbed metal ion equilibria are absent and metal - chelate dissociation is suppressed following the absorption of nutrients. This could result in nutrient deficiencies as the bioavailable forms of nutrients are depleted [Lin79a],[Wal83d].

Metal chelates have widespread application in soils including those soils supporting the growth of sunflower [Wei54], peach, sweet cherry and apple [Ben57], rice [Cha81] as well as to plants growing in hydroponic solutions such as mustard and tomatoes [Dek57], soybean [Tif60b], wheat [Lin79b], and bush beans [Wal80a], [Wal83g]. In hydroponic solutions, metal chelates are used predominantly for

maintaining sufficient iron in soluble forms since free iron(III) and iron(II) concentrations are generally low [Chr74], [Wal83f], [Wal84a] and [Wal84b]. Increases in the micronutrient concentrations of potassium, magnesium and calcium as well as the sulphate, chloride and nitrate anions have been shown to further enhance the uptake of iron from FeEDDHA in corn plants growing in nutrient solutions [Oer74].

The aminopolycarboxylic acid EDTA was among the first synthetic chelates to be used for correcting iron deficiency in plants growing in slightly acidic soils [Wei54]. Use of FeEDTA on neutral or alkaline soils has met with little success. DTPA, CDTA and EDDHA have been found to be more successful in supplying plants with iron and other essential minerals in alkaline and calcareous soils [Wal55], [Mar57], [Tif60a], [Nor69], [Nor72b]. FeEDDHA has been reported to be the most stable and effective chelate for supplying iron to plants in soils particularly at high pH [Kro57] and [Wal83c].

Wallace et. al. [Wal57] and Tiffin et. al. [Tif61] using isotopically labelled metal chelates have confirmed the presence of some chelated metal in plants following absorption as has Weinstein [Wei54] who, using the split root system found that some EDTA had migrated from one portion of the root system to another. Spectrophotometric evidence for the absorption of FeEDTA by plants has been reported [Hil57] as well as the absorption of iron - polymaleic acid by wheat plants [Lin78a].

It is apparent from the paucity of literature available that less attention has been given to the study of the interactions between naturally occurring chelates and metal ions in soils. Naturally occurring chelates such as fulvic acids could also play an important role in solubilizing and mobilizing metal ions in soils solutions. Singh has

found that fulvic acid extracted from a Mollisol soil maintained sufficiently high (for the purposes of plant nutrition) concentrations of zinc and copper in solution in calcareous and alkaline soils [Sin89]. The solubilities of copper(II) and zinc(II) ions are strongly pH dependent decreasing 100-fold for each unit increase in pH. In calcareous soils their solubilities could approach critical levels below which deficiencies could occur [Lin78c]. Humic acids have been shown to decrease the uptake of iron by wheat plants growing in hydroponic solutions [Lin78b]. Chand et. al. examined the effect of ZnEDTA and ZnDTPA on zinc uptake in plants and found that the aforementioned chelates were far superior to fulvate and sulphate in maintaining high levels of soluble zinc [Cha81].

pH-stability diagrams, showing the speciation of ligands and metals over a pH range, were first introduced by Lindsay, Hodgson and Norvell. They applied various iron - chelates to sorghum crops to correct iron deficiency and found that the availability of iron from the chelates corresponded well with the predicted behaviour obtained from the pH-stability diagrams [Lin67]. It is thus more appropriate to use theoretical results as a basis for predicting the behaviour of chelating agents in soil systems of different pH and soil composition rather than to generalize from the application of metal chelates to a specific soil. The use of pH-stability diagrams is now widespread as a means for understanding the simultaneous equilibria of metals and chelating compounds in nutrient and soil solutions [Lin69], [Nor72a], [Hal72b] (see figure 1.4), [Lin79a], [Lin88] and [Tho88].

Nitrilotriacetic acid, NTA (**VII**) is structurally related to N-Phosphonomethyl iminodiacetic acid, (**IV**) and has been used as a chelating agent in soils and in hydroponic solutions. Although NTA is not as strongly binding as EDTA, DTPA and EDDHA, it does complex with all of the essential metals [Nor72a] and its

divalent metal-chelates are reported to be more readily absorbed than those of EDTA by plants growing in hydroponic solutions [Dek57].

$(HO_2C\text{-}CH_2)_2\text{-}N\text{-}CH_2\text{-}CO_2H$

Nitrilotriacetic acid (VII)

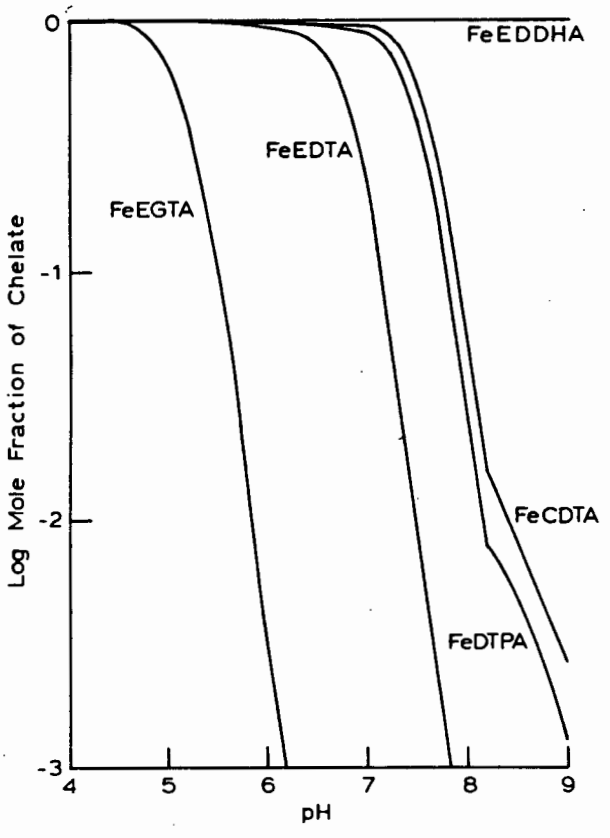


Figure. 1.4 Diagram showing the mole fraction of EGTA,EDTA,DTPA,CDTA and EDDHA complexed with Fe^{3+} at 0.0003 atmospheres CO_2 [Hal72b].

NTA applied at 1.3 X 10^{-2} mol.dm^{-3} (2500 ppm) has been reported to be slightly toxic to bush beans growing in soil [Wal74]. Slightly lower concentrations of NTA resulted in increased concentrations of iron, zinc, manganese, copper, molybdenum,

cobalt, nickel and aluminium in leaves. Applications of 100 to 1000 ppm of NTA to soybeans also increased the concentrations of several heavy metals as well as that of calcium, magnesium and potassium in leaves without any decrease in yield. Wallace et. al. have found that FeNTA showed promise as a source of iron for corn plants growing in hydroponic solutions of pH 6 and may be a satisfactory source of iron for other monocotyledonous plants as well [Wal83e]. Chelate dissociation at the root surface of monocotyledonous plants is low and FeNTA with a lower stability constant than the iron(III) chelates of EDTA, DTPA and EDDHA ought to increase the availability of Fe. De Kock and Mitchell have reported that trivalent metal ions are absorbed in chelated form [Dek57]. NTA among other chelating compounds has been shown to alleviate aluminium toxicity and chelation is a possible mechanism involved in the tolerance that plants show towards the presence of heavy metals [Muc88].

Application of a specific metal chelate to remedy an apparent metal ion deficiency need not necessarily be successful as the metal ion bound to the chelate may be displaced by other metal ions [Lin67]. This results in a loss of mobility of the metal ion concernerned and could even result in precipitation. Metal chelates are also known to adsorb to soil particles and the extent to which this occurs depends on the composition of the insoluble soil component and the nature of the chelate [Hil57] and [Nor69].

The equilibria of synthetic and natural chelates with metal ions in soils and hydroponic solutions is extremely complex and indeed very delicately poised. Any major disturbance of this balance could cause irreversible damage to plants. Nevertheless, a careful choice of metal chelates based on theoretical calculations could enable one to have an excellent control over the availability of metal ions to plants, particularly in the less intricate hydroponic solution systems.

Metal-chelate equilibria studies have been in progress for four decades and Wallace reported that after three decades there was still some controversy as to the interactions of chelating agents with metal ions and their ability to alter its availability to plants [Wal83b]. It would appear as if this still holds true today.

1.6 PLANT NUTRIENT BIOAVAILABILITY

Growing plants efficiently depends in part on nutrient supply from the soil solution. The processes which could play an important role in controlling soil solution speciation have been discussed in sections 1.1 to 1.5 and summarised in figure 1.3. These include the interactions between the essential elements of plant nutrition, elements beneficial to plants, toxins and soil organic matter.

Plant root exudates have received increasing attention by researchers in recent times. Despite the uncertainties in the mechanisms by which iron becomes available to plants as well as the role of compounds released by plants, it is clear that plant root exudates do affect soil solution and nutrient solution pH, redox and speciation and may have a profound effect on the availability of nutrients and perhaps even toxins to plants.

Synthetic organic compounds have been used effectively for solubilising and moving metal ions to plant roots by the process of chelation. This needs to be carefully monitored since an over abundance of metal ions regarded as essential for plant growth could lead to toxicities.

Plant growth regulators are an interesting class of compound since they possesss functional groups capable of binding to metal ions and could therefore alter soil solution speciation.

1.7 OBJECTIVES OF THIS STUDY.

Approximate concentrations of ions in soil solutions can be determined by analytical methods but it is not always possible to determine the various physico-chemical forms of the species in solution. Computer modelling is an excellent technique for calculating soil solution speciation. Sposito and Mattigod successfully used computer modelling to examine soil solution speciation [Spo81]. In their studies they focussed on the principle species of cadmium as generated by their computer model and found a good correlation between their speciation results and the actual species of cadmium as found in the shoots of corn plants.

A computer model can be used effectively to predict trends that may occur in a real system. If the limitations of the model, such as a fixed pH, and the absence of adsorbtion equilibria, are clearly understood and always borne in mind, the computer simulated results may be interpretted within these confines.

Plant growth regulators contain functional groups capable of binding to metal ions in the soil solution. As reported in the literature [Nic82], there is a great deal of inconsistency in the effects of plant growth regulators on plant growth. Similar quantities of the same plant growth regulator applied to the same plant species under apparently similar conditions have resulted in different plant responses. A knowledge of the soil solution speciation is expected to represent an important step in understanding the mode of action of plant growth regulators and their possible effects on plants. It is important to note that the binding strength of N-Phosphonomethyl iminodiacetic acid (**IV**) as established in this study,(Chapter 3), is approximately one log unit greater than that of NTA (**VII**) [Mar74] for the various metal ions under consideration. Since the latter has been found to affect soil solution speciation, it is reasonable to expect that applications of the herbicide N-

Phosphonomethyl iminodiacetic acid would alter metal ion speciation in soil and consequently its availability to plants.

Chemical modelling represents an excellent technique for examining the possible effects of compounds such as (**I**), **(II)**, **(III)** and **(IV)** on soil solution speciation and consequently on the availability of metal ions to plants.

The objectives of this study are thus:

1. To conduct a literature search in order to establish the various factors and components that contribute to the chemical speciation of a soil solution as well as the present state of knowledge of selected plant growth regulators.

2. To synthesize and characterize four structurally related organophosphorus plant growth regulators; viz, N-(Phosphonomethyl) glycine, **(I)**, N,N'[Phosphinicobis(methylene) bis glycine], **(II)**, N,N-bis(Phosphonomethyl) glycine, **(III)** and N-(Phosphonomethyl) iminodiacetic acid, **(IV)**.

3. To determine protonation and metal ion equilibrium constants of compounds **(I)**, **(II)**, **(III)** and **(IV)** using glass electrode potentiometry.

4. To examine the aqueous equilibria of compounds **(I)**, **(II)**, **(III)** and **(IV)** using ^{1}H, ^{13}C and ^{31}P nuclear magnetic resonance spectroscopy with a view to determining the exact sites of deprotonation.

5. To construct a computer model of a soil solution to simulate the effects of selected plant growth regulators on soil solution speciation

6. To examine and discuss the speciation results as calculated by the chemical model.

CHAPTER 2

SYNTHESIS

CONSISTING OF

INTRODUCTION

EXPERIMENTAL

RESULTS AND DISCUSSION

2.1 INTRODUCTION

The four plant growth regulators **(I)**, **(II)**, **(III)** and **(IV)** used in this study have all been synthesised. The synthetic method used to prepare compound **I** has been devised in this laboratory and is presented in this chapter. Compound **IV** was prepared by employing reported methods for the synthesis of similar compounds whereas compounds **II** and **III** were prepared using methods which are fully described in the literature.

$$H_2O_3PCH_2NHCH_2CO_2H \quad (I)$$

N - (Phosphonomethyl) glycine (Ligand 1)

$$HO_2P(CH_2NHCH_2CO_2H)_2 \quad (II)$$

N,N'[Phosphinicobis(methylene)] bis glycine (Ligand 2)

$$(H_2O_3PCH_2)_2NCH_2CO_2H \quad (III)$$

N,N - bis(Phosphonomethyl) glycine (Ligand 3)

$$H_2O_3PCH_2NH(CH_2CO_2H)_2 \quad (IV)$$

N - (Phosphonomethyl) iminodiacetic acid (Ligand 4)

Aminomethylphosphonic acids of the type **(I)**, **(III)** and **(IV)** are generally synthesised by the addition of an aldehyde or ketone to a mixture of a phosphite diester, such as diethyl phosphite, and a primary or secondary amine to give substituted aminomethyl phosphonic esters [Fie52]. This can also be achieved by the Mannich - type reaction of an amine, formaldehyde and phosphorous acid which proceeds according to the general equation described by the scheme below [Moe66].

$$R_{3-n}NH_n + nCH_2O + nHP(O)(OH)_2 \downarrow R_{3-n}N[CH_2P(O)(OH)_2]_n + nH_2O$$

R is any alkyl group

The synthesis of (II) also is based on the above scheme except that hypophosphorous acid is used as a precursor, instead of phosphorous acid, since it contains two acidic protons bound to the phosphorus atom [Ole80].

2.2 EXPERIMENTAL

All the chemical reagents used in the synthetic work were commercially available and where possible, were purified before use by conventional methods. In the characterisation of compounds, melting point determinations were measured on a Fisher - Johns melting point apparatus and the microanalyses were determined using a Heraeus universal combustion analyser. The nuclear magnetic resonance spectra were determined in D_2O on a Varian VXR - 200 superconducting FT spectrometer.

N - (Phosphonomethyl) glycine (I) was prepared according to the following procedure. Methyleneaminoacetonitrile was synthesised by adding a solution of sodium cyanide dropwise to a stirring solution of 35% formaldehyde and ammonium chloride at 0 °C [Ada32]. When half the sodium cyanide had been added, a solution of glacial acetic acid was then added dropwise to the reaction mixture at a rate such that its addition and that of the remaining sodium cyanide was completed at the same time. The product started crystallising from solution when the glacial acetic acid was added. The product was filtered under suction, washed with cold water,

dried and characterised by microanalysis, proton nuclear magnetic resonance and melting point determination.

A 12.2 g (0.176 mol.) sample of methyleneaminoacetonitrile was dissolved in 48 cm^3 (0.372 mol.) of freshly distilled (b. p. 84 to 87 ^oC / 12 mm Hg) diethyl phosphite and dry HCl was passed with stirring into the solution for 3 hours at room temperature. The resulting precipitate was filtered off, washed with cold diethyl ether , dried and recrystallised from methanol to give the hydrochloride salt of N - (Diethylphosphonomethyl) aminoacetonitrile. In the above reaction, the dry HCl was generated by adding a concentrated HCl solution dropwise to a concentrated solution of H_2SO_4.

A 10.0 g sample of of N - (Diethylphosphonomethyl) aminoacetonitrile was dissolved in 120 cm^3 of concentrated HCl and the solution was heated under reflux for 6 hours. The solvent was removed on a rotary evaporator, yielding 10.3 g (97%) of a 1 : 1 mixture (as determined by elemental analysis) of N - (Phosphonomethyl) glycine.HCl and ammonium chloride. A 5.0 g amount of this mixture was dissolved in 50 cm^3 of water and the solution was passed through a cation - exchange column (Amberlite IR - 12H) to separate the hydrochloride salt of (**I**) from the ammonium chloride. Two bed volumes of deionized water were used to elute the product. The solution was approximately neutralised with respect to HCl using NaOH, after which about 80% of the solvent was removed on a rotary evaporator. On standing, (**I**) crystallised from solution (NaCl remained in solution) and was filtered under suction, washed with cold water and dried. The product was recrystallised from water.

N,N'[Phosphinicobis(methylene)] bis glycine (II) was synthesised according to the procedure described by Maier and Smith [Mai80].

35.0 g of N - Benzylglycine hydrochloride (0.174 moles) [Bak49], 11.5 cm^3 of 50% hypophosphorous acid (0.087 moles) and 200 cm^3 of concentrated hydrochloric acid were refluxed for 20 minutes until a clear solution was obtained. 60 cm^3 of 35% aqueous formaldeyhde was added dropwise to the reaction mixture over a period of 30 minutes and the solution was refluxed for a further 2 hours and left at room temperature for 16 hours. The precipitated product was filtered, washed with cold water and dried. In order to remove any unreacted N - Benzylglycine hydrochloride, the product was boiled in 250 cm^3 of 99.7% ethanol and filtered whilst still hot. After cooling, the product, N,N'[Phosphinicobis(methylene)] bis benzylglycine was filtered and dried.

0.12 g of palladium on charcoal (Pd/C) was added to a solution of 2.0 g of N,N'[Phosphinicobis(methylene)] bis benzylglycine in 50 cm^3 of H_2O. This solution was hydrogenated at 30 to 35 ^oC. After about 40% of the theoretically calculated hydrogen had been taken up, an additional 0.12 g Pd/C and 50 cm^3 of absolute ethanol was added. A further 0.12 g Pd/C, 24 cm^3 acetic acid and 0.24 g Pd/C were added after 88%, 96% and 98% respectively of hydrogen had been taken up. After 106 % of the hydrogen had been taken up, the reaction was stopped, the catalyst filtered off, and the filtrate was evaporated. The residue was warmed with water for 12 hours in order to remove impurities after which the solution was filtered and the filtrate evaporated. The colourless product, N,N'[Phosphinicobis(methylene)] bis glycine was then recrystallised from water.

N,N - bis(Phosphonomethyl) glycine (III) was synthesised according to the procedure described by Kireeva et. al. [Kir73].

17.2 g (0.20 moles) of 97% phosphorous acid was added to a solution of glycine (7.5 g, 0.10 moles) in a mixture of water (15 cm^3) and concentrated hydrochloric acid (20 cm^3). This solution was refluxed and 35 cm^3 (0.41 moles) of 35% aqueous formaldehyde was added dropwise after which the solution was refluxed for a further 60 minutes. The reaction mixture was cooled, filtered and the filtrate removed under reduced pressure yielding a viscous oil that crystallised after addition of a small volume of ethanol. The crystalline compound, N,N - bis(Phosphonomethyl) glycine, was filtered and washed with cold ethanol.

N - (Phosphonomethyl) iminodiacetic acid (IV) was prepared similarly to **(III)** starting with 20.1 g (0.151 moles) of iminodiacetic acid, 12.4 g (0.147 moles) of 97 % phosphorous acid and 26 cm^3 (0.328 moles) of 35% aqueous formaldehyde. After the work - up as described in the synthesis of **(III)**, compound **(IV)** was obtained.

2.3 RESULTS AND DISCUSSION

A number of synthetic methods for the preparation of **N - (Phosphonomethyl) glycine (I)** have been established and patented [Fra72], [Smi74], [Mai82], [Chu86] and [Ler88].

Franz has reported the preparation of **I** by condensation of glycine with chloromethylphosphonic acid in aqueous NaOH [Fra72] whereas Smith prepared **I** by heating **IV** under strongly acidic conditions in a closed vessel resulting in the removal of one of the carboxymethyl groups [Smi74]. Maier obtained a 90% yield for **I** following condensation of N - Benzylglycine hydrochloride with formaldehyde (H_2CO) and phosphorous acid $P(OH)_3$ and subsequent debenzylation using hydrogen gas and a Pd/C catalyst [Mai82].

Very recently, Riley et. al. have reported the selective removal of one carboxymethyl group from **IV** to give **I** using cobalt(II) as a catalyst under an oxygen atmosphere [Ril91].

The method for the synthesis of **I** described below has been established in our laboratory [Dha90]. N - (Diethylphosphonomethyl) aminoacetonitrile hydrochloride was prepared by the addition of 100% excess of diethyl phosphite to the trimer methyleneaminoacetonitrile [Joh24]. The nitrile and ester functional groups of this intermediate were then hydrolysed [Sas63] to give a mixture of **(I)**.HCl and ammonium chloride which was separated using a cation exchange resin. Following is a general scheme for the preparation of **(I)**.

$$2\,H_2C{=}O \;+\; NaCN \;+\; NH_4Cl \longrightarrow 1/3\,(CH_2{=}NCH_2CN)_3 \;+\; NaCl$$

$$1/3\,(CH_2{=}NCH_2CN)_3 \;+\; 100\%\ \text{excess}\ (EtO)_2P(O)H$$

$$\downarrow\ HCl(g)$$

$$(EtO)_2P(O)CH_2NHCH_2CN\,.\,HCl$$

$$\downarrow\ \text{conc. HCl}$$

$$(OH)_2P(O)CH_2NH_2CH_2CO_2H\,.\,HCl \;+\; NH_4Cl$$

$$\downarrow\ \text{cation exchange}$$

$$(OH)_2P(O)CH_2NH_2CH_2CO_2H \quad \textbf{(I)}$$

The yields, melting points, proton NMR data and microanalyses of N - (Diethylphosphonomethyl) aminoacetonitrile hydrochloride and N - (Phosphonomethyl) glycine **(I)** are reported below. The proton NMR spectrum of **I** is presented in figure 2.1.

N - (Diethylphosphonomethyl) aminoacetonitrile hydrochloride

Yield :- 23.0 g (54%)

Melting point :- 136 to 138 °C

^{1}H NMR (D_2O) :-

δ 1.37	triplet,	6H,	2 x $C\underline{H}_3CH_2O$-,
δ 3.68	doublet,	2H,	-$C\underline{H}_2P$, J_{HP} = 14 Hz,
δ 4.28	singlet,	2H,	-$C\underline{H}_2CN$,
δ 4.28	d of quart.,	4H,	2 x $CH_3C\underline{H}_2O$-

Microanalysis :- $C_7H_{16}N_2O_3PCl$

	%C	%H	%N
Calculated	34.60	6.60	11.55
Found	34.55	6.35	11.70

N - (Phosphonomethyl) glycine (I)

Yield :- 2.40 g (60%)

Melting point :- 220 to 225 °C (decomp.)

^{1}H NMR (D_2O) :-

δ 3.26	doublet,	2H,	-$C\underline{H}_2P$, J_{HP} = 14 Hz,
δ 3.99	singlet,	2H,	-$C\underline{H}_2CO_2$,

Microanalysis :- $C_3H_8NO_5P$

	%C	%H	%N
Calculated	21.30	4.70	8.20
Found	21.25	4.70	8.25

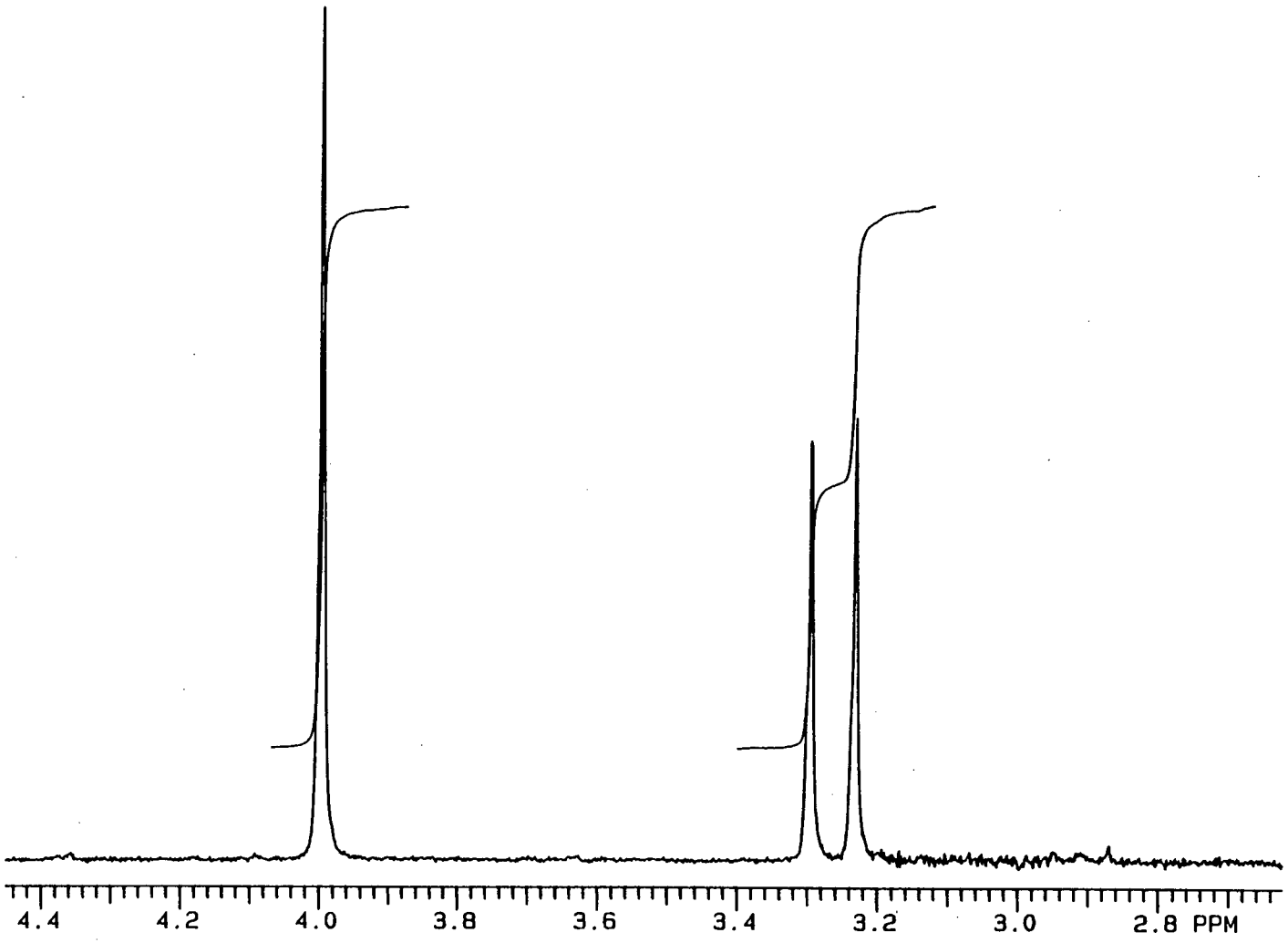


Figure 2.1 ^{1}H NMR spectrum of N - (Phosphonomethyl) glycine (Ligand 1) in D_20.

N,N'[Phosphinicobis(methylene)] bis glycine (II) was synthesised according to a procedure described in the literature [Bak49], [Mai80]. N - benzylglycine hydrochloride, a precursor for the synthesis of **(II)** was prepared following the condensation of benzylamine hydrochloride, formaldehyde and sodium cyanide. This yielded the hydrochloride of N - benzylaminoacetonitrile which upon hydrolysis gave N - benzylglycine hydrochloride. The latter was now reacted with formaldehyde and hypophosphorus acid resulting in N,N'[Phosphinicobis(methylene)] bis benzylglycine which was subsequently hydrogenated using Pd/C giving **(II)**. Following is a general scheme for the preparation of **(II)**.

$$Ph\text{-}CH_2NH_2 + HCl \rightarrow Ph\text{-}NH_3^+ Cl^-$$

$$Ph\text{-}NH_3^+ Cl^- + H_2C{=}O + NaCN \rightarrow PhCH_2NH_2CH_2CN \,.\, HCl$$

$$PhCH_2NH_2CH_2CN \,.\, HCl \xrightarrow{H^+/H_2O} PhCH_2NH_2CH_2CO_2H \,.\, HCl$$

$$2\ PhCH_2NH_2CH_2CO_2H \,.\, HCl + 2\ H_2C{=}O + H_3PO_2$$

$$\downarrow$$

$$(HO)P(O)[CH_2N(CH_2Ph)CH_2CO_2H]_2$$

$$\downarrow\ H_2\,(g),\ Pd/C$$

$$(HO)P(O)[CH_2NCH_2CO_2H]_2 \quad \textbf{(II)}$$

The yields, melting points, proton NMR data and microanalyses of N,N'[Phosphinicobis(methylene)] bis benzylglycine and N,N'[Phosphinicobis(methylene)] bis glycine **(II)** are reported below. The proton NMR spectrum of **II** is presented in figure 2.2.

N,N'[Phosphinicobis(methylene)] bis benzylglycine

Yield :- 23.4 g (59%)

Melting point :- 200 to 205 °C (lit. 211 to 214 °C)

^{1}H NMR (D_2O) :-

δ 3.50	doublet,	4H,	2 x -C$\underline{H_2}$P,	J_{HP} = 14 Hz,
δ 4.08	singlet,	4H,	2 x -C$\underline{H_2}$CO$_2$,	
δ 4.60	singlet,	4H,	2 x -C$\underline{H_2}$Ph	
δ 7.54	singlet,	10H,	2 x -CH$_2$$\underline{Ph}$	

Microanalysis :- $C_{20}H_{25}N_2O_6P.HCl$

	%C	%H	%N
Calculated	52.60	5.70	6.10
Found	51.80	5.30	6.00

N,N'[Phosphinicobis(methylene)] bis glycine (II)

Yield :- 0.44 g (42%)

Melting point :- 272 to 278 °C (decomp.) (lit. 279 to 282 °C [Mai80])

^{1}H NMR (D_2O) :-

δ 3.48	doublet,	4H,	2 x -C$\underline{H_2}$P,	J_{HP} = 14 Hz,
δ 3.88	singlet,	4H,	2 x -C$\underline{H_2}$CO$_2$,	

Microanalysis :- $C_6H_{13}N_2O_6P$

	%C	%H	%N
Calculated	30.00	5.42	11.67
Found	29.75	5.50	11.50

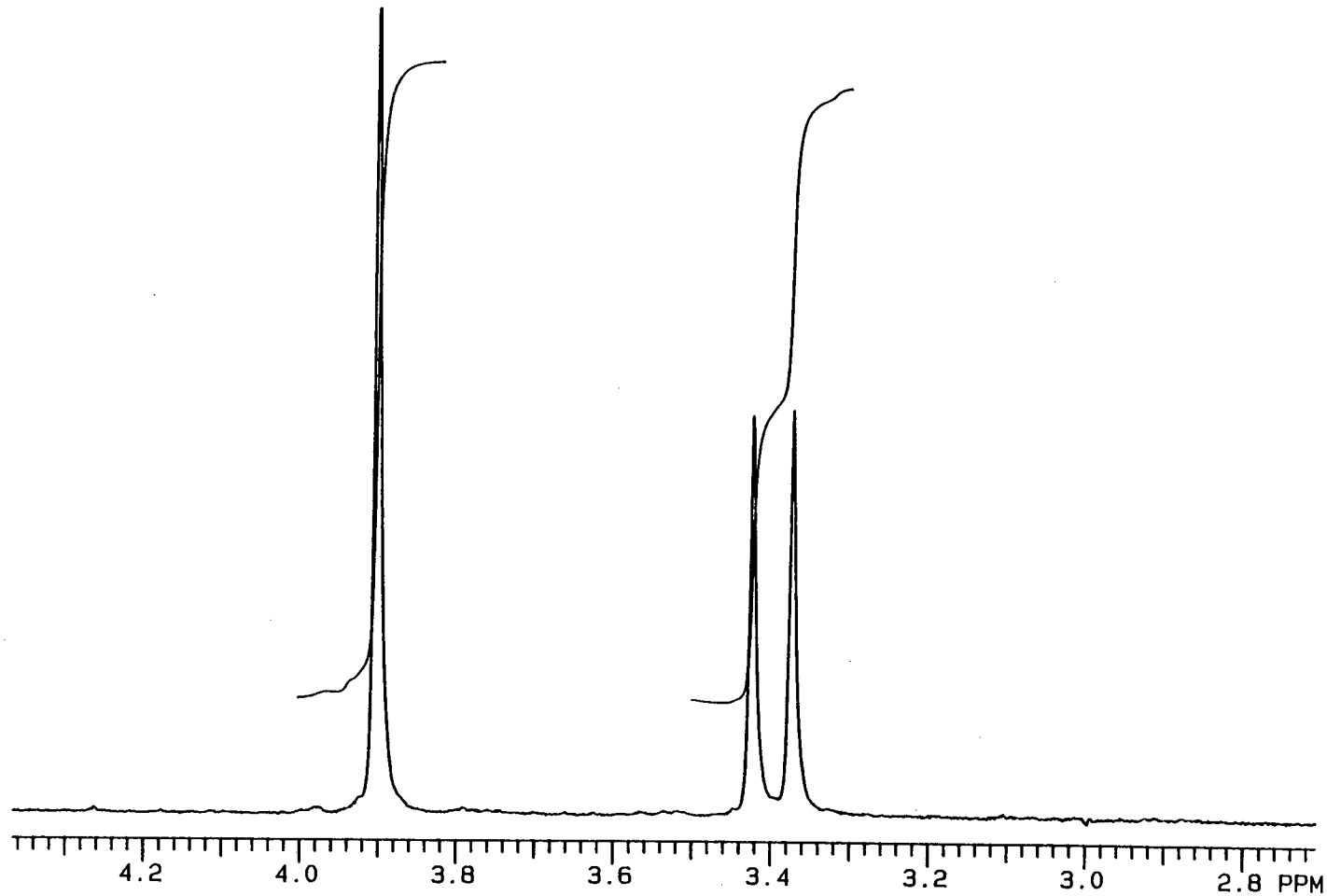


Figure 2.2 ^{1}H NMR spectrum of N,N' [Phosphinicobis(methylene) bis glycine (Ligand 2) in D_2O.

The synthesis of **N,N - bis(Phosphonomethyl) glycine (III)** was relatively simple in comparison with **(I)** and **(II)** and was based on the condensation of glycine with formaldehyde and phosphorous acid in a strongly acidic solution. Following is a general scheme for the preparation of **(III)**.

$$H_2NCH_2CO_2H + 2\ H_3PO_3 + 2\ H_2C{=}O \xrightarrow{HCl} (H_2O_3PCH_2)_2NCH_2CO_2H\ \textbf{(III)}$$

The yield, melting point, proton NMR data and microanalysis of N,N - bis(Phosphonomethyl) glycine **(III)** is reported below. The proton NMR spectrum of **III** is presented in figure 2.3.

N,N - bis(Phosphonomethyl) glycine (III)

Yield :- 26.3 g (66%)

Melting point :- 189 to 193 ^oC (decomp.)

^1H NMR (D_2O) :- δ 3.72 doublet, 4H, 2 x -$C\underline{H}_2P$, J_{HP} = 14 Hz,
δ 4.44 singlet, 2H, -$C\underline{H}_2CO_2$,

Microanalysis :- $C_4H_{11}NO_8P_2$

	%C	%H	%N
Calculated	18.25	4.20	5.30
Found	18.25	4.20	5.30

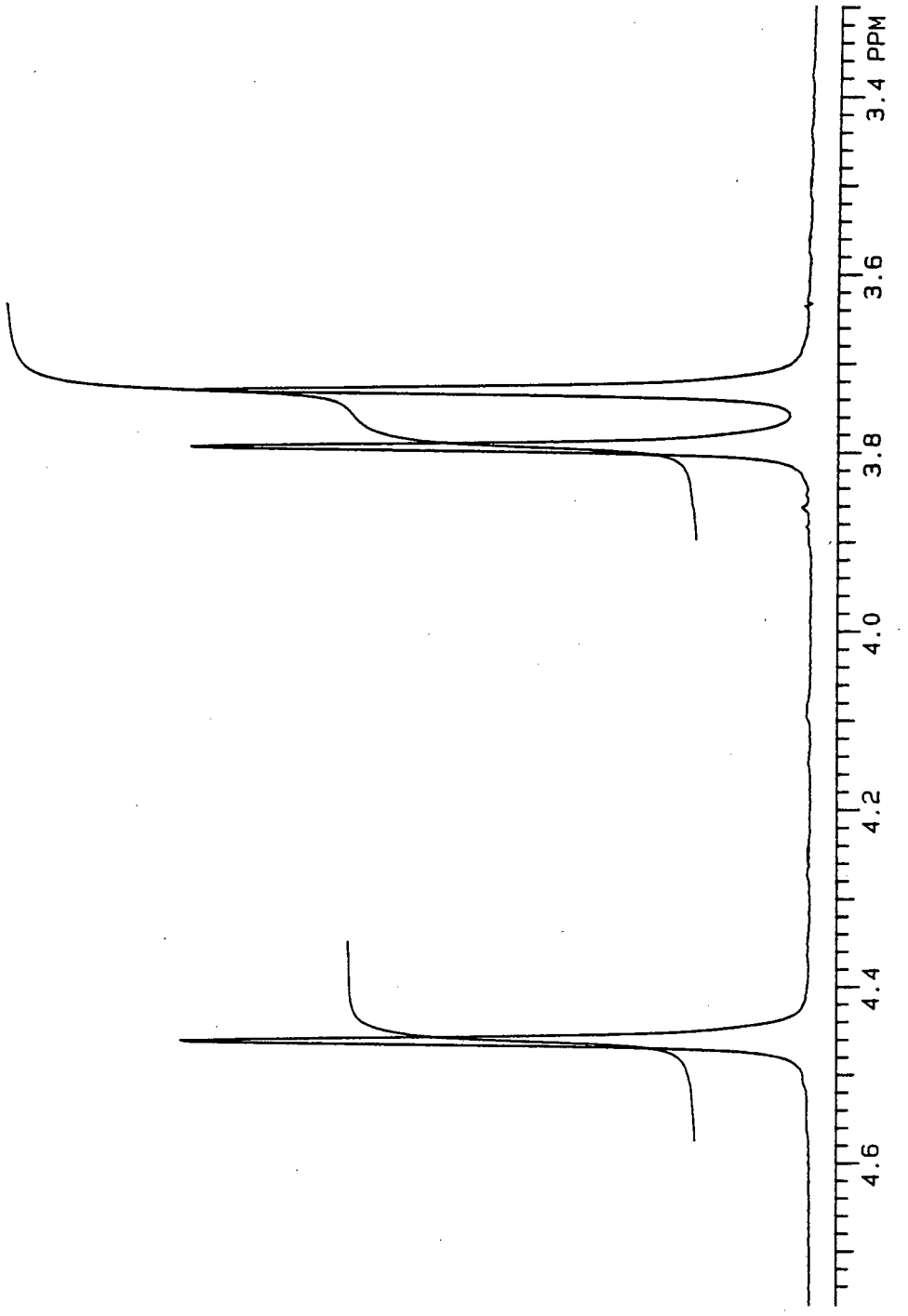


Figure 2.3 ^{1}H NMR spectrum of N,N - bis(Phosphonomethyl) glycine (Ligand 3) in D_20.

N - (Phosphonomethyl) iminodiacetic acid (IV) was prepared under similar reaction conditions to **(III)**. Equimolar quantities of iminodiacetic acid, phosphorous acid and formaldehyde were condensed under acidic conditions. Following is a general scheme for the preparation of **(IV)**.

$$HN(CH_2CO_2H)_2 + H_3PO_3 + H_2C{=}O \xrightarrow{HCl} H_2O_3PCH_2N(CH_2CO_2H)_2 \ \textbf{(IV)}$$

The yield, melting point, proton NMR data and microanalysis of N - (Phosphonomethyl) iminodiacetic acid **(IV)** is reported below. The proton NMR spectrum of **IV** is presented in figure 2.4.

N - (Phosphonomethyl) iminodiacetic acid (IV)

Yield :- 24.1 g (72%)

Melting point :- 214 to 218 °C (decomp.)

^{1}H NMR (D_2O) :-

	δ 3.56	doublet,	2H,	$-C\underline{H}_2P$, J_{HP} = 14 Hz,
	δ 4.30	singlet,	4H,	2 x $-C\underline{H}_2CO_2$,

Microanalysis :- $C_5H_{10}NO_7P$

	%C	%H	%N
Calculated	26.43	4.40	6.17
Found	26.40	4.35	6.15

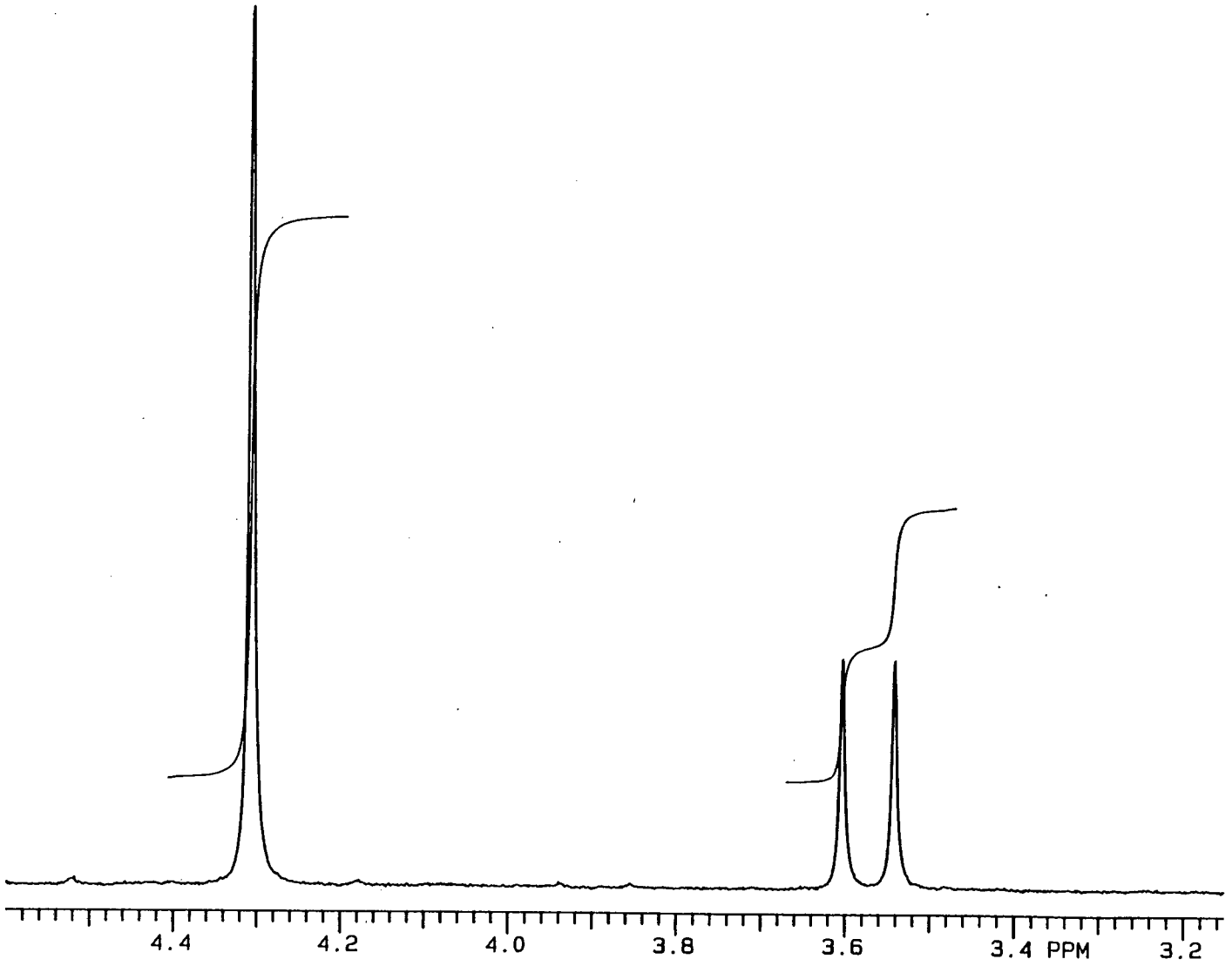
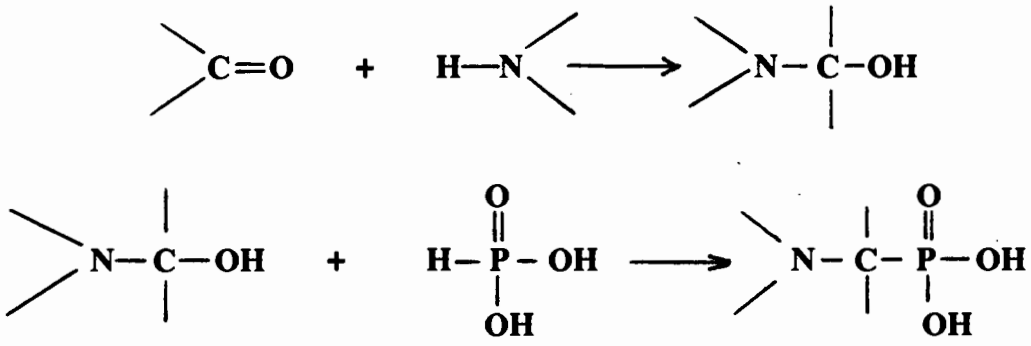


Figure 2.4 ^{1}H NMR spectrum of N - (Phosphonomethyl) iminodiacetic acid (Ligand 4) in D_20.

There are two possible mechanisms for reactions of the type described in this section. The first is condensation of the aldehyde with the amine followed by reaction with the phosphorous containing substrate as described by the following general scheme.



The alternative mechanism is reaction of the aldehyde with the phosphorus substrate resulting in an α - hydroxyalkylphosphonic acid, followed by reaction with an amine. However, this mechanism is unlikely since α - hydroxymethylphosphonic acids only react with amines at very high temperatures [Fie52].

CHAPTER 3

POTENTIOMETRY

CONSISTING OF

INTRODUCTION

THEORY

EXPERIMENTAL PROCEDURE

COMPUTATIONAL PROCEDURE

RESULTS AND DISCUSSION

PLAUSIBLE STRUCTURES OF COMPLEXES

3.1 INTRODUCTION

Ligands, protons and metal ions interact in solution giving rise to numerous co-ordination complexes of varying stability. A stability constant is an effective means of representing the affinity of a ligand for a metal ion in solution.

Stability constants are required to determine the nature of complexes under a variety of conditions in many scientific disciplines. In analytical chemistry, stability constants are required for developing methods for the separation of selected metal ions from mixtures. In medicine, the choice of correct antedote to counteract the effects of ingested toxic metals can only be made from a knowledge of stability constants. In environmental science, toxic metals from industry eventually find their way into the environment and complex with naturally occuring ligands which seriously disrupts the bioavailability of essential metal ions to plants. In mining, the extraction of precious metals from ores is dependent on the selective complexing of extracting agents. In agriculture, organic compounds are carefully selected, from a knowledge of their complexing capabilities, to supply metal ions to plants by increasing their solubility and mobility [Lin84a], [Mar88].

In this laboratory, stability constants have been used to (i) model blood plasma using low molecular weight complexes [May76], [May77], (ii) model the effect of fulvic acids on metal ions in a soil solution [Mur82], (iii) develop a urine model to investigate the factors associated with urolithiasis [Lit84], (iv) model the effect of caffeic acid on metal ion speciation in a plant nutrient solution [Voy85] and (v) examine the speciation of metal ions in sea water by computer simulation [Meu90].

In this thesis, stability constants of metal ions with selected plant growth regulators are required for simulating their effects on the soil solution speciation of metal ions by computer modelling.

Any experimental technique that can be used to measure the concentration of one of the components in equilibrium can be used to determine stability constants provided that the total analytical concentrations of all the components are known. Methods such as spectrophotometry, colorimetry, nuclear magnetic resonance spectroscopy and polarography can all be used to determine stability constants [Ros78], [Har80] and [Mel88]. Potentiometry is widely used as one of the most accurate and sensitive techniques for determining stability constants and is the chosen method in this study. When complexes are exeedingly stable at low pH values, displacement techniques such as ligand-ligand or metal-metal competition may be employed and monitored potentiometrically [Mot80], [Mar88] and [Bec90]. Motekaitis and Martell utilised the strong tendency of gallium(III) to undergo hydrolysis, to determine stability constants of Ga(III) ions and various ligands [Mot80]. In the aforementioned systems, all ligands were displaced from the metal ion by hydroxyl ions at high pH.

In a potentiometric investigation involving a ligand and a strong acid, the hydrogen ion concentration can be measured as a function of the volume of titrant (NaOH) added. In order to determine the protonation constant, the hydrogen ion concentration can be compared to its expected concentration in the absence of any ligand. The resulting difference is of course due to ligand-proton complexation. The protonation constants can be determined by an optimization procedure using any of the many computer programs presently available [Leg85] and [Mel88]. Prior to the availability of computers, potentiometric data were graphically analysed. The methods of Rossotti and Rossotti [Ros61], were among those most commonly used. Owing to the complexity of systems containing even a few species, most of the graphical techniques were based on approximations.

Numerous computer programs for processing potentiometric data have been developed. LETAGROP [Ing64], SCOGS [Say68], MINIQUAD [Sab74], BEST [Mot82] and SUPERQUAD [Gan85] are among the more frequently used optimization procedures. Whilst each of these programs fulfill the basic requirement of refining stability constants, they each have their own subtle variations arising out of the specific needs of their authors. ESTA, (Equilibrium Simulation for Titration Analysis), consists of a suite of programs allowing one to handle virtually every type of calculation in a potentiometric investigation and is one of the most compact and efficient programs presently available [May85], [May88a].

In a solution containing metal ions, a ligand and a strong acid, the hydrogen ion concentration of the solution can be compared with that of a solution consisting of uncomplexed ligand. This comparison gives an indication of the degree of metal ion complexation. In principle, the extent of metal ion complexation ought to be determined more accurately by using a metal ion sensitive electrode. This would allow for the direct measurement of the free metal ion concentration rather than determining this indirectly via the effect that the metal complexation has on the release or complexation of hydrogen ions by the ligand as measured by a hydrogen specific electrode. Metal ions such as copper, lead, and cadmium exhibit reversible half reactions and are thus satisfactory metal ion specific electrodes. However, iron, cobalt and nickel develop non-reproducible potentials and are thus not suitable for electrodes [Sko86]. Some metal ion electrodes that are available have slow response times or are sensitive to the presence of other metals which of course ultimately leads to inaccurate determination of stability constants [Bas83].

In this study, glass electrodes, figure 3.1, have been used to measure the hydrogen ion concentration of all metal-ligand-proton systems investigated. A glass electrode is used in conjunction with a reference electrode, for example the calomel electrode,

figure 3.2. Glass electrodes are vastly superior to other ion selective electrodes and are used widely due to their ease of preparation and constancy of potential [Bas83].

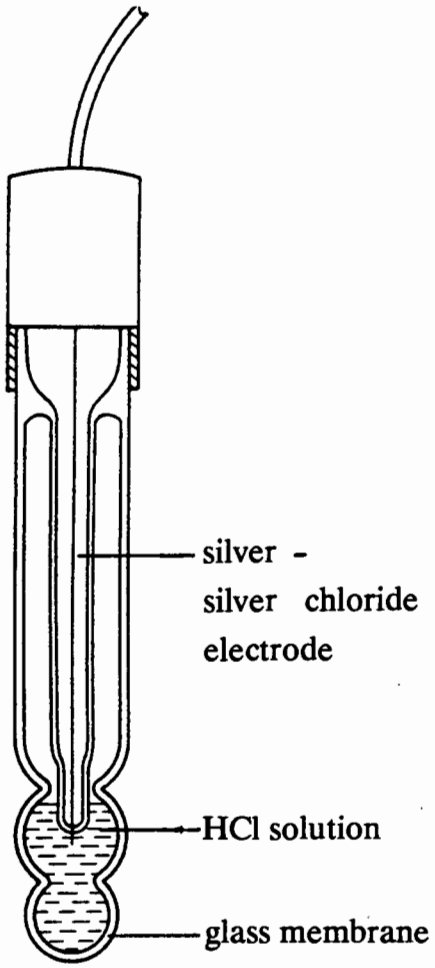


Figure 3.1

The glass electrode

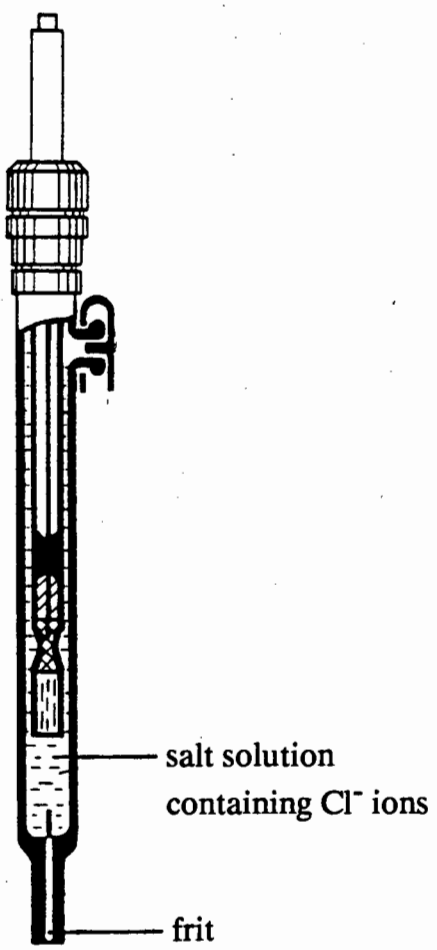


Figure 3.2

The calomel electrode

The glass electrode is an example of a membrane electrode. The potential developed between the outer surface of the glass membrane and the solution is a function of the pH of the solution and can be used to measure the hydrogen ion concentration of a solution. Provided that the internal HCl solution is maintained at a constant concentration, the potential of the silver-silver chloride electrode inserted into it will remain constant. This also applies to the potential between the HCl and the inner surface of the glass bulb. The only potential which can vary is that

existing between the outer suface of the glass bulb and the test solution into which it is immersed. Thus the overall potential of the electrode is governed by the hydrogen ion concentration of the test solution. Within the layer of glass between the inner and outer hydrated layers of the bulb, conductivity is due to the migration of sodium ions within the silicate lattice [Bas83].

In this study, the protonation constants of four selected organophosphorus plant growth regulators, Ligand 1, Ligand 2, Ligand 3 and Ligand 4 are determined.

Ligand 1 N - (Phosphonomethyl) glycine **(I)**

Ligand 2 N,N' - [Phosphinicobis(methylene)] bisglycine **(II)**

Ligand 3 N, N - bis(Phosphonomethyl) glycine **(III)**

Ligand 4 N - (Phosphonomethyl) iminodiacetic acid **(IV)**

In addition to this, the aqueous equilibria between each of the above ligands and Ni^{2+} ions as well as that of Ligand 4 and Mn^{2+}, Fe^{2+}, Co^{2+} and Zn^{2+} ions have been established. The Cu^{2+} - Ligand 4, Cu^{2+} - Ligand 3 and Fe^{3+} - Ligand 4 systems were also studied potentiometrically, but due to the high stability of the complexes formed at low pH, the data could not be processed. The Cu^{2+} - Ligand 4 system was successfully analysed in the presence of a competing ligand. A stability constant for the ML species of the Fe^{3+} - Ligand 4 system was graphically estimated and used in the modelling section of this study.

The ligands used in this study are structural analogues of IDA, IDP, NTA and NTP and their protonation behaviour and complexing properties with metal ions are expected to be similar to those of Ligands 1, 2, 3 and 4. Protonation and stability constants of IDA, IDP, NTA and NTP have been reported in the literature and the observed trends of these constants and those determined in this study are discussed.

IDA Iminodiacetic acid **(V)**

IDP Iminodi(methylenephosphonic acid) **(VI)**

NTA Nitrilotriacetic acid **(VII)**

NTP Iminotri(methylenephosphonic acid) **(VIII)**

The ligands used in this study as well as their structural analogues all include some or all of the functional groups, R-NH_2, -CO_2^- and -PO_4^{3-} and could thus be described as hard bases [Bur88] and [Bec90]. The metal ions Mn^{2+} and Fe^{3+} are hard acids while the ions Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} are classified as borderline (ie nether hard nor soft) [Bur88] and [Bec90]. Since hard metal ions form stable complexes with hard ligands, the stability constants of complexes formed between the metals and ligands of interest in this study are expected to be high.

There are huge discrepancies in the literature for stability constants of the same metal-ligand-proton systems determined under the same experimental conditions of temperature and ionic strength. A detailed description of the experimental procedure used in this study is given in chapter 3.3. Great care was taken in ensuring that the purest materials were used and that they were carefully standardised according to known and recommended procedures. The endpoints observed in the standardisation of metal ions are reported in detail and compared with those reported in the literature. Despite using fresh supplies of both metal ions and indicators, it is clear that colour changes in the region of the endpoint are not as sharp as one would like for potentiometric purposes. This could have lead to significant systematic errors which would have differed from one researcher to another since the final choice of endpoint is often a matter of opinion. For example, a difference of 0.04 cm^3 in the final choice of endpoint for a 10 cm^3 sample of zinc is

a difference of 0.4% in the final concentration of EDTA. This error is now carried through to the other metal ions which are standardised against EDTA.

The conditions under which the potentiometric studies were conducted as well as the procedure used for the conditioning, calibration and maintainance of the electrodes are discussed in detail.

3.2 THEORY

The concentrations of chemical species formed in solution, as a result of the presence of metal ions (M), ligands (L) and protons (H), are dependent on many factors such as the concentrations of the individual components, the pH of the solution, but most importantly, the equilibrium constant, K, of each reaction. The types of complexes that could possibly form include mononuclear binary species (ML_n), protonated species (ML_nH_m), ligand protonated species (LH_n), hydroxy species ($ML(OH)_n$), oligonuclear species ($L_nM\text{-}ML_n$) and metal hydroxy species ($M(OH)_n$).

For the reaction

$$M + L + H \rightleftharpoons MLH$$

the conditional equilibrium constant, K_1, is defined as

$$K_1 = [MLH]/[M][L][H] \qquad \text{...eq. 3.1}$$

where [ ] is the concentration in $mol.dm^{-3}$ of each of the species.

On addition of a further proton, (H) to the above reaction product, K_2 for the reaction

$$MLH + H \rightleftharpoons MLH_2$$

is defined as

$$K_2 = [MLH_2]/[MLH][H] \qquad \text{...eq. 3.2}$$

In reality, complex formation is accompanied by the displacement of solvent molecules from the co-ordination sphere of the metal ion and equation 3.1 ought to be

$$K_1^* = [MS_{n-i}LH]\,[S]^i / [MS_n]\,[L]\,[H] \qquad \text{...eq 3.3}$$

where n is the number of solvent molecules and
i is the number of solvent molecules substituted and is often the denticity of the ligand

By convention, solvent molecules are generally not included in expressions of equilibrium constants.

The formation of hydroxy complexes is different to that of other complexes in that OH^- does not displace a water molecule from the ligand but is produced as a result of the dissociation of a proton from one of the water molecules in the co-ordination sphere of the metal ion.

In general, the trend is for K_n to decrease as n increases provided that factors such as a change in co-ordination number of the metal ion or intramolecular hydrogen bonding does not lead to added stability of the complex.

The products of individual equilibrium constants give rise to characteristic values called overall or cumulative stability constants represented as ß.

$$\text{Thus } ß_2 = K_1.K_2 = [MLH]/[M][L][H] \,.\, [MLH_2]/[MLH][H]$$
$$= [MLH_2]/[M][L][H]^2 \qquad \text{...eq. 3.4}$$

Expressing a reaction product as a stability constant leads to greater clarity as all species are then expressed in terms of their individual components. For example, the reaction product leading to K_2 could have been formed by the reaction

$$ML + 2H \rightleftharpoons MLH_2$$

resulting in a different value of K_2.

Equation 3.4 thus has the general form

$$ß_n = \prod_{i=1}^{n} K_i \qquad \text{...eq. 3.5}$$

The law of mass action is only valid when stability constants are determined in terms of the activities of the individual components. However, it is only practicable to determine stability constants in terms of concentrations since single ion activities cannot be determined by any physical technique.

The activity or effective concentration of a species is related to its actual concentration by an activity coefficient

$$a = \gamma \times c$$

where c is the concentration in $mol.dm^{-3}$,

γ is the molar activity coefficient and

a is the activity of the species.

The cumulative thermodynamic stability constant for the general reaction

$$pM + qL + rH \rightleftharpoons M_pL_qH_r$$

$$\text{is } {}^{T}\beta_{pqr} = \{M_pL_qH_r\}/\{M\}^p\{L\}^q\{H\}^r \qquad \text{...eq. 3.6}$$

where { } is the activity, and p, q and r are the stoichiometric coefficients of metal, ligand and protons respectively.

The overall stability constant of the above reaction expressed in terms of concentrations,

$$\text{is } \beta_{pqr} = [M_pL_qH_r]/[M]^p[L]^q[H]^r \qquad \text{...eq. 3.7}$$

and is related to the thermodydamic stability constant by the equation

$${}^{T}\beta_{pqr} = \beta_{pqr} \times Q \qquad \text{...eq. 3.8}$$

where Q is the quotient of the activity coefficients for the products and reactants

$$Q = \gamma_{MpLqHr} / \gamma_M{}^p \cdot \gamma_L{}^q \cdot \gamma_H{}^r$$

In an experiment of varying pH, the concentrations of reactants and products change, thus affecting the ionic strength, I, of the solution.

$$I = {}^1/_2 \sum_{i=1}^{n} c_i z_i^2 \qquad \text{...eq. 3.9}$$

where c_i is the concentration (mol.dm^{-3}) of species i and
z_i is the charge of species i.

From an expression of the Debye-Hückel equation, eq. 3.10, it can be seen that a change in ionic strength affects the activity coefficients which in turn affects Q.

$$\log \gamma_i = -Az_i^2 I^{0.5} / (1 + å_i B I^{0.5}) \qquad \text{...eq. 3.10}$$

where I is the ionic strength
γ_i is the activity coefficient of ion i
z_i is the charge on ion i
A and B are constants characteristic of the solvent
(A = 0.509 and B = 0.328 for water at 25 °C)
$å_i$ is an ionic size parameter

In order to determine a stability constant where the ionic strength remains constant throughout the course of a titration, an inert background electrolyte is used in large excess. This effectively masks the changing charge effects of the reacting species and allows for the determination of a stability constant at "constant" ionic strength.

Concentration based stability constants that are determined are thus only valid at specific temperatures and ionic strengths. Since it is tedious to determine stability constants for the same reaction at different ionic strengths, estimates can be determined by applying correction factors from the many published equations that are available. An extended form of the Debye - Hückel equation , eq. 3.11, has been found to work well for small changes in ionic strength [Lin82b].

$$\log \gamma_i = -Az_i^2 I^{0.5} / (1 + åBI^{0.5}) + CI \qquad \text{...eq. 3.11}$$

where C is an additional constant.

The experimental data accumulated from the potentiometric investigations were processed by the computer program ESTA [May85] and [May88a]. ESTA enables one to generate a series of plots from the observed data which assists in the identification of major species in solution. Once a model has been proposed, the calculated stability constants are used to generate theoretical plots. In comparing the "goodness of fit" between the experimental and theoretical plots, one gets an indication of the validity of the proposed model.

The experimental proton formation function, Z_H^{exp}, is defined as the average number of protons bound to ligand in the absence of metal ions and is derived as follows

$$\begin{aligned} Z_H^{exp} &= [\text{Bound H}] / [\text{Ligand not bound to metal}] \\ &= [\text{Bound H}] / T_L \\ &= T_H - [H] + K_W[H]^{-1} / T_L \end{aligned} \qquad \text{...eq. 3.12}$$

where T_H is the total observed proton concentration,

T_L is the total observed ligand concentration,

[H] is the observed free proton concentration and

K_W is the ionic product of water.

The theoretical proton formation function, Z_H^{calc}, can be determined as follows

$$\begin{aligned}
[\text{Bound H}] &= [LH] + 2[LH_2] + 3[LH_3] + ... + N[LH_N] \\
&= [H][L]\beta_{011} + 2[H]^2[L]\beta_{012} + ... \\
&= [L] \sum_{1}^{n} j[H]^j\beta_{01j} \\
\text{and } T_L &= [L] + [H][L]\beta_{011} + [H]^2[L]\beta_{012} + ... \\
&= [L] \sum_{1}^{n} [H]^j\beta_{01j}
\end{aligned}$$

where [L] is the observed free ligand concentration.

Therefore, $$Z_H^{calc} = \sum_{1}^{n} j[H]^j\beta_{01j} / \sum_{1}^{n} [H]^j\beta_{01j} \qquad \text{...eq. 3.13}$$

The experimental and calculated values of Z_H are plotted as a function of pH.

The experimental metal formation function, Z_M^{exp}, is defined as the average number of ligand molecules bound to metal and is derived as follows

$$\begin{aligned}
Z_M^{exp} &= [\text{Ligand bound to metal}] / [\text{Total metal}] \\
&= [\ T_L - (\text{Ligand not bound to metal})] / T_M \\
&= [\ T_L - (\text{Bound H}) / Z_H^{exp}\ ] / T_M \qquad \text{... eq. 3.14}
\end{aligned}$$

where T_M is the total observed metal concentration.

The theoretical metal formation function, Z_M^{calc}, is determined as follows

$$\begin{aligned}[\text{Ligand bound to metal}] &= [ML] + 2[ML_2] + 3[ML_3] + \ldots \\ &= [M][L]\beta_{110} + 2[M][L]^2\beta_{120} + \ldots \\ &= [M]\sum_{1}^{n} j[L]^j\beta_{1j0}\end{aligned}$$

where [M] is the observed free metal concentration

$$\begin{aligned}T_M &= [M] + [ML] + [ML_2] + \ldots \\ &= [M] + [M][L]\beta_{110} + [M][L]^2\beta_{120} + \ldots \\ &= [M]\sum_{1}^{n}[L]^j\beta_{1j0} \\ \text{therfore } Z_M^{calc} &= \sum_{1}^{n} j[L]^j\beta_{1j0} / \sum_{1}^{n}[L]^j\beta_{1j0} \qquad \ldots\text{eq. 3.15}\end{aligned}$$

The experimental and theoretical values of Z_M are plotted as a function of the negative logarithm of the free ligand concentration, p[L].

The experimental deprotonation function, Q_M^{exp}, is defined as the average number of protons released per metal ion as a result of complexation and is defined as follows

$$Q_M^{exp} = (T_H^* - T_H) / T_M \qquad \ldots\text{eq. 3.16}$$

where T_H^* is the calculated total concentration of protons in the system at the observed pH ignoring the presence of all metal complexes. A proton formation function, n, is defined for the ligand system in solution and is plotted together with Q_M^{exp} as a function of pH where

$$n = (T_H^* - [H] + K_W[H]^{-1}) / T_L \qquad \ldots\text{eq. 3.17}$$

The following mass balance equations are solved for T_H^* and T_L.

$$T_H^* = [H] - K_W[H]^{-1} + \Sigma r[M_pL_qH_r]$$
$$\text{and } T_L = [L] + \Sigma q[M_pL_qH_r]$$

where p = 0.

The theoretical value of the deprotonation function, Q_M^{calc}, is determined from the following equation

$$Q_M^{calc} = [L] \Sigma [H]^j\beta_{01j} - r \Sigma \beta_{pqr}[M]^p[L]^q[H]^r / [M] \Sigma [L]^j\beta_{1j0} \quad ...eq.3.18$$

Both Z_M and Q_M are calculated under the assumption that only mononuclear binary species of the type LH_n and ML_n are formed.

A rough estimate of the stepwise proton and metal formation constants can also be obtained graphically from the pH values of Z_H^{exp} and the -log[L] values of Z_M^{exp} using the Bjerrum half Z-bar method [Bje41].

The principles of stability constant determination from potentiometric data are as follows. At every titration point, the total concentration of each component can be calculated as the sum of the individual species together with that of the uncomplexed component. The total metal concentration, T_M^{calc} can be determined as follows

$$T_M^{calc} = [M] + [ML] + [ML_2] + [ML_3] + ...$$
$$+ [MLH] + [MLH_2] + ...$$
$$+ [M_2L] + [M_2LH] + ...$$
$$+ [MLH^{-1}] + ...$$

and can be expressed in terms of the free concentration of the component and the stability constant, therefore

$$T_M^{calc} = \sum_p \sum_q \sum_r \beta_{pqr} [M]^p [L]^q [H]^r \quad \text{...eq. 3.19}$$

similarly,

$$T_L^{calc} = q \sum_p \sum_q \sum_r \beta_{pqr} [M]^p [L]^q [H]^r \quad \text{...eq. 3.20}$$

and

$$T_H^{calc} = r \sum_p \sum_q \sum_r \beta_{pqr} [M]^p [L]^q [H]^r \quad \text{...eq. 3.21}$$

At every titration point, each of the equations 3.19, 3.20 and 3.21 can be equated with their real (experimental) concentrations, 3.22, 3.23 and 3.24 respectively, as determined from the initial volume, V^i, the initial component concentrations,(T_M^i, T_L^i, T_H^i), and the total volume, V, of base, C_H^{base}, added at that particular point.

$$T_M^{exp} = T_M^i \times V^i / V^i + V \quad \text{...eq 3.22}$$

$$T_L^{exp} = T_L^i \times V^i / V^i + V \quad \text{...eq 3.23}$$

$$T_H^{exp} = T_H^i \times V^i - C_H^{base} \times V / V^i + V \quad \text{...eq 3.24}$$

Hence for each titration point, we have N_{mbe} mass balance equations with a total of M (N_{mbe} X N_{pts}) mass balance equations for N_{pts} titration points. Experimentally, at each titration point we can determine at least one of the free component concentrations. In this study the glass electrode emf reading allows one to determine the $[H^+]$ ion concentration from the equation

$$E = E_o + 59.16 \log [H^+] \qquad \text{...eq. 3.25}$$

At each titration point we therefore have

$$N_{mbe} - N_e(\text{number of electrodes}) = N_c$$

number of unknown free concentrations or a total of $N_c \times N_{pts}$ unknown free concentrations per titration. Assuming that the number of unknown ß's are N, we then have $(N + N_c \times N_{pts})$ unknowns which have to be solved from M simultaneous equations.

In ESTA, a Gauss-Newton method is used to minimise an objective function, U, by simultaneously optimizing N_p parameters.

$$U = (N_{pts}-N_p)^{-1} \Sigma N_e^{-1} \Sigma W_{ni}(Y_{ni}^{exp} - Y_{ni}^{calc})^2 \qquad \text{...eq. 3.26}$$

where W_{ni} = weight of the i^{th} residual at the n^{th} point. The sum of the squares of the residuals may be minimised with respect to either the emf of electrode i at the n^{th} titration point ($Y_{ni} = E_{ni}$) or with respect to the total concentration of the electrode ion i at the n^{th} titration point ($Y_{ni} = T_{ni}$).

The goodness of fit between the experimental curves and that of the calculated curves is expressed by the R-factor, R_f, which is expressed as follows

$$R_f = \{ U / \Sigma W_n(emf_n^{exp})^2 \}^{0.5} \qquad \text{...eq. 3.27}$$

Ideally, R_f should be equal to R_{lim} where

$$R_{lim} = \{ N_{pts} / \Sigma W_n(emf_n^{exp})^2 \}^{0.5} \quad \text{...eq. 3.28}$$

if the model describes the system perfectly. However, R_{lim} can only be applied strictly if all errors are non-systematic which is not true for the analysis of potentiometric data. For example, an error in the electrode intercept, E_0, acts as a systematic error on all titration points. Nevertheless, a comparison between R_f and R_{lim} is a reasonable measure of the goodness of fit. From experiment, an R_f value less than 0.01 usually indicates that all of the major species have been found and that minor species may or may not be present.

The final choice of complexes modelling each of the metal-ligand-proton systems was made using the follwing criteria, U, R_f, Z_H, Z_M and Q_M.

3.3 EXPERIMENTAL PROCEDURE

3.3.1 CHEMICALS USED : -

Water:- Deionised and distilled

Sodium Chloride:- BDH Aristar grade

Sodium Hydroxide:- Merck ampoules

Hydrochloric Acid:- Merck ampoules

Potassium Hydrogen Phthalate:- Merck (min. 99.9%)

Titriplex III (EDTA-Disodium salt):- Merck (min. 99%)

Ligand 1:- Synthesised

Ligand 2:- Synthesised

Ligand 3:- Synthesised

Ligand 4:- Synthesised

4-Nitrocatechol:- Merck (min. 97%)

$MnCl_2.4H_2O$:- Merck (min. 99%)

$FeCl_2.4H_2O$:- Merck (min. 99%; max. 0.2% Fe^{3+})

$FeCl_3.6H_2O$:- Merck (min. 99%)

$CoCl_2.6H_2O$:- Merck (min. 99%)

$NiCl_2.6H_2O$:- Merck (min. 98%)

$CuCl_2.2H_2O$:- Merck (min. 99%)

Zn (granular):- Merck (min. 99.9%)

3.3.2 STANDARDISATION OF SOLUTIONS : -

Standardization of all solutions was carried out by titrating one sample delivered by a Radiometer ABU80 autoburette with a minimum increment of 0.01 cm^3 against another sample delivered by a calibrated pipette into a conical flask. The concentrations of the solutions used in this study were of the following order; HCl 0.01 $mol.dm^{-3}$, NaOH 0.05 $mol.dm^{-3}$, metal ion 0.01 $mol.dm^{-3}$ and ligand 0.01 $mol.dm^{-3}$.

The **water** (deionised and distilled) used to prepare all solutions was boiled before use to remove carbon dioxide.

An exceedingly pure grade of **sodium chloride** was used as a background electrolyte since it was being used in much greater quantities than the components under investigation and any impurities would magnify errors and lead to incorrect stability constants. All solutions prepared had a chloride $(Na^+)[Cl^-]$ concentration of 0.1 $mol.\ dm^{-3}$. The chloride ion contributions of metal ions and that from HCl were also taken into consideration when preparing solutions.

Sodium hydroxide solutions were prepared under a purified nitrogen atmosphere and protected from atmospheric carbon dioxide by soda lime. The solutions, which were not kept for more than five days, were standardised against dried potassium hydrogen phthalate using an automatic burette.

Hydrochloric acid solutions were standardised against sodium hydroxide using an automatic burette. A number of titrations were performed using two different glass electrodes, adding the NaOH in small increments throughout. The data was later used for determining the electrode intercepts, E_o's, using the optimization task OBJE of ESTA.

Titriplex III (EDTA-Disodium salt) solutions were prepared by accurately weighing quantities, which had been thoroughly dried at 80 ^{o}C and dissolving them in boiled water in calibrated flasks. This calculated concentration was merely used as a check against the standardised EDTA concentration. EDTA solutions were standardised against zinc solutions (primary standard) using pH buffer tablets as an indicator [Merck]. The reported end colour change is from red to green. Adding EDTA in increments of 0.01 cm^3 towards the endpoint and allowing sufficient time for complexation to take place, the following sequence of colour changes was observed; crimson - steel grey - grey green - green. The first permanent colour of green was taken as the endpoint. Standardised EDTA concentrations usually agreed with the calculated concentrations to within 0.2%.

Titrations involving **Ligand 1**, **Ligand 2** and **Ligand 3** were carried out by weighing quantities of recrystallised material on a Sartorius 6-decimal place balance.

Potentiometric investigations involving **Ligand 4** were initially carried out by weighing quantities of material but this failed to give reproducible results for

interactions with metal ions. A stock solution of Ligand 4 was then prepared and standardised against sodium hydroxide. Ligand 4 has four dissociable protons and neutralisation of the third proton resulted in a sharp endpoint. Standardised concentrations were of the order of 1.5% less than that determined by weighing.

The microanalysis of Ligand 4 carried out after drying under vacuum at 30 ^{o}C is as follows:

	%C	%H	%N
Calculated	26.43	4.40	6.17
Observed	26.40	4.35	6.15

The Ligand 4 sample was checked for the presence of other organic impurities by thin layer chromatography using the following solvent systems; (i) 80% ethyl acetate/20% benzene, (ii) methanol and (iii) 20% water/80% metanol. The results showed that Ligand 4 was free from contamination of other organic substances. Ligand 4 was suspected of being hygroscopic and a small quantity was dried over phosphorus pentoxide, (P_2O_5), and weighed after 16 hours and again after 48 hours. The results showed a decrease in mass of 0.5% and 1.3% respectively with the display readings being unstable in both cases suggesting that atmospheric moisture was being absorbed rapidly.

It was then concluded that Ligand 4 was hygroscopic and it was subsequently prepared as a stock solution and standardised against sodium hydroxide. Since ligand 4 has four dissociable protons, titration against a basic solution results in four endpoints. In the above instance, the third endpoint was the sharpest and therefore used to calculate the concentrations of ligand 4 solutions. The third endpoint was subsequently established as the neutralisation of the phosphonic acid functional group (chapter 4).

4-Nitrocatechol (X) was twice recrystalised from distilled water and yielded the following analyses.

	%C	%H	%N
Calculated	46.46	3.22	9.03
Observed	46.60	3.10	9.10

A proton NMR spectrum was determined in D_2O with dioxane as an internal standard. The results were as follows:

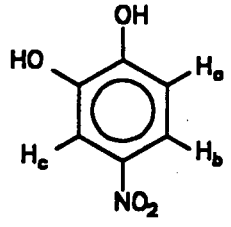


Figure 3.3 4-Nitrocatechol (X)

Doublet, 1H, 6.90, (ortho coupling, 8.8Hz), H_a

Multiplet, 2H, 7.68, H_b and H_c

4-Nitrocatechol was used by weighing quantities for potentiometric investigation.

Solutions containing **manganese(II) ions** were standardised against Titriplex III using eriochrome black T indicator [Sch57]. The reported colour change is red to blue. The observed colour changes were pink - various intensities of purple - purple blue - blue. The first permanent shade of blue was taken as the endpoint.

Solutions containing **iron(II) ions** were freshly prepared every 48 hours under a nitrogen atmosphere and standardised against Titriplex III using salicylic acid as indicator [Che53], [Mer89]. Before titrating in the Titriplex solution, all the Fe^{2+} ions are converted to Fe^{3+} ions [Merck]. The indicators tiron [Merck], 5-

sulphosalicylic acid [Merck] and variamine blue [Sch57] all failed to give clear endpoints making the standardization difficult. The freshly prepared Fe^{2+} solutions were tested for the presence of Fe^{3+} ions using the sensitive potassium thiocyanate test [Fei72]. The results were positive as a maximum of 0.2% Fe^{3+} (specified by Merck) is well within the identification limits of the test.

Solutions containing **iron(III) ions** were prepared in acid solution using 30% suprapur hydrochloric acid (Merck), to prevent hydrolysis of the metal ions. Solutions were standardised against Titriplex III using salicylic acid as indicator [Che53]. The reported endpoint is purple to yellow. The observed endpoint was purple - yellow (with a purple tinge) - yellow. The disappearance of the last purple tinge was taken as the endpoint. The **H^+ ion** content in the Fe^{3+} ion solution was determined by ion exchange. A known volume of Fe^{3+}/H^+ ion solution was passed down an Amberlite IR-120H resin column. Seven to eight bed volumes of previously boiled water was used to elute all the H^+ ions. After four bed volumes had been eluted, the pH of the eluent was close to 7 indicating that most of the acid had already passed down the column. This solution was then standardised against sodium hydroxide. Having previously determined the Fe^{3+} ion concentration, the H^+ ions displaced from the column could be calculated. The H^+ ion concentration originally in the Fe^{3+} solution was then determined.

Solutions containing **cobalt(II) ions** were standardised against Titriplex III using xylenol orange indicator [Merck]. The reported endpoint is violet to yellow. The observed endpoint was violet - violet red - red yellow - yellow. The disappearance of the last shade of red was taken as the endpoint.

Solutions containing **nickel(II) ions** were standardised against Titriplex using murexide indicator [Bas83]. The reported endpoint colour change is yellow to violet.

The endpoint was taken as the disappearance of the last shade of yellow as the solution varied from yellow - yellow with a violet tinge - violet.

Solutions containing **copper(II) ions** were standardised against Titriplex III using fast sulphon black as indicator [Bas83]. The reported endpoint is purple to dark green. The disappearance of the last shade of purple leaving a clear green solution, was taken as the endpoint.

Solutions containing **zinc(II) ions** were prepared as a standard solution by dissolving zinc granules in acidic solution in a calibrated flask. The HCl (PAL Chemicals) content of the solution was determined by standardizing against sodium hydroxide.

3.3.3 CONDITIONING AND CALIBRATION OF ELECTRODES : -

Since sodium chloride was chosen as the background electrolyte, the **calomel electrode** was filled with a 5M NaCl solution. The solubility of NaCl in water is 6.15 moles per dm^3 and it was found that by using an unsaturated solution, crystallisation of NaCl was avoided which in turn prevented any clogging of the frit. This ensured a consistent performance from the calomel electrode.

The **glass electrodes** were always stored in a 0.1M HCl solution. From time to time the HCl solution was replaced and the electrodes were allowed to soak for at least 48 hours before recalibration

At 25 °C, the emf reading, E, of the electrode is related to -log $[H^+]$ as described by equation 3.25. The electrode intercept, E_0, varies with time and by reguarly performing strong acid strong base titrations, valid intercept values were used in all calculations. As previously reported, acid - base data were processed using ESTA. Results of this nature can also be processed by MAGEC [May82].

The two glass electrodes used in this study, Electrode A and Electrode B, were regularly checked to see if they showed Nernstian behaviour. By plotting the observed emf readings against the calculated -log[H^+] values for an acid - base titration, one obtains a plot with a Nernstian slope and an intercept E_o. As presented in figure 3.4, both electrodes behaved linearly even below pH values of 2.

Electrodes are also prone to fluctuation and drifting. Extreme care was taken in this regard to ensure that the electrodes behaved in a manner preventing the accumulation and processing of erroneous data.

3.3.4 APPARATUS : -

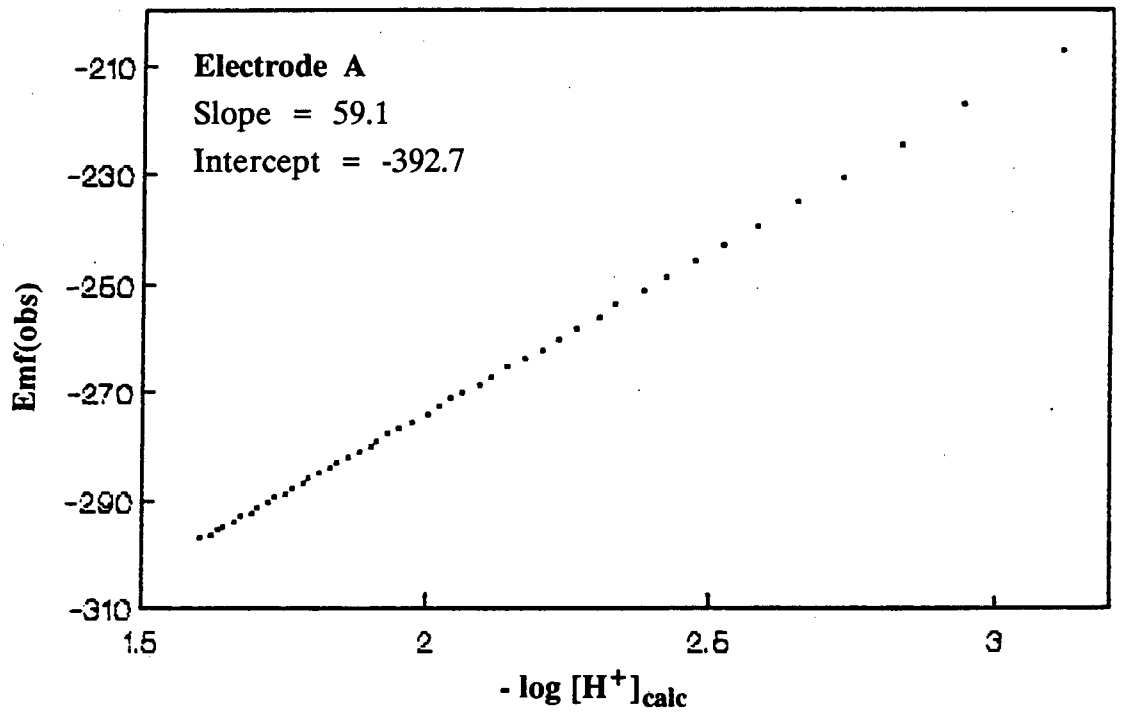
Titration vessel:-	Metrohm EA876-20, double walled
Glass electrodes:-	Metrohm EA109
Calomel electrode:-	Metrohm EA404
Burette:-	Radiometer ABU80 Autoburette
pH Meter:-	Radiometer PHM64

3.3.5 EXPERIMENTAL CONDITIONS : -

The laboratory temperature was controlled by an air conditioner and fixed at 20 °C.

All glassware used such as volumetric flasks and pipettes were thoroughly cleaned by soaking in 10% HCl solutions and then calibrated by accurately weighing the volumes of water delivered. The water temperature was measured and the volumes were corrected to give readings at the laboratory temperature of 20 °C [Bas83].

In order to exclude carbon dioxide and oxygen from the reaction vessel, a purified nitrogen atmosphere was maintained. A high purity nitrogen gas, (Afrox), was first



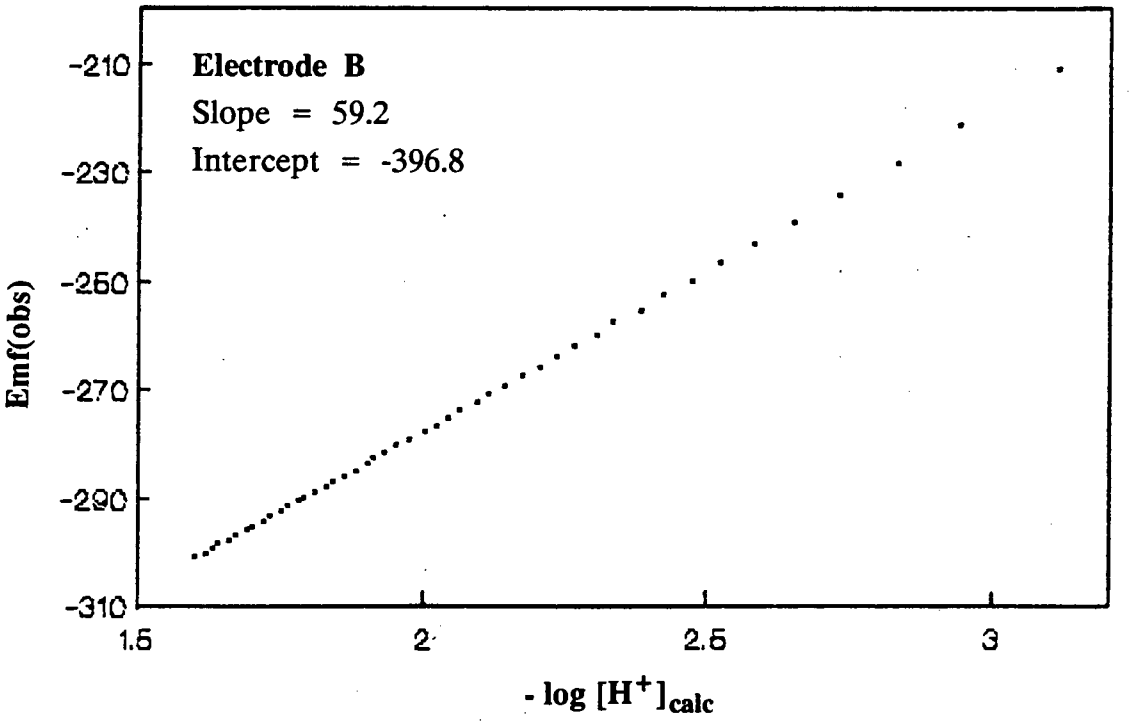


Figure 3.4 Plot of Emf (observed) vs -log[H^+] (calculated) for the glass electrodes used in this study.

passed through a series of solutions for further purification and these are in sequence:-

1. 50% KOH, (potassium hydroxide), solution to remove carbon dioxide.
2. Fieser's solution [Alb62] to remove oxygen.
3. Boiled distilled water.
4. An empty bottle (trap).
5. A 0.1M sodium chloride solution thermostatted at 25 °C.

The nitrogen gas was released from the air tight reaction vessel via a trap containing 0.1M sodium chloride solution which prevented the back diffusion of atmospheric gases.

Water thermostatted at 25 °C was circulated through the walls of the reaction vessel and titrations were only commenced once the reaction solution had reached this temperature.

3.3.6 POTENTIOMETRIC INVESTIGATIONS : -

In the examination of a metal-ligand-proton system, in most cases two titrations were carried out at each of the following ligand : metal ratios 1 : 2, 1 : 1, 3 : 2, 2 : 1, 5 : 2 and 3 : 1. Owing to the high denticity of the ligands used in this study, it was felt that higher ligand : metal ratios such as 5 : 1 and 10 : 1 would serve no purpose. In each of these titrations at a specific ratio, different, independently standardised ligand and metal solutions as well as different electrodes were used. Overlapping of experimental curves in the aforementioned cases thus ensured that the system was reproducible.

Before commencing any titration, the emf value of the HCl solution, E_{HCl}, was measured and compared with the E_{HCl} value of the acid-base titration used to determine E_o. Any difference in value affects E_o but this usually differed by no more than 0.2 mv. This was regarded as acceptable and although used as a check from time to time, E_o values determined in the initial acid-base titrations were used in subsequent computations.

The HCl and metal solutions were pipetted into the reaction vessel. The ligand solution was either weighed or pipetted if prepared as a stock solution. The solution was gently stirred with a teflon coated magnetic stirrer as vigorous stirring led to fluctuation of emf readings.

The titration vessel was fitted with a glass electrode, a calomel electrode, a thermometer and a burette delivery tube fitted with a non-return valve and allowed to equilibrate to a temperature of 25 ^oC under a purified nitrogen atmosphere. Figure 3.5 shows a potentiometric titration vessel with the necessary accessories. All titrations were carried out by delivering predetermined quantities of sodium hydroxide to the reaction vessel. Sodium hydroxide concentrations were such that roughly 80 to 120 experimental points were recorded per titration at increments of 0.1 cm^3 to 0.15 cm^3.

Reaction solutions were carefully monitored during the titrations to check for the precipitation of metal hydroxides or other products. Samples of all solutions were kept after the titrations for observation. The solutions were allowed to settle since fine precipitates are not easily detectectable in a stirring solution. Fortunately, precipitation never occured in any of the systems investigated in this study.

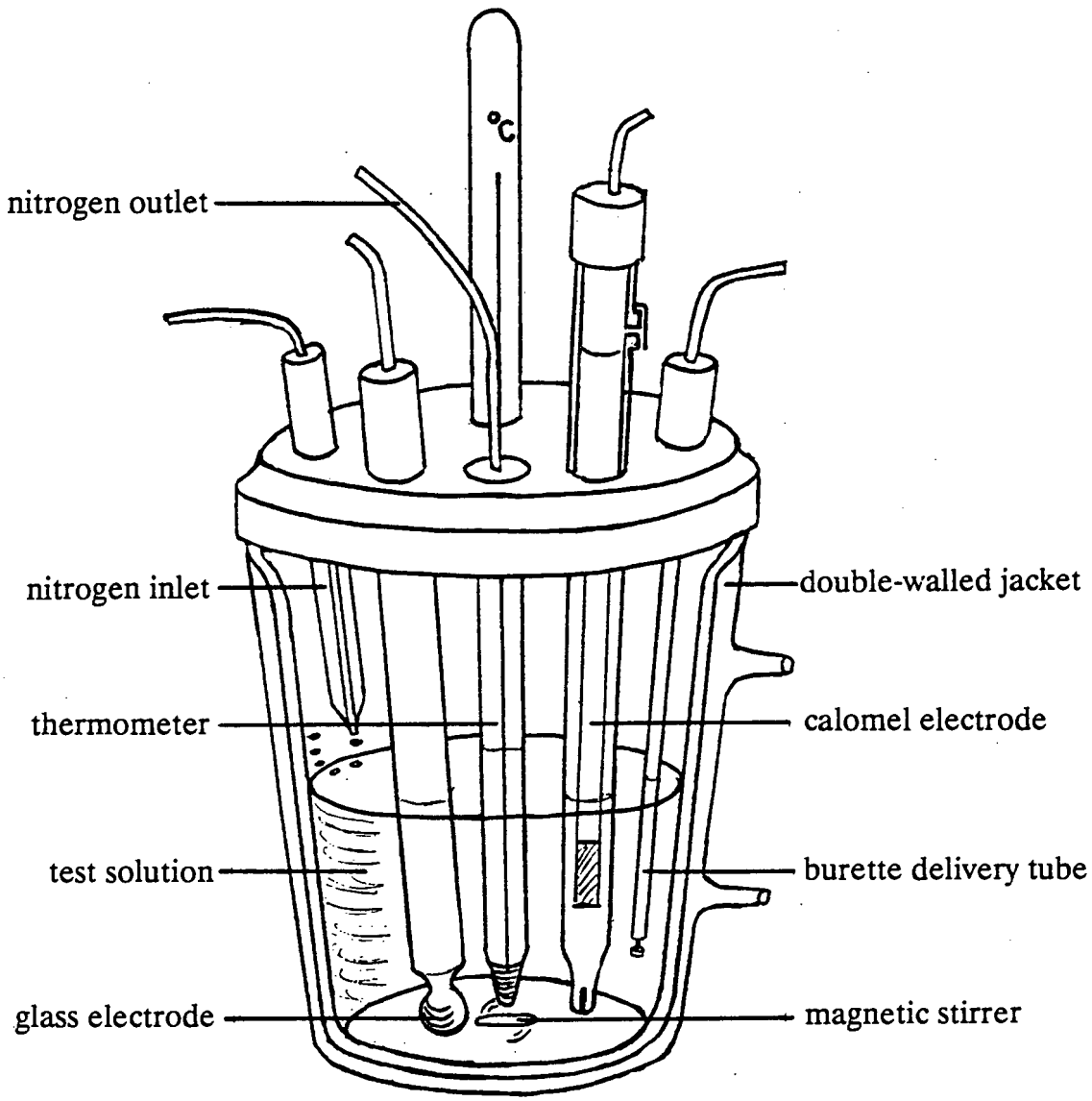


Figure 3.5 Diagram of a potentiometric titration vessel with accessories

The burette and pH meter were interfaced with a Bondwell personal computer which recorded the emf reading and total volume of titrant added at each experimental point. Data are simultaneously recorded on floppy disc as well as on paper allowing one to check immediately for discrepancies between observed and recorded readings.

A common source of erroneous data is a failure to allow the reaction solution to reach equilibrium, after the addition of a sodium hydroxide increment, before recording the emf reading [Mar88]. Computer software written by researchers in this laboratory allows for emf readings to be compared after a fixed delay time to check whether equilibrium has been reached. If the two readings are not the same, a further time interval is allowed for equilibrium to be reached before recording the emf value and adding the next titre increment. Typically, a maximum delay time of 60 seconds is allowed for equilibrium to be reached after an increment of sodium hydroxide has been delivered. By selecting a delay time of 10 seconds, one allows for six successive comparisons of emf readings to be made before recording takes place. Failure to reach equilibrium within 60 seconds, (reasonable for the addition of 0.1 cm^3 to a total volume of between 30 to 40 cm^3), allows for an emf and titre reading to be recorded with a "maxtime". Titrations showing an excess of "maxtimes" are discarded although this is more the exception than the norm.

3.4 COMPUTATIONAL PROCEDURE

The experimental data collected from all the potentiometric investigations in this study, were processed using the appropriate task and module of ESTA. Following is a description of the computational procedure used for analysing the potentiometric data of a metal-ligand-proton system.

The electrode intercept, E_o, and the dissociation constant of water, pKw, were refined from data accumulated from HCl-NaOH titrations. It is important that these are the same solutions used in the metal complexation studies as electrode intercepts vary all the time. The refined values of pK_w were always in the range 13.69 to 13.72.

Before the metal ion speciation of any system can be established, the ligand protonation constants have to be determined in a separate potentiometric study. The dissociation constant of water, the electrode intercept and the protonation constants are fixed in any computation of a metal-ligand-proton system and so too are the metal hydrolysis constants for the specific metal ion under investigation. Table 3.1 lists the hydrolysis constants for the various metal ions at 25 ^oC and I = 0.1 $mol.dm^{-3}$ [Bae76] as used in the respective computations.

The initial volume of the reaction solution as well as the concentrations of HCl, NaOH, ligand and metal ions are also required. The electrode slope was always fixed at its theoretical value of 59.16 since the glass electrodes generally behaved very well and deviations from this value as obtained from calibration curves were always small. The number of dissociable protons on the ligand is also specified. This represents the basic requirements for the execution of any ESTA task.

Table 3.1

Metal hydrolysis constants used in this study [Bae76]

T = 25 °C, I = 0.1 mol.dm^{-3}.

Hydrolysis reaction								log β_{por}
Mn^{2+}	+	H_2O	$\rightleftharpoons$	$Mn(OH)^+$	+	H^+		-10.79
Fe^{2+}	+	H_2O	$\rightleftharpoons$	$Fe(OH)^+$	+	H^+		-9.71
Fe^{2+}	+	$2H_2O$	$\rightleftharpoons$	$Fe(OH)_2$	+	$2H^+$		-20.82
Fe^{2+}	+	$3H_2O$	$\rightleftharpoons$	$Fe(OH)_3^-$	+	$3H^+$		-31.00
Fe^{3+}	+	H_2O	$\rightleftharpoons$	$Fe(OH)^{2+}$	+	H^+		-2.56
Fe^{3+}	+	$2H_2O$	$\rightleftharpoons$	$Fe(OH)_2^+$	+	$2H^+$		-6.20
$2Fe^{3+}$	+	$2H_2O$	$\rightleftharpoons$	$Fe_2(OH)_2^{4+}$	+	$2H^+$		-2.84
Co^{2+}	+	H_2O	$\rightleftharpoons$	$Co(OH)^+$	+	H^+		-9.85
Ni^{2+}	+	H_2O	$\rightleftharpoons$	$Ni(OH)^+$	+	H^+		-10.06
Cu^{2+}	+	H_2O	$\rightleftharpoons$	$Cu(OH)^+$	+	H^+		-7.85
$2Cu^{2+}$	+	$2H_2O$	$\rightleftharpoons$	$Cu_2(OH)_2^{2+}$	+	$2H^+$		-10.40
Zn^{2+}	+	H_2O	$\rightleftharpoons$	$Zn(OH)^+$	+	H^+		-9.15
$2Zn^{2+}$	+	H_2O	$\rightleftharpoons$	$Zn_2(OH)^{3+}$	+	H^+		-8.89

If any or all of the parameters are to be weighted in subsequent calculations, the necessary standard deviations may be supplied and the weighting block activated. Initially, experimental metal formation, Z_M^{exp}, and metal deprotonation, Q_M^{exp}, curves are determined from the experimental data. The protonation formation, metal formation and metal deprotonation curves are all used to identify the major species in solution. For example, when the metal formation curves of a metal-ligand system at different metal to ligand ratios overlap, one can assume that only

mononuclear binary species of the type ML_n have formed. If the highest value of Z_M^{exp} levels off at an integer value, q, then the highest mononuclear complex formed is ML_q. If Z_M^{exp} reaches a maximum value of say 1.5, one can safely assume that an ML_2 species has formed to some extent. The presence of hydroxy species is indicated by the back-fanning pattern of the Z_M^{exp} vs -log[L] curves at high pH. Systems that include protonated species show high Z_M^{exp} values at low pH which tend to dip as the pH is increased before increasing to a maximum again.

The metal deprotonation curve is particularly useful in determining the stoichiometry of protonated species. From the expression

$$r = (q \times n) - (Q_M^{exp} \times p)$$

one can determine the average stoichiometric coefficient, r, (assuming that the complex is fully formed) for any given metal (M) and ligand (L) stoichiometry, p and q. For example, if p and q are both 1, n = 2 and $Q_M^{exp} = 1$, then r = 1 indicating the presence of an MLH complex. If Q_M^{exp} exceeds n at low or intermediate pH, the system should be examined for ML_2 and ML_3 species. At high pH values this indicates the presence of hydroxy species.

Initial estimates of the possible major species are obtained using the BETA task of the simulation module of ESTA, ie ESTA1. The initial estimates are then refined using the OBJT task of the optimization module ESTA2. OBJT permits the optimization of parameters using an unweighted least squares objective function based on emf residuals.

By calculating theoretical metal formation and metal deprotonation curves and comparing these with the experimental curves, one can establish whether any of the

major species have been omitted. An R_f value between 0.01 and .015 usually indicates that all the major species have been found.

Once the major species have been established, their stability constants are temporarily fixed and the metal formation and metal deprotonation curves are carefully scanned for likely minor species. The BETA task is used again to determine rough estimates of likely minor species and if any are found, these are refined together with the major species using OBJT. If the BETA task is unable to provide an estimate for the stability constant of a minor species, it responds by producing a default value of 111.11. If it does provide an estimate, this is no guarantee that either of the optimization tasks will in fact refine a constant. Refinement of a constant for a minor species is also no guarantee ~~the~~ that the complex is an integral part of the model. At this stage of the modelling process, the principles of coordination chemistry should be borne in mind as "computer complexes" could quite easily find their way into the model. This does not imply that one should overlook these principles when looking for the major species, except that major species almost always make good chemical sense.

The ERR% task of ESTA determines the percentage, (%), of any complex at each titration point using simulated emf values and volumes. The species are expressed as a % of the total concentration of the metal ion. A good model usually indicates an excellent agreement (within 2%) between the % of each complex based on emf values and on volume at each experimental point. The ligands used in this study all complex strongly with metal ions and at 1:1 ratios, all of the ligand is eventually bound to metal at some pH value. Consequently, any complex consisting of less than 5% of the total metal metal was either a computer complex or a minor species having little or no effect on the objective function and R_f value of the model. Such species were discarded from the model.

The OBJE task of ESTA2 optimizes parameters using a weighted or unweighted least squares objective function based on emf residuals. This task is now used to further refine the stability constants of the chosen model. By specifying standard deviations, poor experimental points in the unbuffered region of the titrations, have less effect on the optimized values of parameters [May88b]. The standard deviations used in this study are as follows:

Metal ion concentration:-	0.2%
All other concentrations:-	0.1%
Initial volume:-	0.1%
Electrode intercept, E_o:-	0.1 mv
Electrode slope:-	0.05 mv/pH
Titre volume:-	0.005 cm^3
emf readings:-	0.1 mv

In all potentiometric investigations in this study the R-factor, R_f, for the final model obtained by refining the stability constants using OBJE with weighting, are all well below 0.01 and comparisons between experimental and theoretical metal formation and metal deprotonation curves are all reasonable and acceptable.

By refining the stability constants for all final models on their own, the random errors of all other parameters are absorbed into these constants. Further refinement of constants with these parameters, eg. ß's and E_o's, ß's, E_o's and $[H^+]$, ß's, E_o's, $[H^+]$ and [L] etc, removes these errors from the stability constants and improves their refined values. This process was continued until the parameters were found to be correlated with the stability constants or when the refinement process broke down.

The final model in each of the potentiometric studies was chosen using the criteria, R_f, U, Z_H, Z_M and Q_M. In cases where models differed in a minor species with no improvement in the statistical data, Ockham's razor was applied and the simpler model was chosen [Tel80].

Figure 3.6 summarises the computational procedure used for analysing potentiometric data of a metal-ligand-proton system as a flowchart.

The procedure followed in the ligand protonation studies was similar to that described above except that the QBAR task is only used for systems containing metal ions. It is also unnecessary to use the BETA task for obtaining estimates of the protonation constants since the optimization module is very robust and will refine these constants from virtually any starting value supplied.

Results of each of the metal-ligand-proton systems studied, have been tabulated. β_{pqr} has been defined as in equation 3.7. In the protonation studies, β_{01r} has been defined and is in fact a special case of β_{pqr}, with p=0 and q=1. A stepwise protonation constant, K_n, has been defined as

$$K_n = [LH_n]/[LH_{n-1}][H] \qquad \text{...eq. 3.29}$$

In the presentation of figures in this thesis, theoretical protonation, metal formation and metal deprotonation curves are represented as a solid line for comparison with their experimental counterparts which are indicated as symbols. For each of the chemical systems investigated, the total number of data points used to refine the stability constants, is included as part of the statistical analysis in the tabulated results. For the purposes of plotting, duplicate titrations have been omitted from the

figures presented and those titration curves which have been presented, have alternate points deleted to facilitate the comparison of experimental and theoretical data. Z_H, Z_M and Q_M have been plotted against -log[H^+], -log[Ligand] and -log[H^+] respectively where [ ] is expressed in moles per dm^3.

Speciation plots of the percentage of metal ion (or ligand) as a function of pH have also been generated from the refined stability (protonation) constants. The pH range used for the presentation of the speciation plots often exceeds the actual experimental range in which the systems were studied. The experimental pH range for each system investigated, has been tabulated.

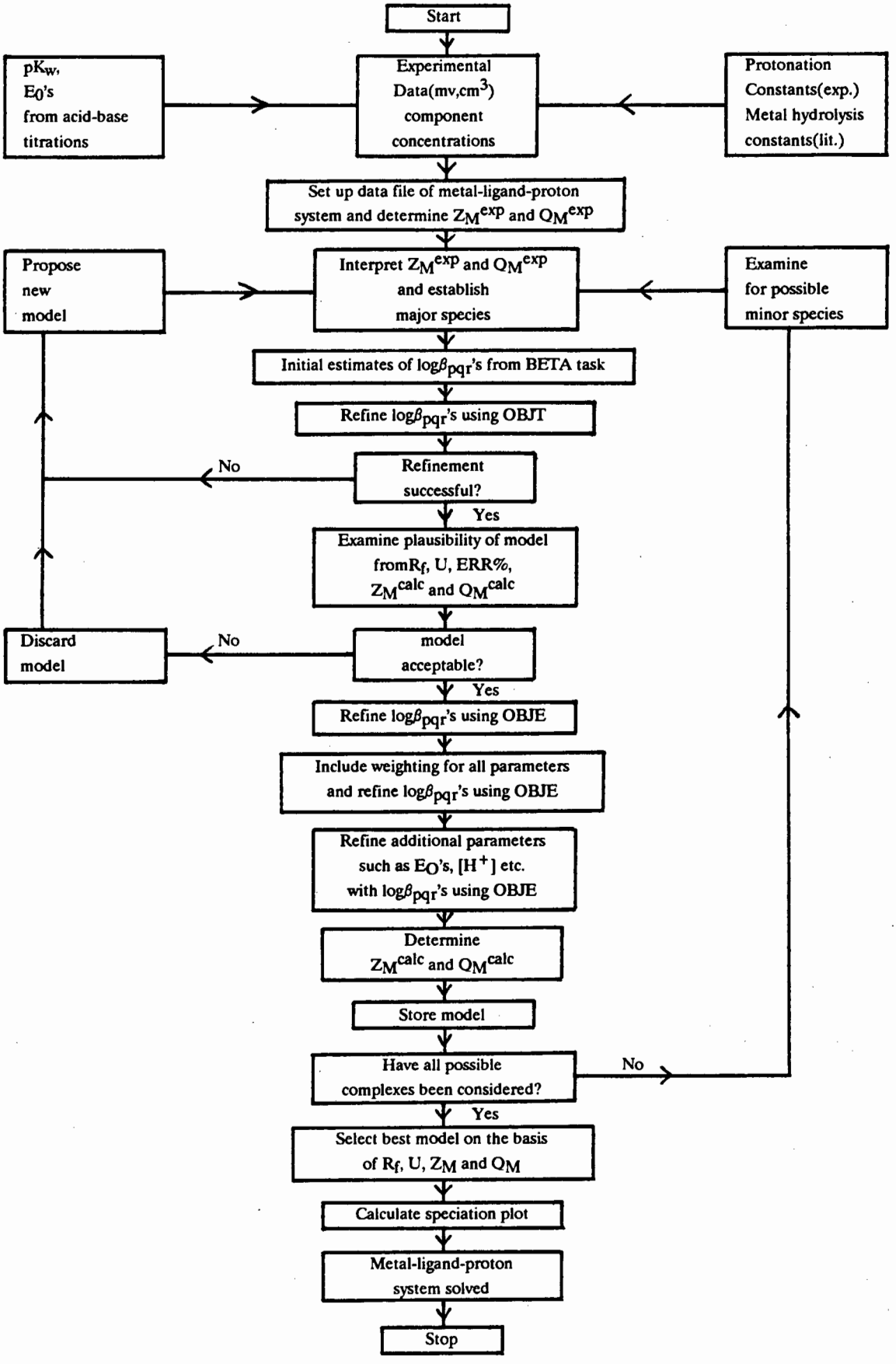


Figure 3.6 Flowchart describing the computational procedure used to analyse potentiometric data for metal-ligand-proton systems.

3.5 RESULTS AND DISCUSSION

3.5.1 LIGAND 1 PROTONATION

N - Phosphonomethyl glycine has been defined as a triprotic ligand, LH_3, in this study and its protonation behaviour has been examined in the pH range 2 to 11. The experimental and theoretical proton formation curves presented in figure 3.7 show a satisfactory agreement. The stepwise and overall protonation constants together with the relevant statistics are reported in table 3.2. The results obtained in this study compare favourably with those obtained by Motekaitis and Martell [Mot85] who examined the protonation of Ligand 1 under the same conditions of temperature and ionic strength but in a slightly narrower pH range, estimated to be 2.7 to 10.8 from the equilibrium curves presented. The species distribution curves of ligand 1 against pH are presented in figure 3.8 and show four distinct regions corresponding to the various states of protonation.

Table 3.2

Statistical analysis and logarithms of the stepwise, $\log K_n$, and overall, $\log \beta_{01r}$, protonation constants of Ligand 1, determined at 25 °C and 0.1 mol.dm^{-3} (Na^+)[Cl^-].

Complex	pqr	$\log K_n$	$\log \beta_{01r}$	Std. dev.
LH	011	10.06	10.06	0.0058
LH_2	012	5.42	15.48	0.0110
LH_3	013	2.11	17.59	0.0258

Objective Function:-	3.73×10^1
R-factor, R_f:-	0.00412
R-limit, R_l:-	0.00068
No of titrations:-	5
No of data points:-	564
[Ligand] range, mol.dm^{-3}:-	0.009957 - 0.015051
pH range:-	2.0 - 11.0

Literature Data

Constants determined potentiometrically at 25 °C and I = 0.1 mol.dm^{-3} KNO_3 [Mot85].

Complex	pqr	$\log K_n$	$\log \beta_{01r}$	Std. dev.
LH	011	10.14	10.14	-
LH_2	012	5.46	15.60	-
LH_3	013	2.23	17.83	-

Figure 3.7 Experimental (symbols) and theoretical (solid line) proton formation curves for Ligand 1.

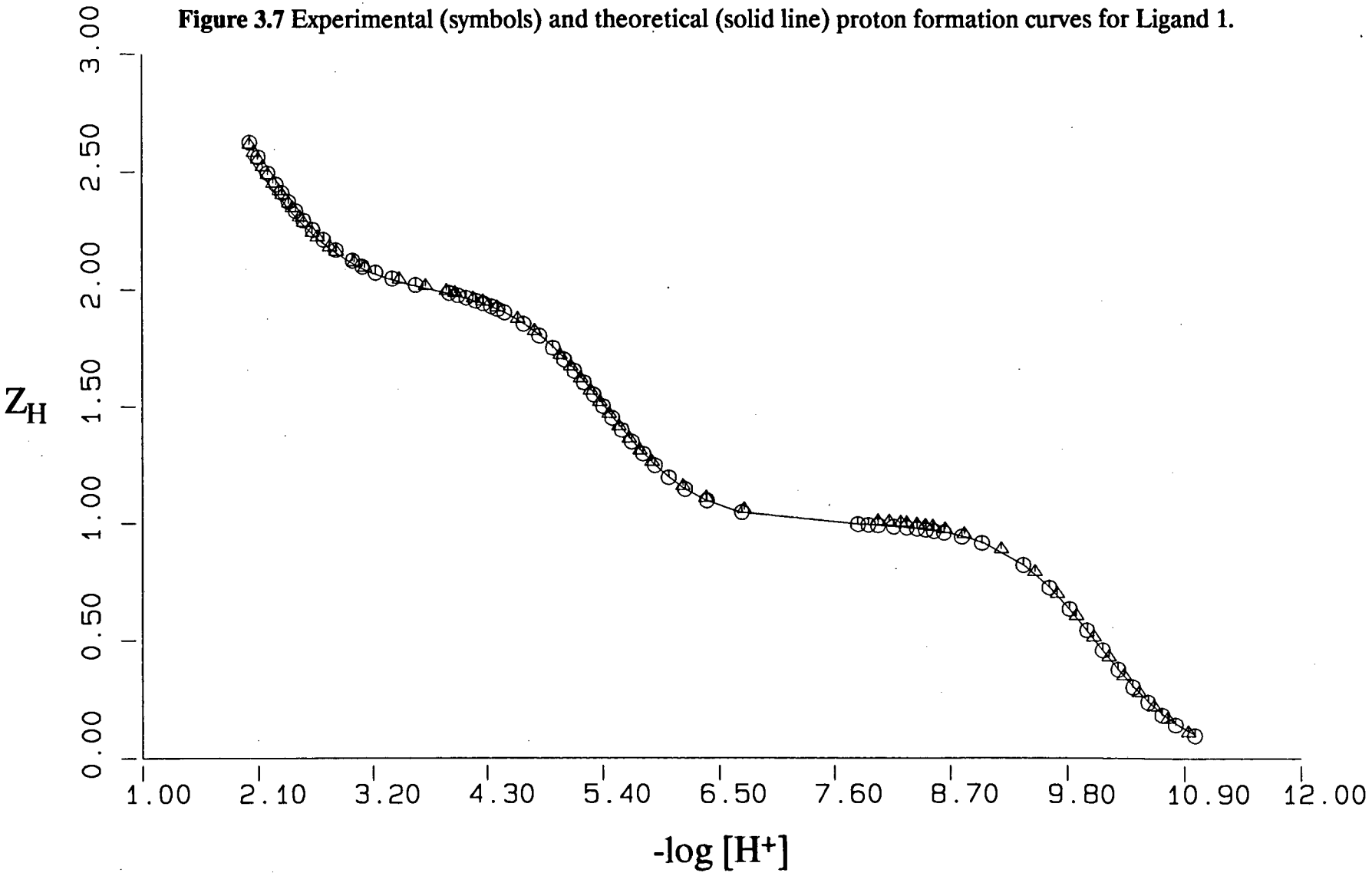
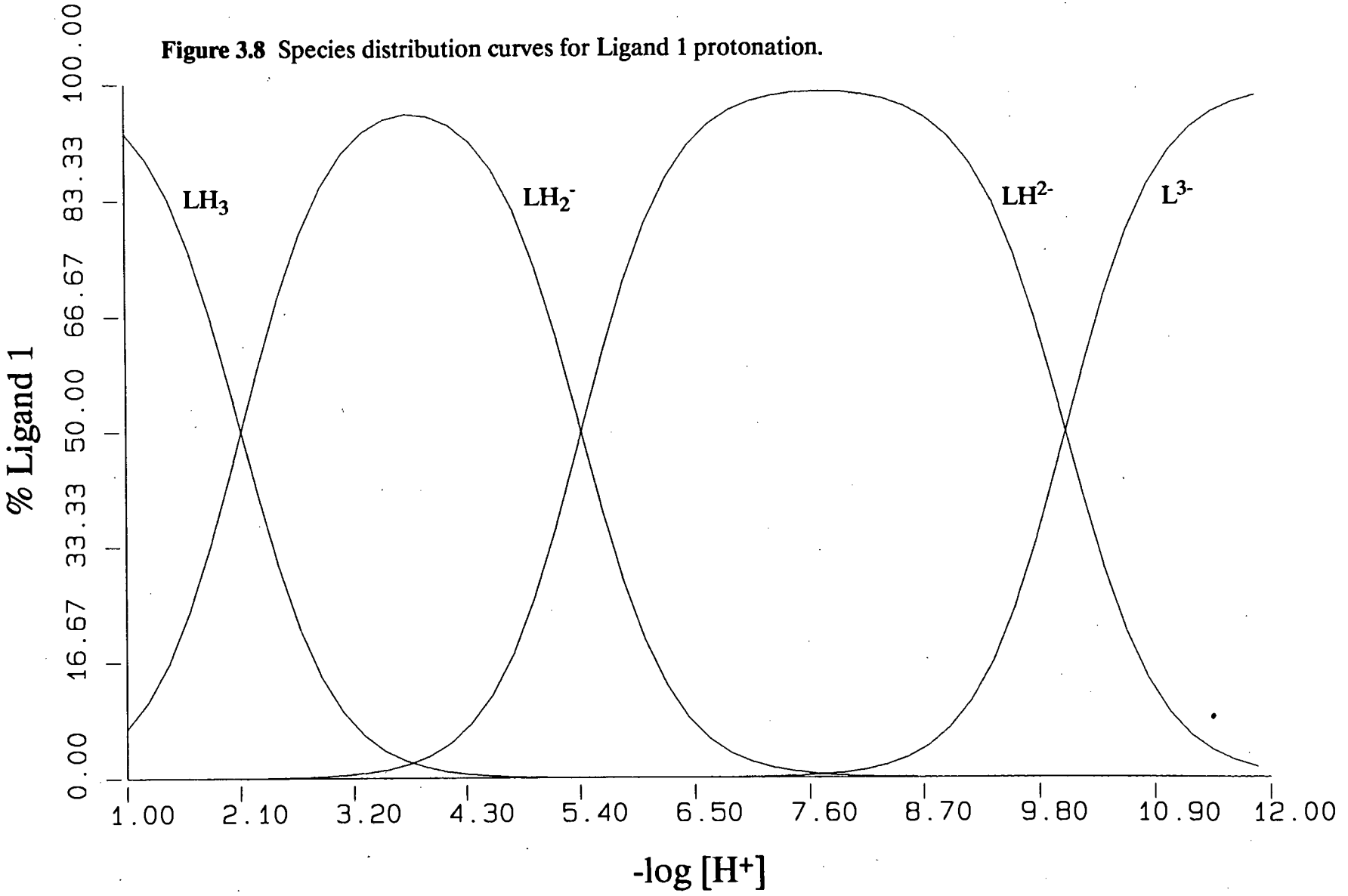


Figure 3.8 Species distribution curves for Ligand 1 protonation.



3.5.2 LIGAND 2 PROTONATION

N, N' - [Phosphinicobis(methylene)] bisglycine has been defined as a triprotic ligand, LH_3, and the stepwise and overall protonation constants determined from experimental data in a pH range of 2 to 11 are presented in table 3.3. The experimental and theoretical proton formation curves presented in figure 3.9 show a satisfactory comparison. The speciation curves of ligand 2 are presented in figure 3.10 and show four clearly defined regions.

Table 3.3

Statistical analysis and logarithms of the stepwise, $\log K_n$, and overall, $\log \beta_{01r}$, protonation constants of Ligand 2, determined at 25 °C and 0.1 mol.dm^{-3} $(Na^+)[Cl^-]$.

Complex	pqr	$\log K_n$	$\log \beta_{01r}$	Std. dev.
LH	011	9.00	9.00	0.0055
LH_2	012	6.55	15.55	0.0083
LH_3	013	2.10	17.65	0.0242

Objective Function:-	5.64×10^0
R-factor, R_f:-	0.00211
R-limit, R_l:-	0.00091
No of titrations:-	4
No of data points:-	138
[Ligand] range, mol.dm^{-3}:-	0.001832 - 0.019290
pH range:-	2.0 - 10.8

Figure 3.9 Experimental (symbols) and theoretical (solid line) proton formation curves for Ligand 2.

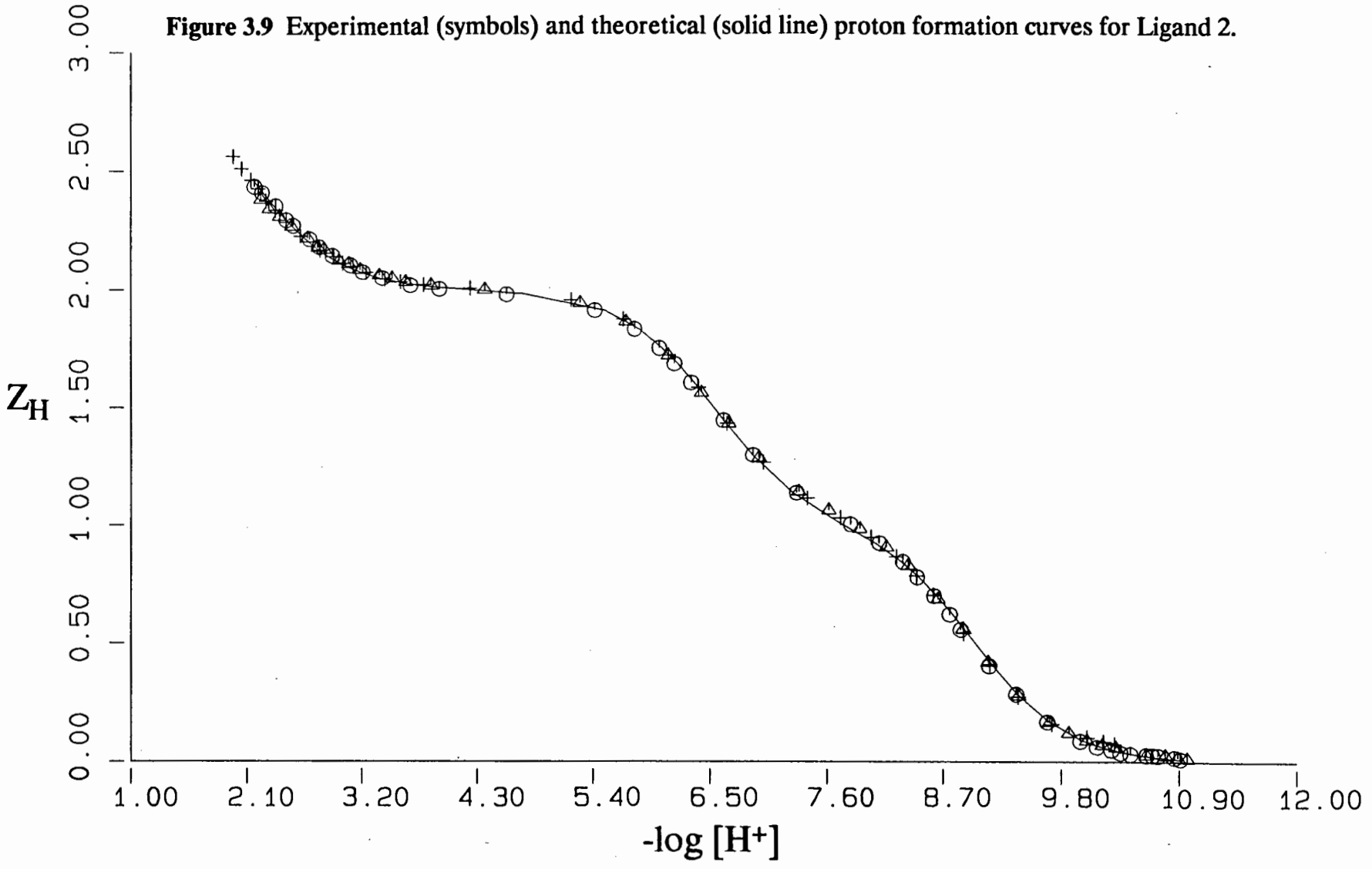


Figure 3.10 Species distribution curves for Ligand 2 protonation.

3.5.3 LIGAND 3 PROTONATION

N, N - bis(Phosphonomethyl) glycine has five dissociable protons and has thus been defined as a pentaprotic acid. Its protonation behaviour has been studied in the pH range 1.7 to 11.4. The experimental data points acrued from the pH region below 2 were found to be reproducible for all the titrations performed. The refined protonation constants are presented in table 3.4 and the experimental and theoretical proton formation curves are presented in figure 3.11. The species distribution curves for ligand 3 are presented in figure 3.12 and show a percentage of 30 to 35% for the LH_5 species at a pH of 1.7.

The results obtained in this study compare favourably with that reported in the literature, Table 3.4 [Wes65], the only discrepancies being between the first and the last protonation constants. Westerback et. al. conducted their protonation studies in the estimated pH ranges of 2.5 to 11.3. Figure 3.12, although determined from the protonation constants of this study, show that at pH 2.5, the major species in solution are LH_4 and LH_3 with LH_5 effectively at zero. This suggests that there must be some uncertainly in the literature value of the last protonation constant. The difference between the first protonation constant as determined in this study and that reported in the literature is not easy to explain.

Table 3.4

Statistical analysis and logarithms of the stepwise, $logK_n$, and overall, $log\beta_{01r}$, protonation constants of Ligand 3, determined at 25 °C and 0.1 mol.dm^{-3} $(Na^+)[Cl^-]$.

Complex	pqr	$logK_n$	$log\beta_{01r}$	Std. dev.
LH	011	11.19	11.19	0.0031
LH_2	012	6.40	17.59	0.0038
LH_3	013	5.02	22.61	0.0040
LH_4	014	2.10	24.71	0.0061
LH_5	015	1.42	26.13	0.0102

Objective Function:-	8.90×10^1
R-factor, R_f:-	0.00535
R-limit, R_l:-	0.00057
No of titrations:-	6
No of data points:-	770
[Ligand] range, mol.dm^{-3}:-	0.005038 - 0.012498
pH range:-	1.7 - 11.4

Literature Data

Constants determined potentiometrically at 25 °C and I = 0.1 mol.dm^{-3} KNO_3 [Wes65].

Complex	pqr	$logK_n$	$log\beta_{01r}$	Std. dev.
LH	011	10.80	10.80	-
LH_2	012	6.37	17.17	-
LH_3	013	5.01	22.18	-
LH_4	014	2.00	24.18	-
LH_5	015	1.73	25.91	-

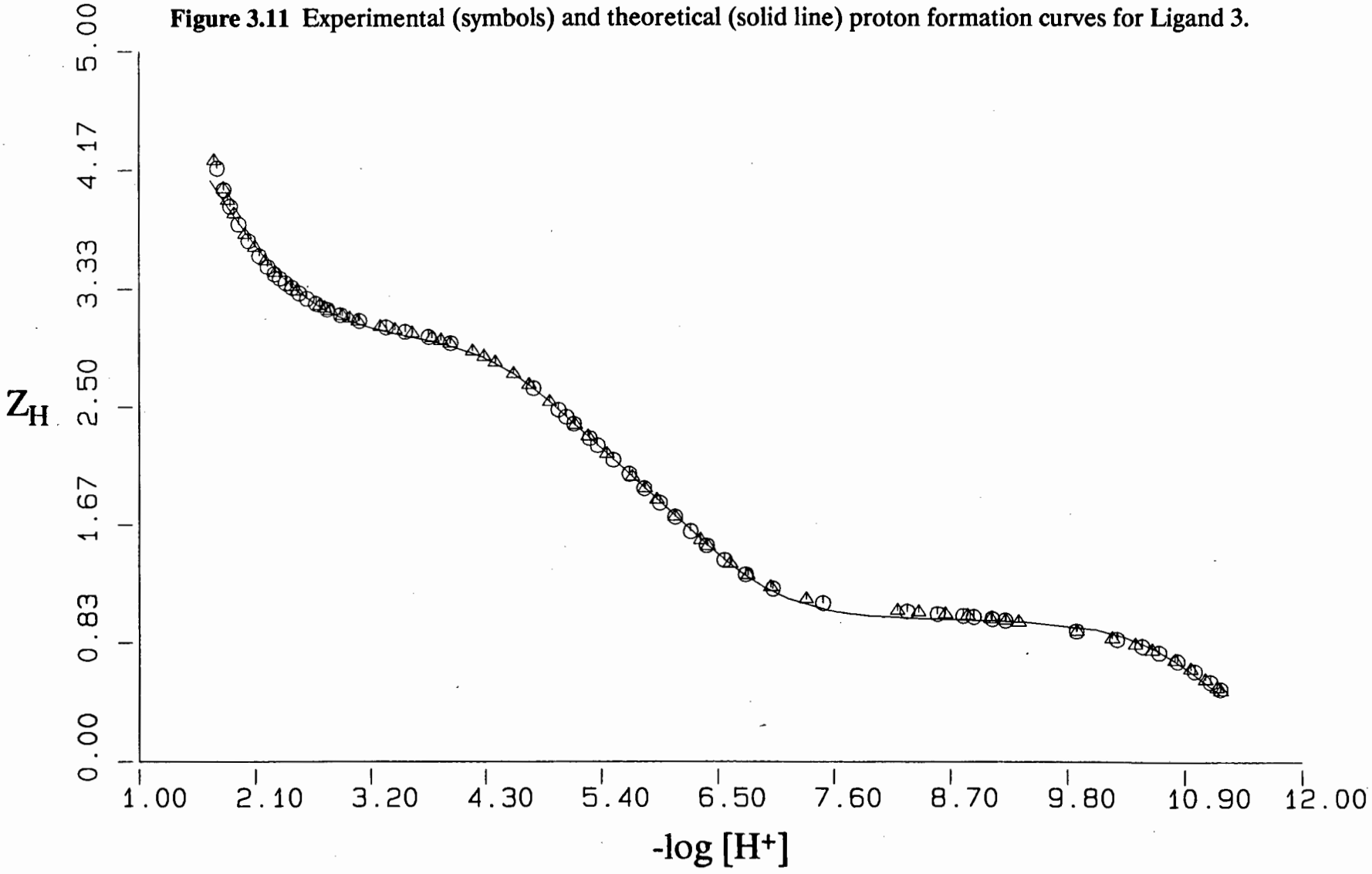
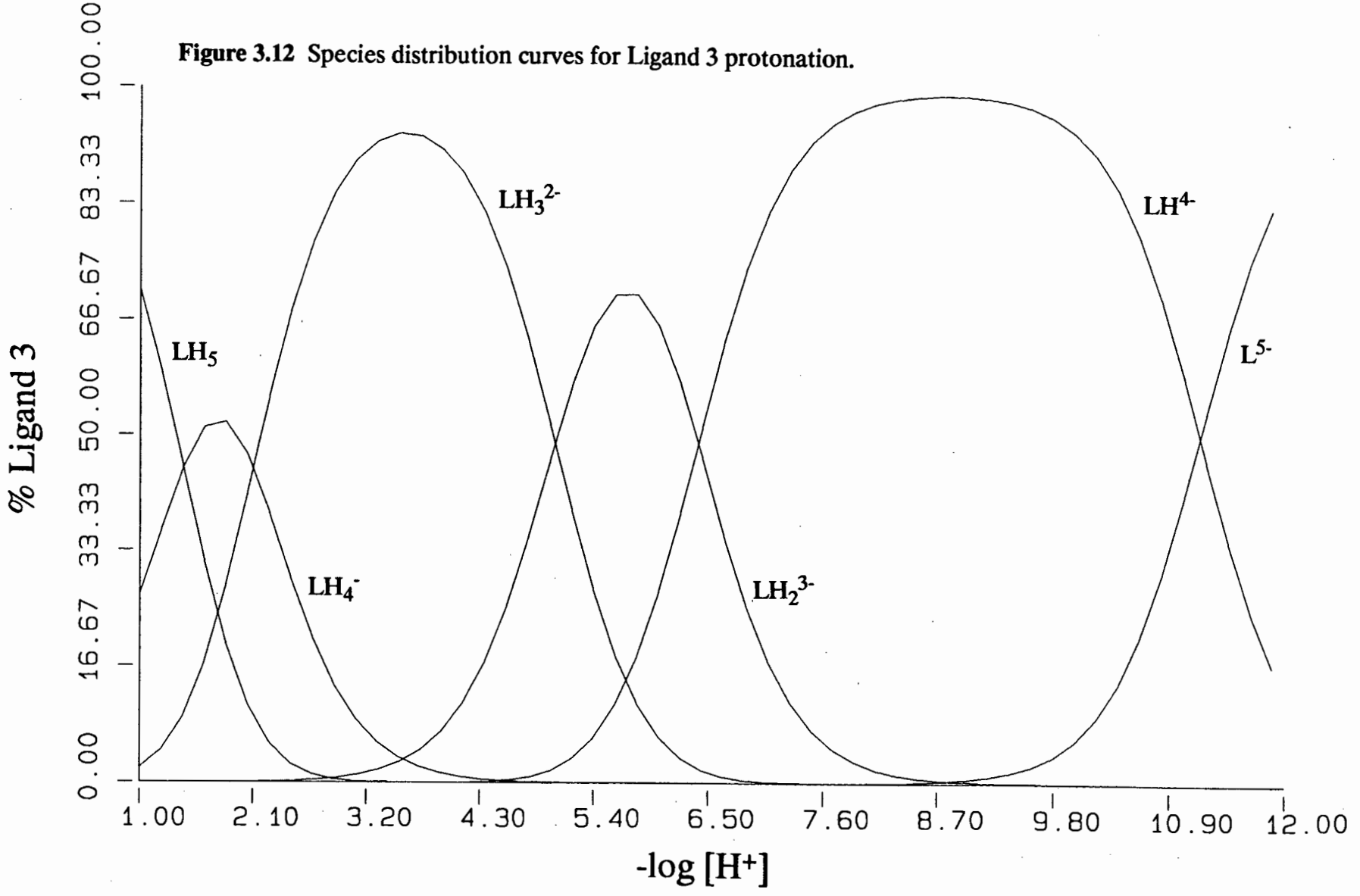


Figure 3.11 Experimental (symbols) and theoretical (solid line) proton formation curves for Ligand 3.

Figure 3.12 Species distribution curves for Ligand 3 protonation.



3.5.4 LIGAND 4 PROTONATION

N - (Phosphonomethyl)iminodiacetic acid has been defined as a tetraprotic acid and its stepwise and overall protonation constants are reported in table 3.5. Literature constants for ligand 4 have been tabulated and these compare favourably with the results of this study. The experimental and theoretical proton formation curves are presented in figure 3.13 and show a good agreement. The experimental pH range during this investigation was 1.7 to 11.4. The distribution of the various protonated forms of Ligand 4 are presented in figure 3.14 and it shows that the species LH_2 and LH predominate over most of the pH range studied.

The protonation results reported here differ slightly from those previously reported by Dhansay et. al. [Dha90]. Previous results were obtained by weighing quantities of Ligand 4 for potentiometric investigation but during studies of its interactions with metal ions, it was established that Ligand 4 is hygroscopic (see chapter 3.3.2). The results reported in table 3.5 have been determined from stock solutions of Ligand 4 and have been used as constants in the potentiometric studies with various metal ions.

Table 3.5

Statistical analysis and logarithms of the stepwise, $\log K_n$, and overall, $\log \beta_{01r}$, protonation constants of Ligand 4, determined at 25 °C and 0.1 mol.dm^{-3} (Na^+)[Cl^-].

Complex	pqr	$\log K_n$	$\log \beta_{01r}$	Std. dev.
LH	011	10.11	10.11	0.0016
LH_2	012	5.55	15.66	0.0024
LH_3	013	2.30	17.96	0.0036
LH_4	014	1.48	19.44	0.0061

Objective Function:-	6.37×10^0
R-factor, R_f:-	0.00117
R-limit, R_l:-	0.00047
No of titrations:-	4
No of data points:-	348
[Ligand] range, mol.dm^{-3}:-	0.003267 - 0.003310
pH range:-	1.7 - 11.4

Literature Data

Constants determined potentiometrically at 25 °C and I = 0.1 mol.dm^{-3} KNO_3 [Mot80].

Complex	pqr	$\log K_n$	$\log \beta_{01r}$	Std. dev.
LH	011	10.29	10.29	0.02
LH_2	012	5.57	15.86	0.02
LH_3	013	2.44	18.30	0.02
LH_4	014	1.20	19.50	0.02

Figure 3.13 Experimental (symbols) and theoretical (solid line) proton formation curves for Ligand 4.

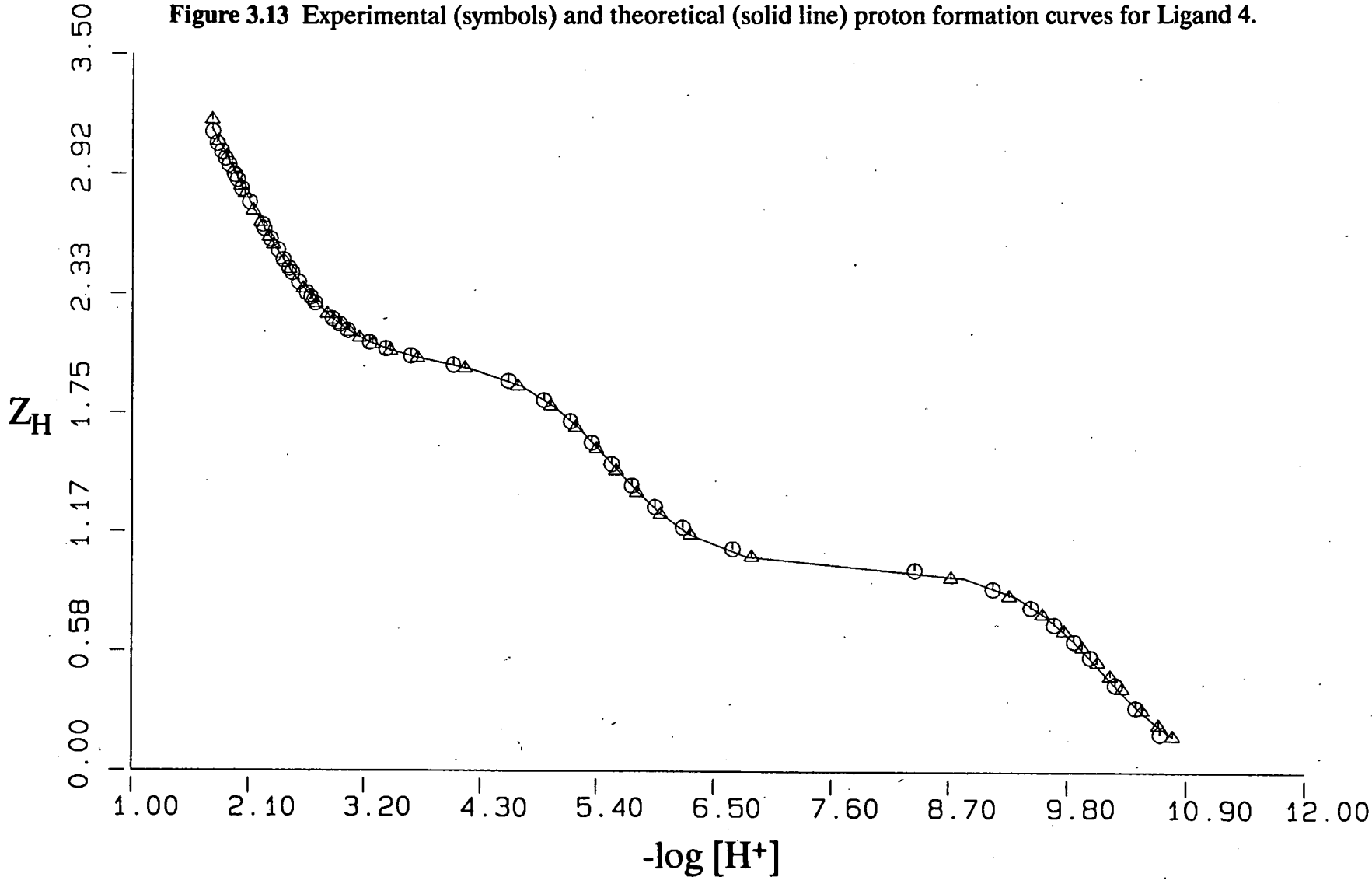
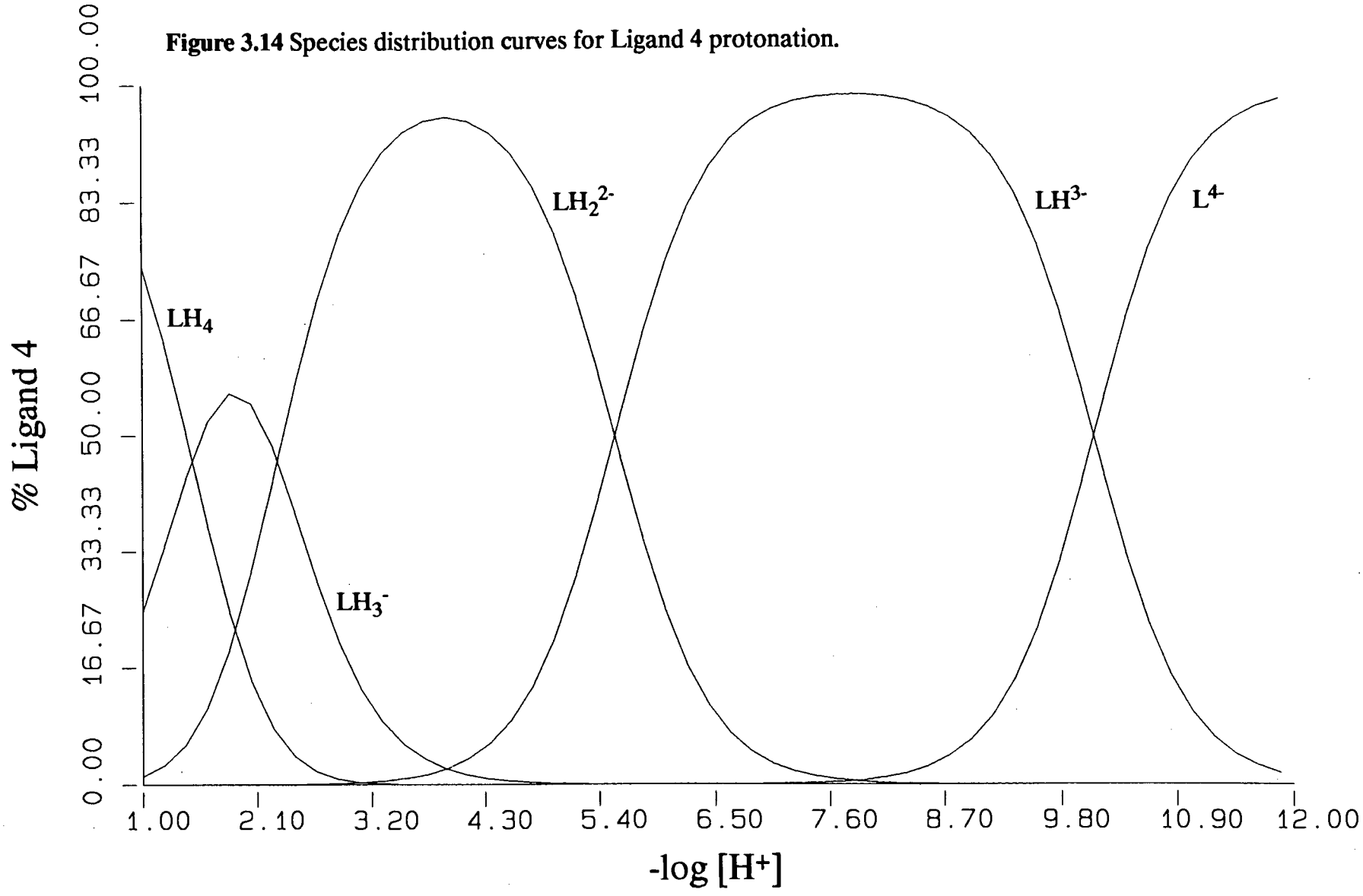


Figure 3.14 Species distribution curves for Ligand 4 protonation.



3.5.5 COMPARISON OF PROTONATION CONSTANTS

The stepwise protonation constants for Ligands 1, 2, 3 and 4 as determined in this study as well as that of four structurally related ligands, viz., IDA (**V**), IDP (**VI**), NTA (**VII**) and NTP (**VIII**) are presented in table 3.6. The structures of ligands 1 to 4 as well as those of the structural analogues have been presented on pages ~~xvii~~ and ~~xviii~~.

An interesting sequence of ligands is that of IDA, Ligand 1 and IDP since successive replacement of carboxylic acid groups by phosphonic acid groups on IDA results in Ligand 1 and IDP. Each of the ligands have three functional groups and by examining the log K_n, for the protonation constants one can establish the sequence of deprotonation by process of elimination. In the above compounds, the order of deprotonation in going from an acidic solution to a basic solution is the carboxylic acid group(s) followed by the phosphonic acid group(s) and then the amino group. The protonation behaviour of Ligands 1, 2, 3 and 4 have also been examined using nuclear magnetic resonance the results of which are presented and discussed in chapter 4.

Using IDA as a reference, introduction of a phosphonic acid group results in an increased electron density at the end of the molecule resulting in an increased basicity of the proton on the central nitrogen atom. This is reflected in the log K_1 for the ligands IDA, Ligand 1 and IDP which are 9.34, 10.06 and 10.79 respectively. The increase in basicity is constant throughout since the changes are 0.72 and 0.73 respectively.

As discussed above, the sequence of ligands, NTA, Ligand 4, Ligand 3 and NTP also show similar trends since the replacement of carboxylic acid groups and introduction of successive phosphonic acid groups to NTA eventually results in NTP. The

Table 3.6

Logarithms of the stepwise protonation constants, $\log K_n$, for ligands used in this study as well as for some structurally related analogues, determined potentiometrically at 25 °C and I = 0.1 mol.dm^{-3}.

Ligand	Complex	$\log K_n$	Reference
IDA	LH	9.34	[Mar89]
	LH_2	2.60	
	LH_3	(1.80)	
LIG1	LH	10.06	[This study]
	LH_2	5.42	
	LH_3	2.11	
IDP	LH	10.79	[Mar89]
	LH_2	6.08	
	LH_3	5.04	
	LH_4	(0.90)	
NTA	LH	9.49	[Mar89]
	LH_2	2.52	
	LH_3	(1.9)	
LIG4	LH	10.11	[This study]
	LH_2	5.55	
	LH_3	2.30	
	LH_4	1.48	
LIG3	LH	11.19	[This study]
	LH_2	6.40	
	LH_3	5.02	
	LH_4	2.10	
	LH_5	1.42	
NTP	LH	(12.1)	[Mar82]
	LH_2	7.30	
	LH_3	5.86	
	LH_4	4.64	
	LH_5	1.50	
	LH_6	0.30	
LIG2	LH	9.00	[This study]
	LH_2	6.55	
	LH_3	2.10	

respective log K_1 values for this sequence is 9.49, 10.11, 11.19 and 12.1 with increases in basicity of 0.62, 1.08 and 0.91 for the amino- nitrogen. The influence of the nett increase in overall charge also affects the protonation constants of the phosphonic acid moieties since log K_2 for the series Ligand 4, Ligand 3 and NTP is 5.55, 6.40 and 7.30 with changes of 0.85 and 0.90 respectively.

Ligand 2 is somewhat different to all of the above-mentioned ligands in that it consists of five functional groups viz., two carboxylic acid, two amino and a phosphinic acid group as opposed to a phosphonic acid group. Since the phosphinic acid moiety only develops a charge of -1 upon deprotonation, the overall electron density on the molecule is not as pronounced as in most of the other ligands under dicussion. This results in a log K_1 of 9.00 for the proton on the amino group which is in fact less than that of all of the ligands listed in table 3.6

3.5.6 NICKEL(II) - LIGAND 1 - H^+ COMPLEXATION

The experimental metal formation and metal deprotonation curves for the Ni^{2+} - Lig1 - H^+ system are presented in figures 3.15 and 3.16 respectively. The metal formation curves show a tendency to level off at both $Z_M = 1$ and $Z_M = 2$ indicating the likely presence of an ML and a ML_2 species. The metal deprotonation curves suggest that MLH_2, MLH, ML, and either an ML_2 or an MLOH complex is present. Of these, the model MLH, ML and ML_2 was found to fit the data best. The system was examined for the presence of MLH_2, ML_2H, ML_2H_2, MLOH and $ML(OH)_2$ species, none of which were found. Refined stability constants for the chosen model as well as the relevant statistical analysis are presented in table 3.7.

The theoretical Z_M and Q_M curves fit the experimental data well and the refined constants as well as the model, compare favourably with the literaure data presented in table 3.7. The species distribution curves shown in figure 3.17, show that each of the species of the chosen model are major species.

Table 3.7

Statistical analysis and logarithms of the overall stability constants, $\log\beta_{pqr}$, of nickel(II) ions with Ligand 1, determined at 25 °C and 0.1 mol.dm^{-3} (Na^+)[Cl^-].

Complex	pqr	$\log\beta_{pqr}$	Std. dev.
MLH	111	13.22	0.0042
ML	110	7.90	0.0041
ML_2	120	12.27	0.0098

Objective Function:-	1.65×10^0
R-factor, R_f:-	0.00307
R-limit, R_l:-	0.00254
No of titrations:-	4
No of data points:-	125
[Ligand] range, mol.dm^{-3}:-	0.002005 - 0.004582
[Metal] range, mol.dm^{-3}:-	0.001829 - 0.002098
Ligand:Metal ratios:-	1:1, 2:1
pH range:-	2.8 - 10.1

Literature Data

Constants determined potentiometrically at 25 °C and I = 0.1 mol.dm^{-3} KNO_3 [Mot85].

Complex	pqr	$\log\beta_{pqr}$	Std. dev.
MLH	111	13.36	-
ML	110	8.10	-
ML_2	120	12.25	-

Figure 3.15 Experimental (symbols) and theoretical (solid line) metal formation curves for the Nickel(II) - Ligand 1 system.

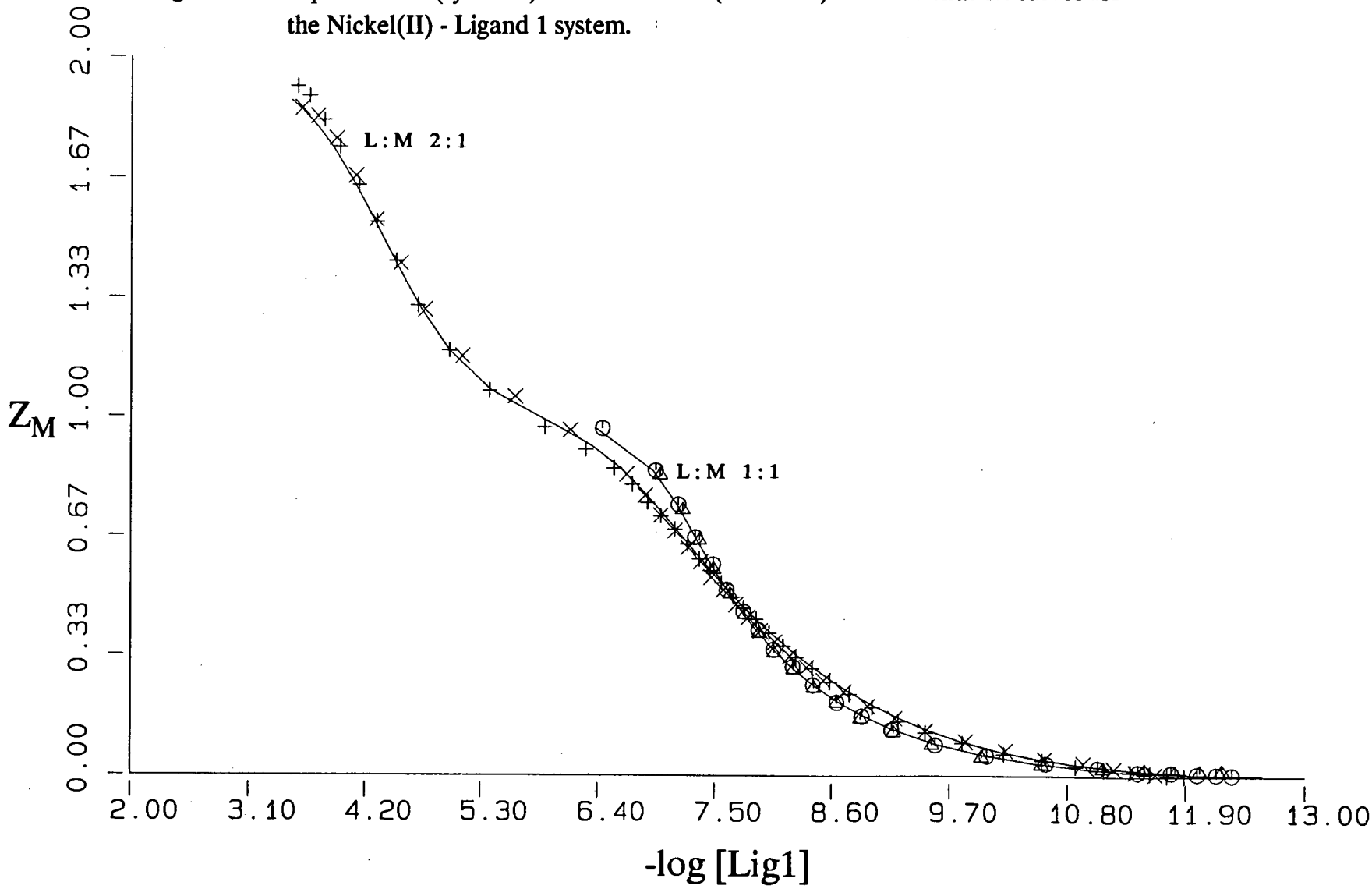


Figure 3.16 Experimental (symbols) and theoretical (solid line) metal deprotonation curves for the Nickel(II) - Ligand 1 system.

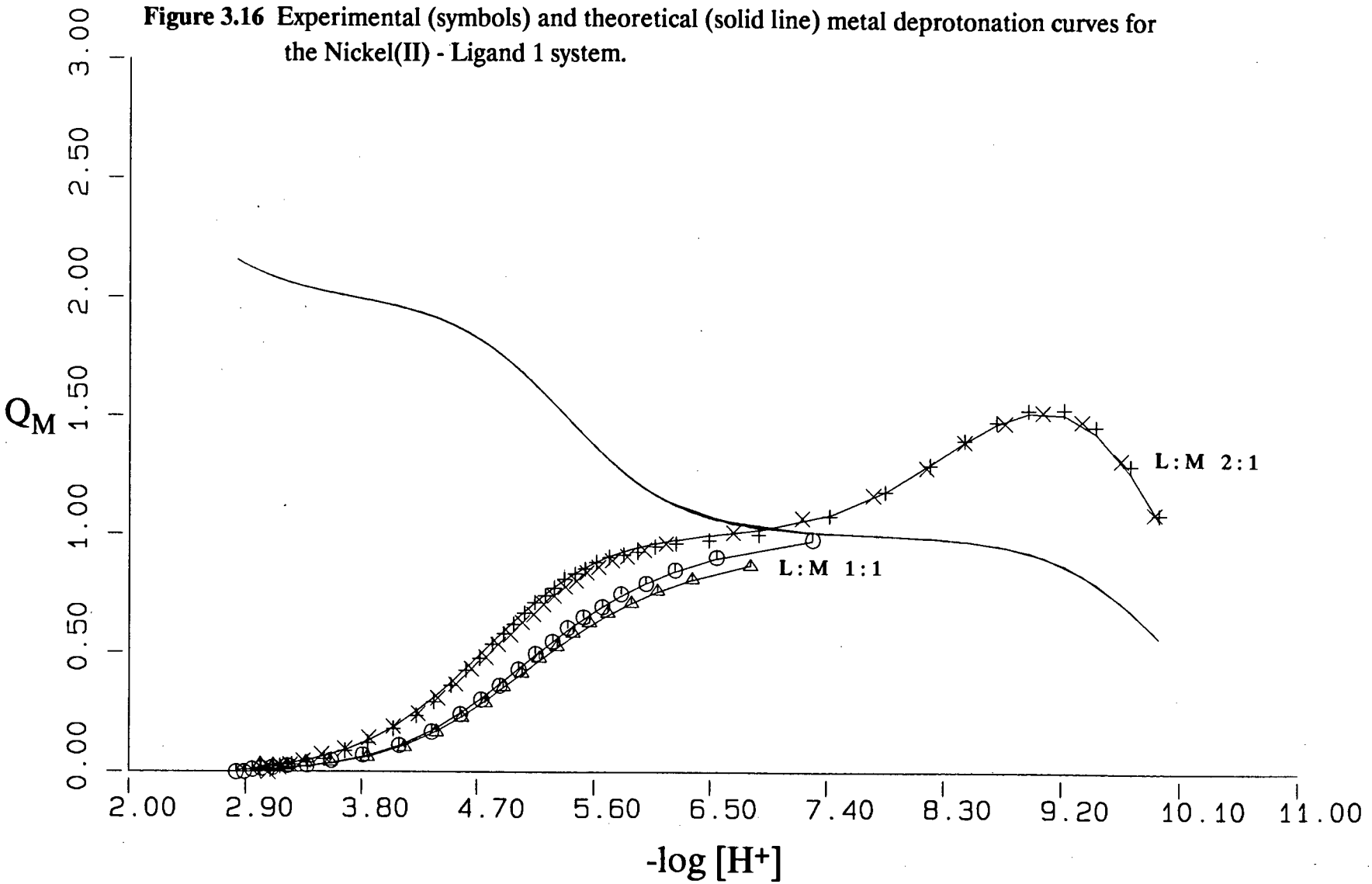
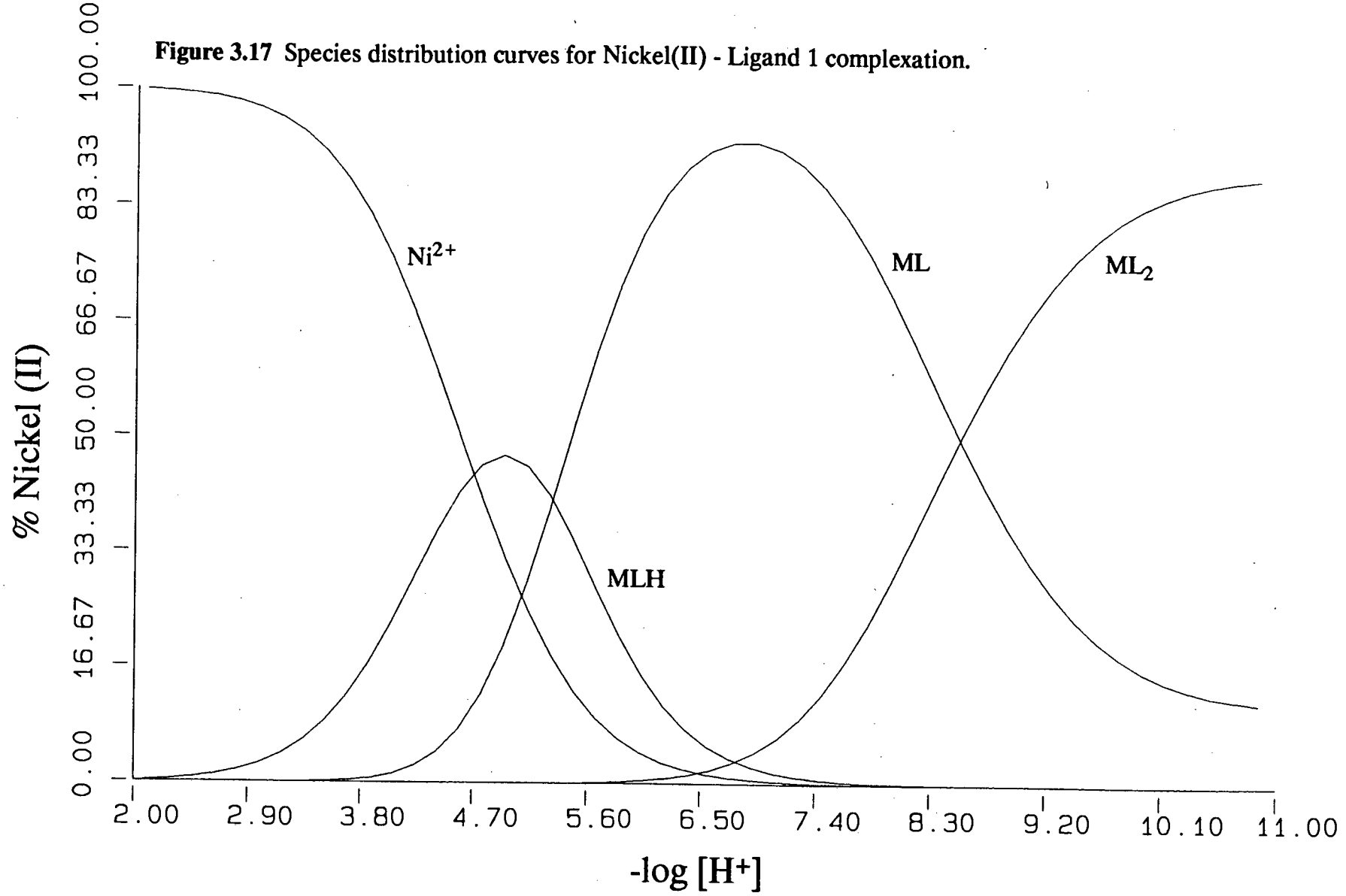


Figure 3.17 Species distribution curves for Nickel(II) - Ligand 1 complexation.



3.5.7 NICKEL(II) - LIGAND 2 - H^+ COMPLEXATION

The experimental metal formation and metal deprotonation curves for the Ni^{2+} - Lig2 - H^+ system are presented in figures 3.18 and 3.19 respectively. The metal formation curves show a levelling off at Z_M = 1 while the metal deprotonation curves indicate that MLH_2, MLH and ML are all likely species. Of these, the only complex that was found was the ML species. At higher pH values, the experimental formation curves fitted the theoretical curves poorly despite suggesting that no further complexation took place. The data was analysed for the presence of ML_2, MLOH and a M_2L species although there was no experimental evidence for their presence. These complexes were not found in the system and the ML species was thus the only complex in the model. In order to refine a good value for the ML species, data points above a pH of 4 were excluded, leaving a very narrow experimental range. The refined constant and data analysis is presented in table 3.8. The relatively uncomplicated speciation curve is presented in figure 3.20.

Table 3.8

Statistical analysis and logarithm of the overall stability constant, $\log\beta_{pqr}$, of nickel(II) ions with Ligand 2, determined at 25 °C and 0.1 mol.dm^{-3} (Na^+)[Cl^-].

Complex	**pqr**	**$\log\beta_{pqr}$**	**Std. dev.**
ML	110	12.24	0.00476

Objective Function:-	1.31×10^1
R-factor, R_f:-	0.00294
R-limit, R_l:-	0.00084
No of titrations:-	8
No of data points:-	159
[Ligand] range, mol.dm^{-3}:-	0.001624 - 0.004965
[Metal] range, mol.dm^{-3}:-	0.001990 - 0.003328
Ligand:Metal ratios:-	1:2, 2:3, 1:1, 3:2, 2:1
pH range:-	2.0 - 4.0

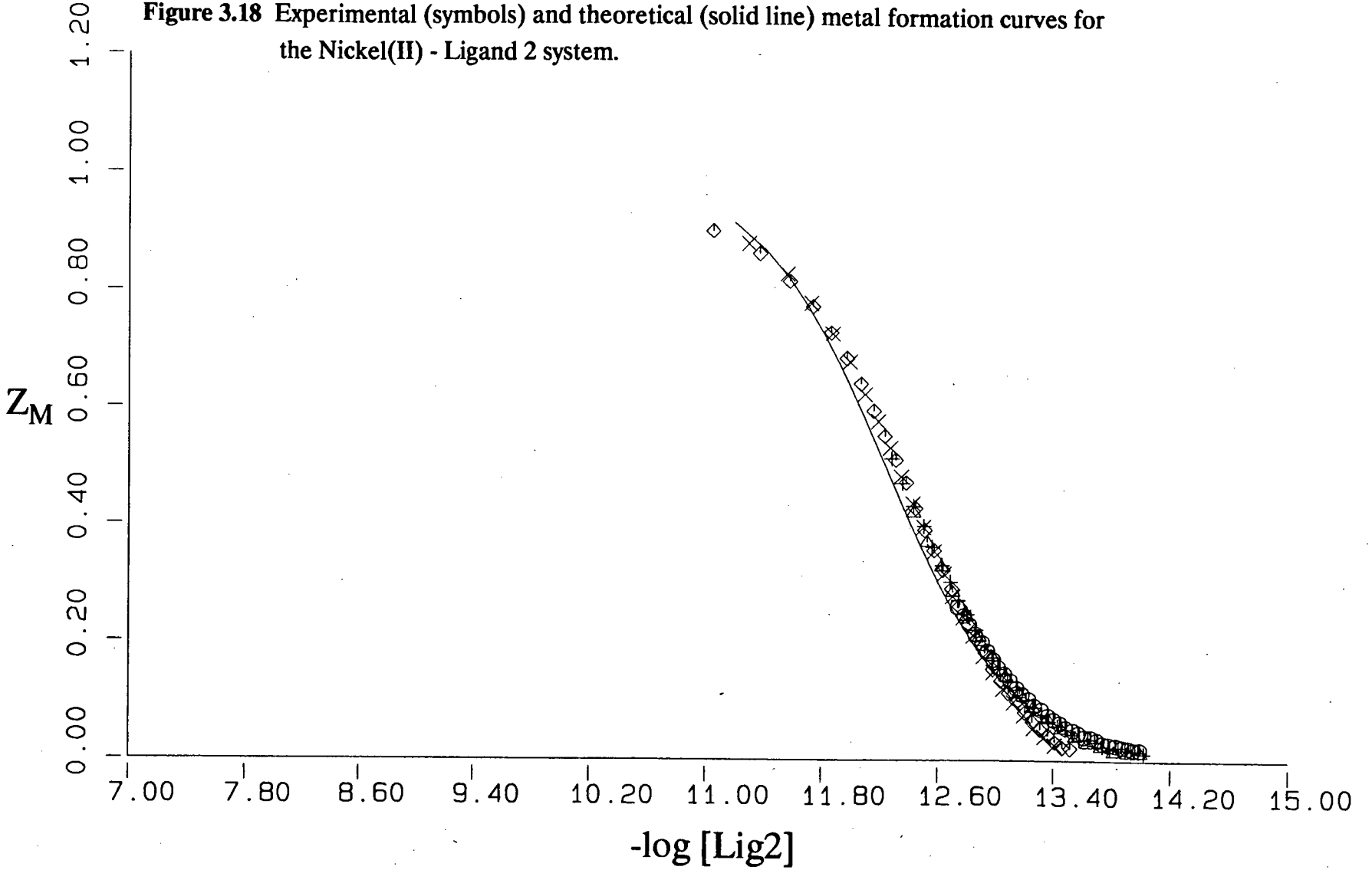


Figure 3.18 Experimental (symbols) and theoretical (solid line) metal formation curves for the Nickel(II) - Ligand 2 system.

Figure 3.19 Experimental (symbols) and theoretical (solid line) metal deprotonation curves for the Nickel(II) - Ligand 2 system.

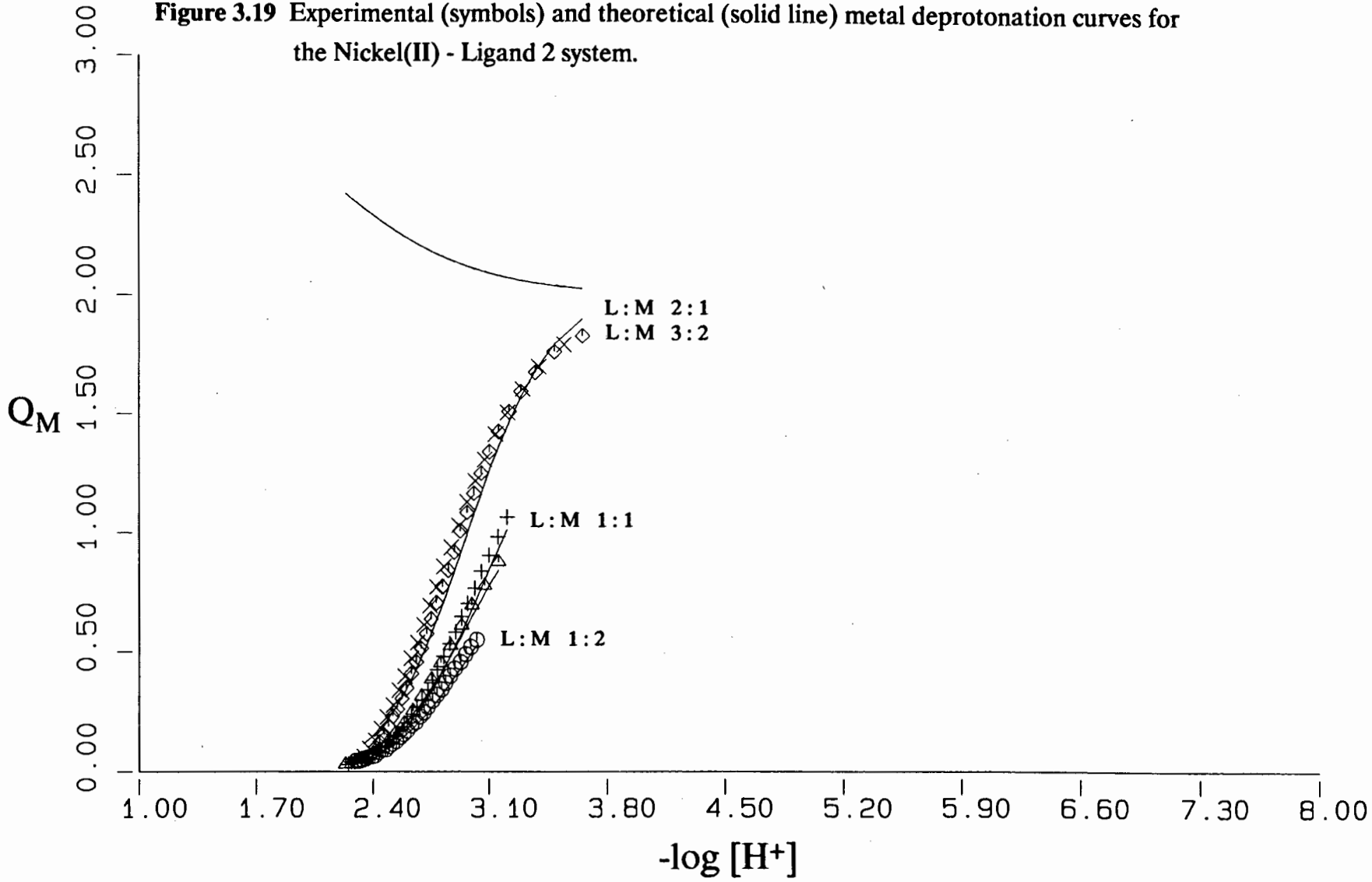


Figure 3.20 Species distribution curves for Nickel(II) - Ligand 2 complexation.

3.5.8 NICKEL(II) - LIGAND 3 - H^+ COMPLEXATION

The experimental metal formation and metal deprotonation curves for the Ni^{2+} - Lig3 - H^+ system are presented in figures 3.21 and 3.22 respectively. The metal formation curves for the metal : ligand ratios of 1 : 1 and 1 : 2 both level off at 1 while the 2:1 ratio reaches a maximum of 0.5. The metal deprotonation curves indicate that at an average of three protons per ligand, the metal displaces 1 suggesting the likely presence of an MLH_2 species. The remaining two protons are rapidly lost between the pH values of 5 and 6. Stability constants were refined for the species MLH_2, MLH and ML and these are presented in table 3.9. The complexes M_2L, ML_2 and MLOH were not found and the above model was thus chosen as the final model.

The stepwise formation constants for the reactions,

$$ML + H \rightleftharpoons MLH$$

$$\text{and} \quad MLH + H \rightleftharpoons MLH_2$$

are 6.25 and 4.83 respectively. This is very similar to the second and third protonation constants of the ligand, viz., 6.40 and 5.02. It appears that the proton displaced by the metal ion upon complexation is that on the central nitrogen atom and the MLH_2 and MLH species are in fact the ML species with protons on each of the phosphonate groups which dissociate as the pH is increased. The species distribution for the system is presented in figure 3.23 and it indicates that all of the species are major species.

Table 3.9

Statistical analysis and logarithms of the overall stability constants, $\log\beta_{pqr}$, of nickel(II) ions with Ligand 3, determined at 25 °C and 0.1 mol.dm^{-3} (Na^+)[Cl^-].

Complex	pqr	$\log\beta_{pqr}$	Std. dev.
MLH_2	112	23.06	0.0080
MLH	111	18.24	0.0095
ML	110	11.99	0.0102

Objective Function:-	9.90×10^1
R-factor, R_f:-	0.00704
R-limit, R_l:-	0.00071
No of titrations:-	5
No of data points:-	308
[Ligand] range, mol.dm^{-3}:-	0.002069 - 0.006592
[Metal] range, mol.dm^{-3}:-	0.001998 - 0.006646
Ligand:Metal ratios:-	1:2, 1:1, 2:1
pH range:-	1.9 - 10.5

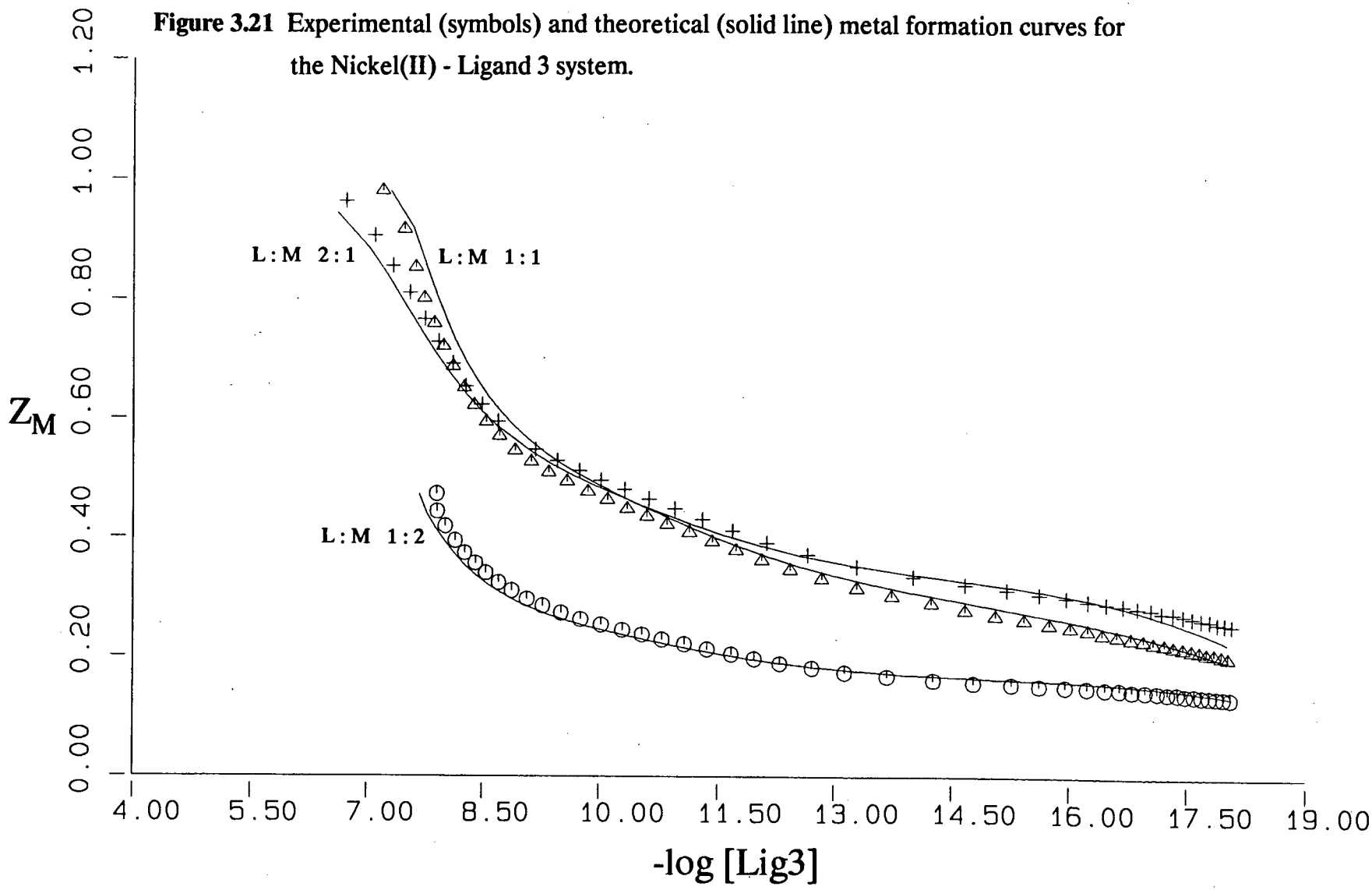


Figure 3.21 Experimental (symbols) and theoretical (solid line) metal formation curves for the Nickel(II) - Ligand 3 system.

Figure 3.22 Experimental (symbols) and theoretical (solid line) metal deprotonation curves for the Nickel(II) - Ligand 3 system.

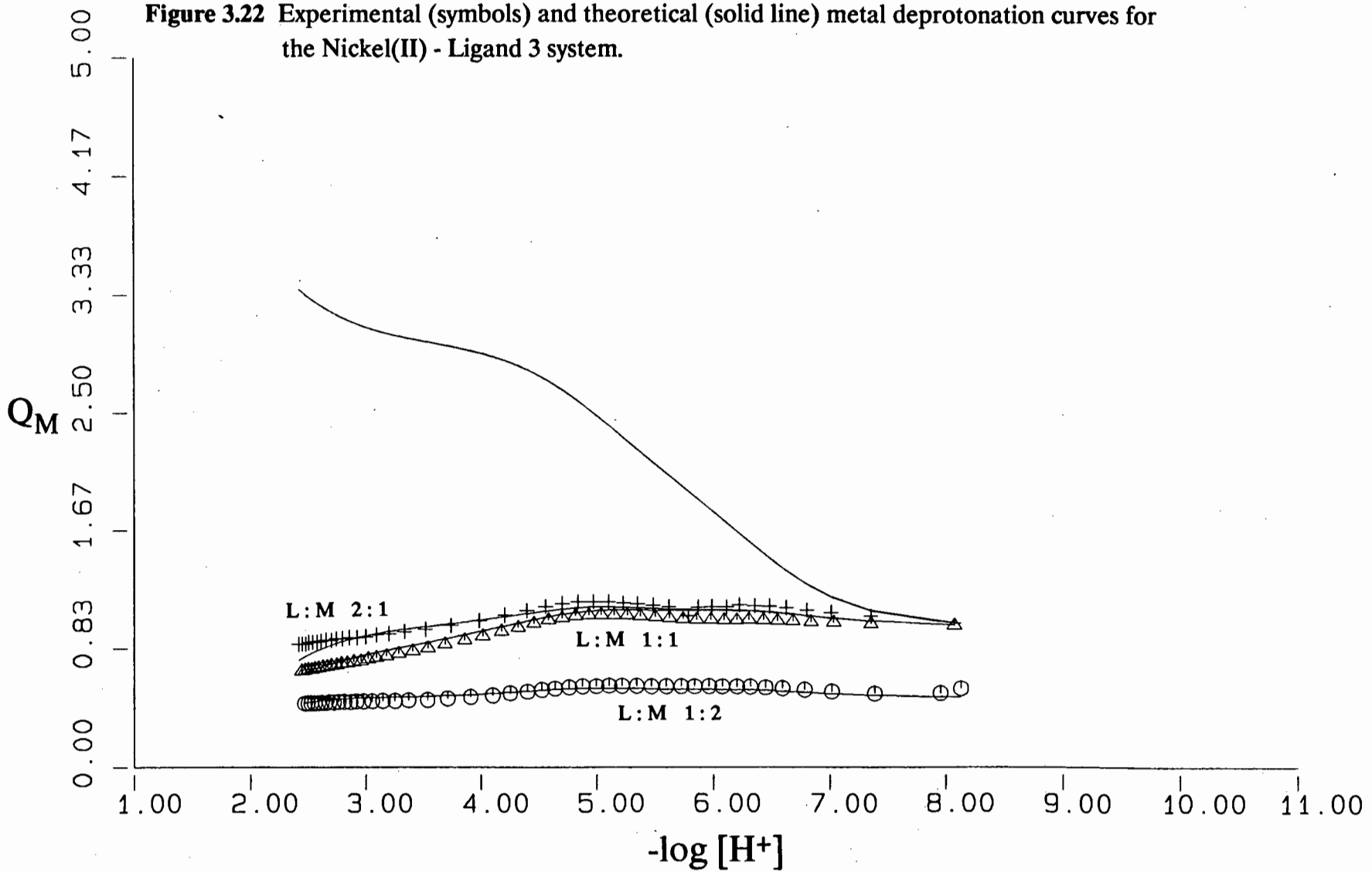
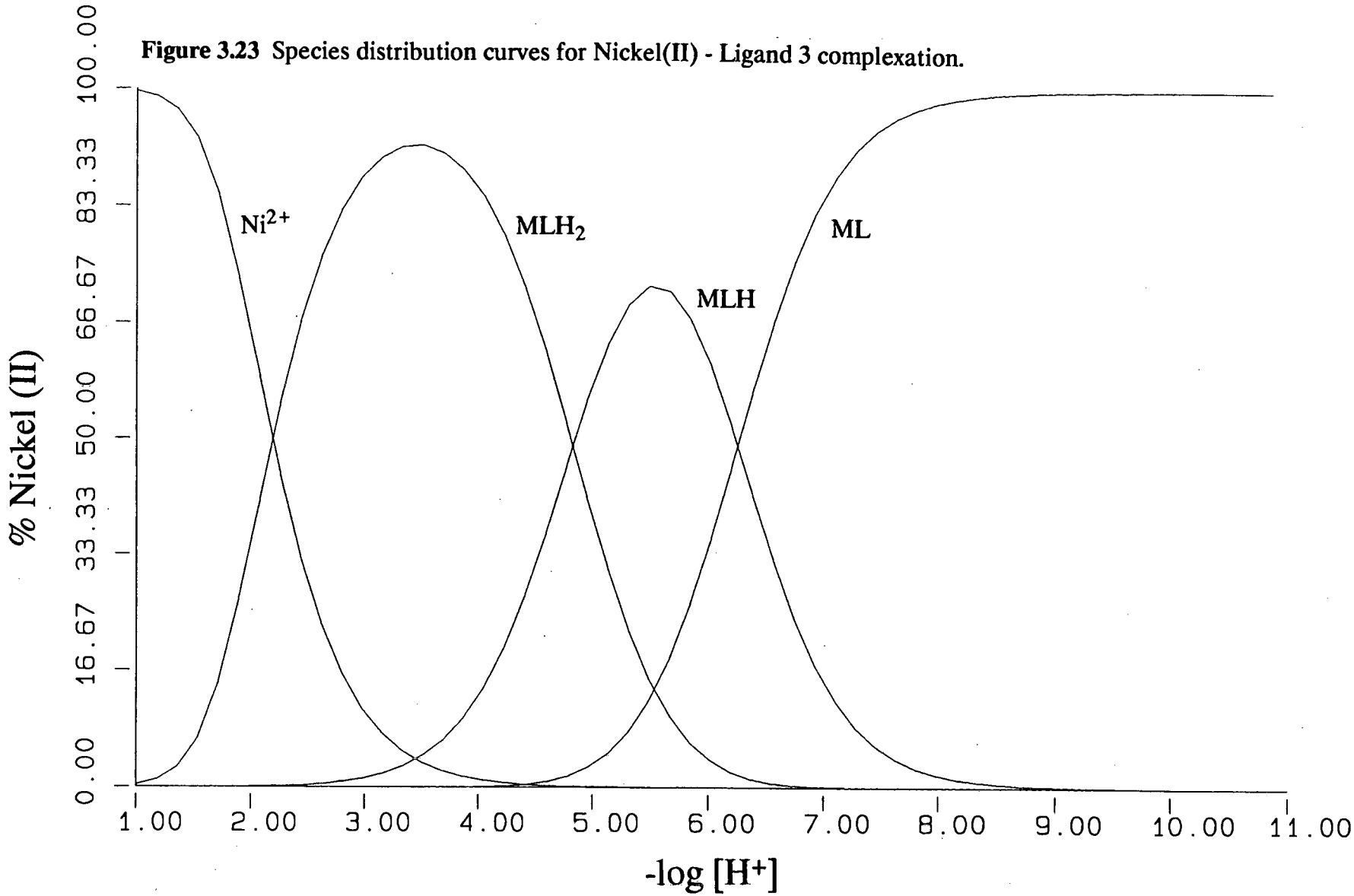


Figure 3.23 Species distribution curves for Nickel(II) - Ligand 3 complexation.



3.5.9 NICKEL(II) - LIGAND 4 - H^+ COMPLEXATION

The experimental metal formation and metal deprotonation curves for the Ni^{2+} - Lig4 - H^+ system are presented in figures 3.24 and 3.25 respectively. The experimental formation curves indicate a relatively high degree of complexation at low pH values with the indications of an ML and ML_2 species being present in solution. The deprotonation curves indicate the presence of an MLH species in addition to the above two species. These three complexes were found to be the basis of the model and no further complexes could be identified. Other complexes examined for in this system include MLH_2, ML_2H, ML_2H_2 and MLOH.

The refined constants for this system are presented in table 3.10 and the species distribution curves are presented in figure 3.26. The stepwise formation constant for the MLH species is 5.46 which is similar to the log K_2, 5.55 for the protonation of the free ligand. A likely protonation site for the MLH species is thus the phosphonate group.

Table 3.10

Statistical analysis and logarithms of the overall stability constants, $\log\beta_{pqr}$, of nickel(II) ions with Ligand 4, determined at 25 °C and 0.1 mol.dm^{-3} (Na^+)[Cl^-].

Complex	pqr	$\log\beta_{pqr}$	Std. dev.
MLH	111	16.82	0.0094
ML	110	11.36	0.0110
ML_2	120	14.48	0.0205

Objective Function:-	2.58 X 10^1
R-factor, R_f:-	0.00349
R-limit, R_l:-	0.00069
No of titrations:-	6
No of data points:-	627
[Ligand] range, mol.dm^{-3}:-	0.002497 - 0.010016
[Metal] range, mol.dm^{-3}:-	0.001990 - 0.004982
Ligand:Metal ratios:-	1:2, 1:1, 2:1, 3:1
pH range:-	2.0 - 11.0

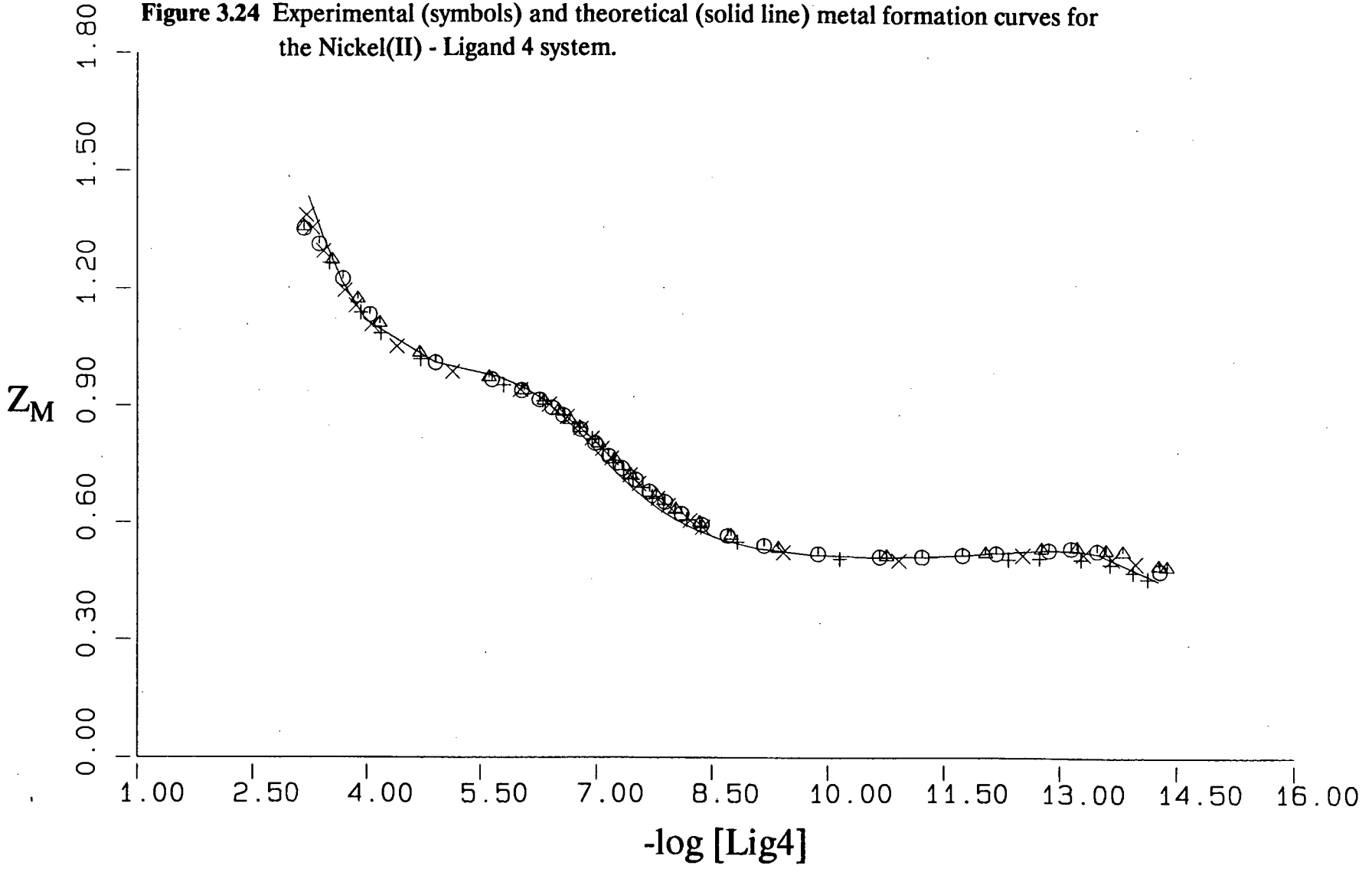


Figure 3.24 Experimental (symbols) and theoretical (solid line) metal formation curves for the Nickel(II) - Ligand 4 system.

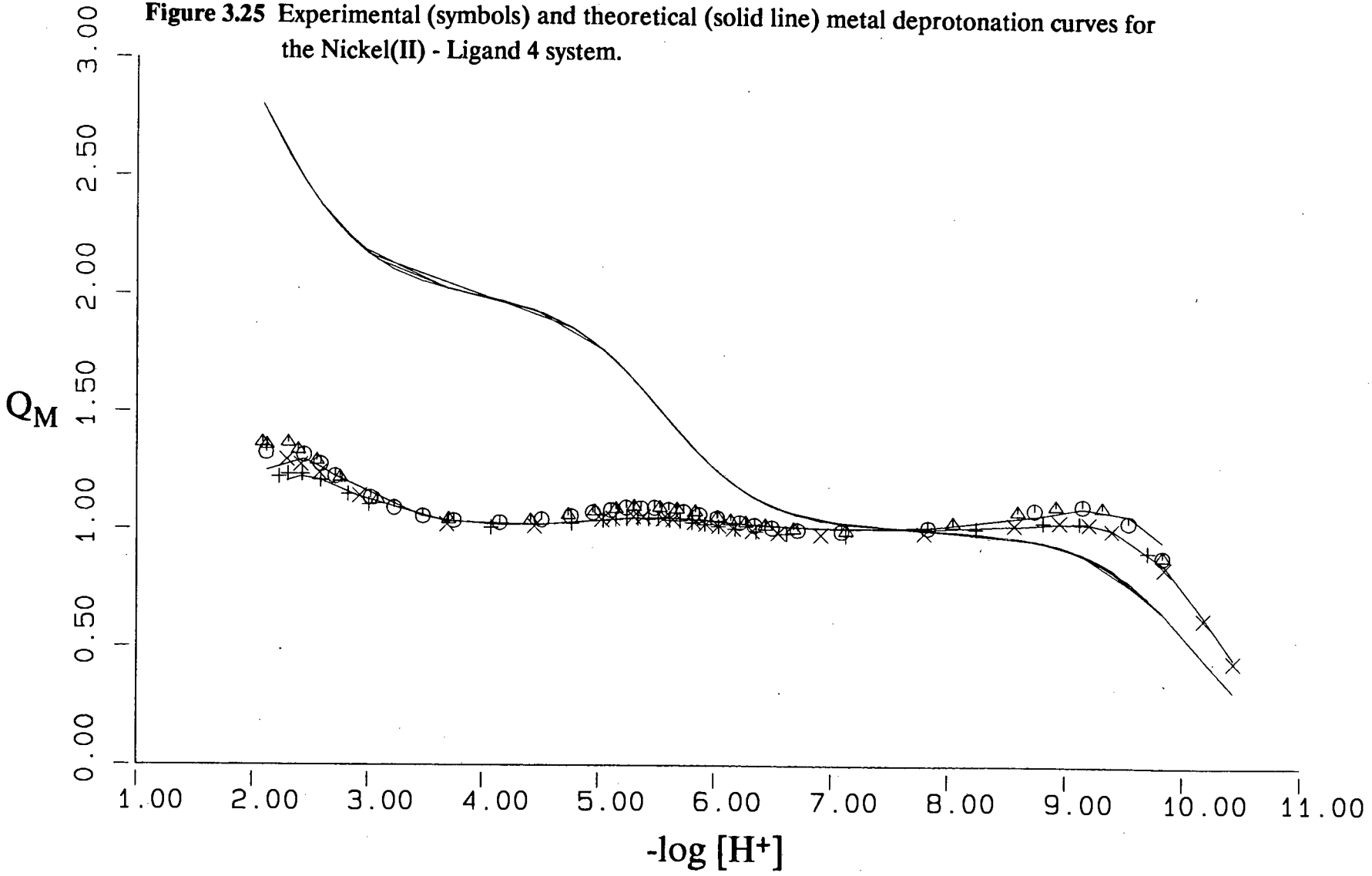


Figure 3.25 Experimental (symbols) and theoretical (solid line) metal deprotonation curves for the Nickel(II) - Ligand 4 system.

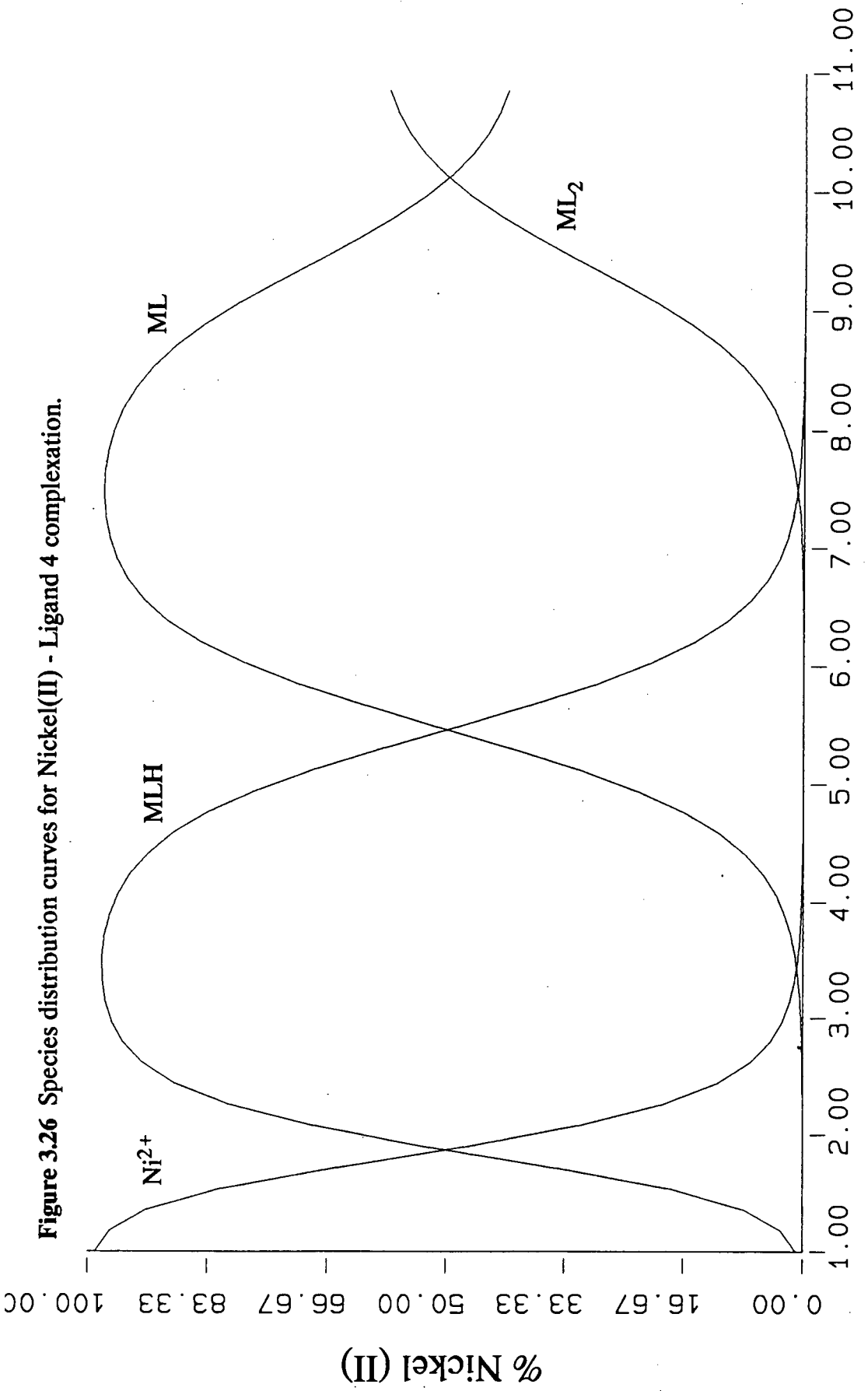


Figure 3.26 Species distribution curves for Nickel(II) - Ligand 4 complexation.

3.5.10 COMPARISON OF NICKEL(II) COMPLEXATION CONSTANTS

Stability constants for the ML species, $\log\beta_{ML}$, of IDA, Lig1, IDP, NTA, Lig4, Lig3 and NTP with the metal ions Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} ions are presented in table 3.11(a). The structures of the abovementioned ligands have been presented on pages ~~xvii~~ and ~~xviii~~.

For the purposes of comparing stability constants, these ligands can be divided into two groups viz. IDA, Lig1, IDP and NTA, Lig4, Lig3 and NTP. For each of the ligands, the stability constants generally obey the Irving-Williams series [Irv53] of $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$.

As reported in section 3.5.5, there is an increase in electron density on the molecule in going from the carboxylic acid ligands to the phosphonic acid ligands since the former functional group develops a charge of -1 while the latter develops a charge of -2 when fully deprotonated. This increase in electron density is reflected in the increase in stability constant with increasing phosphonic acid functionality. It must be said that the overall increase is not as pronounced as one might have expected. For example, the increase in stability for the Cu^{2+} - Lig1 complex in comparison with Cu^{2+} - IDA is 1.37 log units whereas a further substitution of the carboxylic acid group for a phosphonic acid group on Lig1 only increases the stability 0.91 log units as determined from the Cu^{2+} - IDP constant. The increase in electron density around the nucleus of the metal ion in the metal - ligand complex is also subject to charge repulsion and the observed stability constants are thus a nett result of these opposing effects.

A noticable and interesting deviation from the above trend is that of the Ni^{2+} ion which shows a decrease in stability for the Ni^{2+} - Lig1 complex when compared with the Ni^{2+}-IDA complex. The Ni^{2+} - IDP complex also shows no further

Table 3.11(a)

Logarithms of the overall stability constants for the ML species, $\log\beta_{110}$, for ligands used in this study as well as some structurally related ligands with selected metal ions. All constants have been determined potentiometrically at 25 °C and at I = 0.1 mol.dm^{-3}.

METAL	IDA	LIG1	IDP
Mn^{2+}	4.72	5.50	6.26
Fe^{2+}	5.80[a]	6.87	7.70
Co^{2+}	6.96	7.23	7.75
Ni^{2+}	8.30	8.10(7.90)[b]	8.32
Cu^{2+}	10.56	11.93	12.84
Zn^{2+}	7.15	8.74	9.03

METAL	NTA	LIG4	LIG3	NTP
Mn^{2+}	7.46	8.15	8.49[d]	10.2
Fe^{2+}	8.33[c]	9.91	-	-
Co^{2+}	10.38	10.82	12.48[e]	14.4
Ni^{2+}	11.50	11.36	11.69[e](11.99)[b]	11.1
Cu^{2+}	12.94	14.05	15.75[e]	17.4
Zn^{2+}	10.66	11.55	13.48[d]	16.4

References.

IDA, LIG1, IDP, [Mar89]

NTA [Mar74], LIG3 [Nik74], NTP [Mar82]

LIG4 [This study]

a Determined at 20 °C, I = 0.1 mol.dm^{-3} [Mar89]

b This study

c Determined at 20 °C, I = 0.0 mol.dm^{-3} [Mar74]

d Determined at 25 °C, I = 0.1 mol.dm^{-3} [Nik74]

e Determined spectrophotometrically at 25 °C, I = 0.1 mol.dm^{-3} [Nik74]

increase in stability in comparison with the Ni^{2+} - IDA complex. Similarly, there is no general increasing trend in stability for the Ni^{2+} ion complexes of the ligands NTA, Lig4, Lig3 and NTP. However, the increase in stability is clearly evident for the other metal ions. The extent of this anomolous behaviour of Ni^{2+} ions is best illustrated by its stability constant with NTP which deviates from the Irving - Williams series as the Ni^{2+} - NTP stability constant is more than three log units less than that of the Co^{2+} - NTP complex.

In contrast to the above observation, the Ni^{2+} - NTA constant (11.50) is greater than that of the Zn^{2+} - NTA complex (10.66) whereas the reverse is true for all of the other ligands execpt for IDA. It appears as if the Ni^{2+} ion shows a distinct preference for the carboxylic acid functional group since the stability constants of Ni^{2+} - IDA and Ni^{2+} - NTA are greater than expected.

The behaviour of the Ni^{2+} ion with the series of ligands under consideration could perhaps in part be rationalised in terms of the splitting of the 3d orbitals under the influence of the crystal field.

The d orbitals of metal ions are classified as those that lie along the cartesian axes $d(x^2 - y^2)$ and dz^2, collectively known as the e_g orbitals and the d_{xy}, d_{xz} and d_{yz} orditals which lie between the axes and are collectively termed as the t_{2g} orbitals. Since the e_g orbitals lie along the line of approach of any ligand, electrons in these orbitals suffer greater repulsion than would electrons in any of the t_{2g} orbitals.

The Ni^{2+} ion has the electronic configuration of $[Ar]3d^8$. Since the first six electrons completely fill the three t_{2g} orbitals, the two remaining electrons would be unpaired and would each occupy one of the e_g orbitals. This implies that any ligand approaching the Ni^{2+} ion is subject to repulsion irrespective of its line of approach.

This repulsion would be greater with increasing charge on the ligand resulting in an overall decrease in stability. If one were to consider the effect of crystal field splitting on the stability of complexes with other metal ions, it can be seen from the distribution of the outer electrons in the d orbitals that charge repulsion between the metal ion and the ligand is greatest with the Ni^{2+} ion. From the principles of crystal field stabilization energies, Ni^{2+} ions would therefore not necessarily show any nett increase in stability with increasing charge on the ligand.

The trends observed in this study are also observed with EDTA and its phosphonic acid analogue, ethylenediaminetetra(methylenephosphonic acid), EDTP, where the Co^{2+} ion complex stability constant exceeds the Ni^{2+} ion complex stability constant in the case of the latter. Stability constants for the ML species of selected ligands with Co^{2+} and Ni^{2+} ions are presented in table 3.11(b). Ligands containing phosphonate groups deviate from the Irving - Williams series. This is probably as a result of the dianionic charge developed on the functional group when fully deprotonated, as ligands containing monoanionic, ($-CO_2^-$, NO_3^-), and neutral, ($-NH_2$) functional groups tend to obey the Irving - Williams series.

Table 3.11(b)

Logarithms of the overall stability constants, $\log\beta_{pqr}$, for the ML complexes of selected ligands with cobalt(II) and nickel(II) ions determined at 25 °C and I = 0.1 mol.dm^{-3}.

Ligand	$\log\beta_{pqr}(Co^{2+})$	$\log\beta_{pqr}(Ni^{2+})$	Reference
NH_3	2.10[a]	2.81[b]	[Mar76]
NO_3^-	-0.46	-0.22	[Mar76]
Phosphoric acid	2.18	2.08	[Mar76]
Hydrogen diphosphate	6.10	5.94	[Mar76]
Hydrogen triphosphate	6.94	6.75	[Mar76]
EDTA	16.26	18.52	[Mar74]
EDTP	17.11	16.38	[Mar82]
EDDA	11.25	13.65	[Mar74]
DTPA	19.15	20.17	[Mar74]

a = 25 °C, I = 0.2 mol.dm^{-3} b = 30 °C, I = 0.2 mol.dm^{-3}

Table 3.12 lists the overall stability constants of Ni^{2+} complexes with ligands used in this study as well as that of some related ligands. Having discussed the stability constants of the ML species, one observes that the stepwise formation constant for the ML_2 species, log K_{ML2} also decreases for the series of ligands IDA, Lig1 and IDP, (log K_{ML2} = 6.20, 4.37 and 1.52 respectively). This is probably as a result of coulombic charge repulsion since the ML_2 species for Ni^{2+} - $(IDA)_2$ has an overall charge of -2 whereas the Ni^{2+} - $(IDP)_2$ complex has a charge of -6. A similar trend is observed for the ML_2 complexes of NTA and Lig4 with Ni^{2+}ions where log K_{ML2} is 4.82 and 3.12 respectively.

Another interesting observation is that Ni^{2+} is one of only two divalent metal ions (the other being Fe^{2+}) to form an ML_2 complex with Ligand 4. Ligand four is not only bulky, but also tetradendate and could thus occupy four of the six metal binding sites in an ML species. In addition to this, an ML_2 species would have an overall charge of -6. The formation of the Ni^{2+} - $(Lig4)_2$ complex to some extent negates the argument that Ni^{2+} ions are averse to complexes of high overall charge and distinctly points to the Ni^{2+} ion's preference for carboxylate functionality.

There are indeed many possibilities for the structure of an Ni^{2+} - $(Lig4)_2$ complex but a likely arrangement of the two ligands around the metal ion, based on the aforementioned discussion, is that the two amino and four carboxylate functional groups occupy the six metal binding sites with the two charged phosphonate groups in a trans position relative to each other in order to minimise steric hinderence as well as charge repulsion.

Some possible structures for the ligands used in this study are presented in chapter 3.6.

Table 3.12

Logarithms of the overall stability constants, $\log\beta_{pqr}$, of the nickel(II) complexes determined in this study as well as for some structurally related analogues, determined potentiometrically at 25 °C and I = 0.1 mol.dm^{-3}.

Ligand	Complex	$\log\beta_{pqr}$	Reference
IDA	ML	8.3	[Mar89]
	ML_2	14.5	
LIG1	MLH	13.22	[This study]
	ML	7.90	
	ML_2	12.27	
IDP	MLH_2	19.01	[Mar89]
	MLH	14.23	
	ML	8.32	
	ML_2	9.84	
NTA	ML	11.50	[Mar84]
	ML_2	16.32	
LIG4	MLH	16.820.11	[This study]
	ML	11.36	
	ML_2	14.48	
LIG3	MLH_2	23.06	[This study]
	MLH	18.24	
	ML	11.99	
NTP	MLH_2	25.2	[Mar82]
	MLH	19.4	
	ML	11.1	
LIG2	ML	12.24	[This study]

3.5.11 MANGANESE(II) - LIGAND 4 - H^+ COMPLEXATION

The experimental metal formation curves for this system presented in figure 3.27, show a levelling off at Z_M = 1, indicating the likely presence of an ML species. In addition to this, the metal deprotonation curves presented in figure 3.28, indicate the possible presence of an MLH species since Q_M = 1 when the average number of protons on the ligand is two. There is also the possibility that an MLH_2 species might exist in solution in the pH range 2.5 to 4.5.

The model with species ML and MLH were found to fit the experimental data best and their refined stability constants are presented in table 3.13. These complexes were found to exist in the pH range 2.5 to 9.0. In the initial data set which included experimental points to a pH of 11.2, a log β_{11-1}, of -4.13 was refined for an MLOH species. The existence of this species was supported by the back - fanning pattern observed for data points greater than Z_M = 1. However, the fit between the experimental and theoretical data points was poor in this region, resulting in an R - factor of 0.016. It was then decided to eliminate all data points with an experimental $Z_M > 1$.

An estimate of $\log\beta_{pqr}$ = 18.15 for an MLH_2 complex was calculated by the BETA task but neither of the two optimization tasks refined a constant for this complex. A stability constant of 11.76 was refined for an M_2L complex but this was only possible in the absence of the MLH species. The M_2L complex was discarded in favour of the MLH complex owing to the lower R - factor for the model including the latter. The system was also examined for the species M_2LH and M_2L_2 neither of which were found. There is no experimental evidence to suggest the presence of these complexes but they are chemically possible.

The relatively straight forward model of ML and MLH was chosen as the final model and the R - factor of 0.00450 was obtained by simultaneously refining the

stability constants with the electrode intercept, the acid concentration and the ligand concentration. The species distribution curves for the Mn^{2+} - Lig4 - H^{+} system is presented in figure 3.29.

A constant of 14.26 has been reported for an MLH species as determined using paper electrophoresis at 25 ^{o}C and I = 0.1 $mol.dm^{-3}$ [Maj80].

Table 3.13

Statistical analysis and logarithms of the overall stability constants, $\log\beta_{pqr}$, of manganese(II) ions with Ligand 4, determined at 25 ^{o}C and 0.1 mol.dm^{-3} (Na^+)[Cl^-].

Complex	pqr	$\log\beta_{pqr}$	Std. dev.
MLH	111	13.81	0.0054
ML	110	8.12	0.0052

Objective Function:-	1.41 X 10^1
R-factor, R_f:-	0.00450
R-limit, R_l:-	0.00123
No of titrations:-	9
No of data points:-	589
[Ligand] range, mol.dm^{-3}:-	0.003321 - 0.005994
[Metal] range, mol.dm^{-3}:-	0.001988 - 0.003313
Ligand:Metal ratios:-	1:1, 3:2, 2:1, 5:2, 3:1
pH range:-	2.5 - 9.0

Literature Data

Constant determined using paper electrophoresis at 20 ^{O}C and I = 0.1 mol.dm^{-3} KNO_3 [Maj80].

Complex	pqr	$\log\beta_{pqr}$	Std. dev.
MLH	111	14.26	-

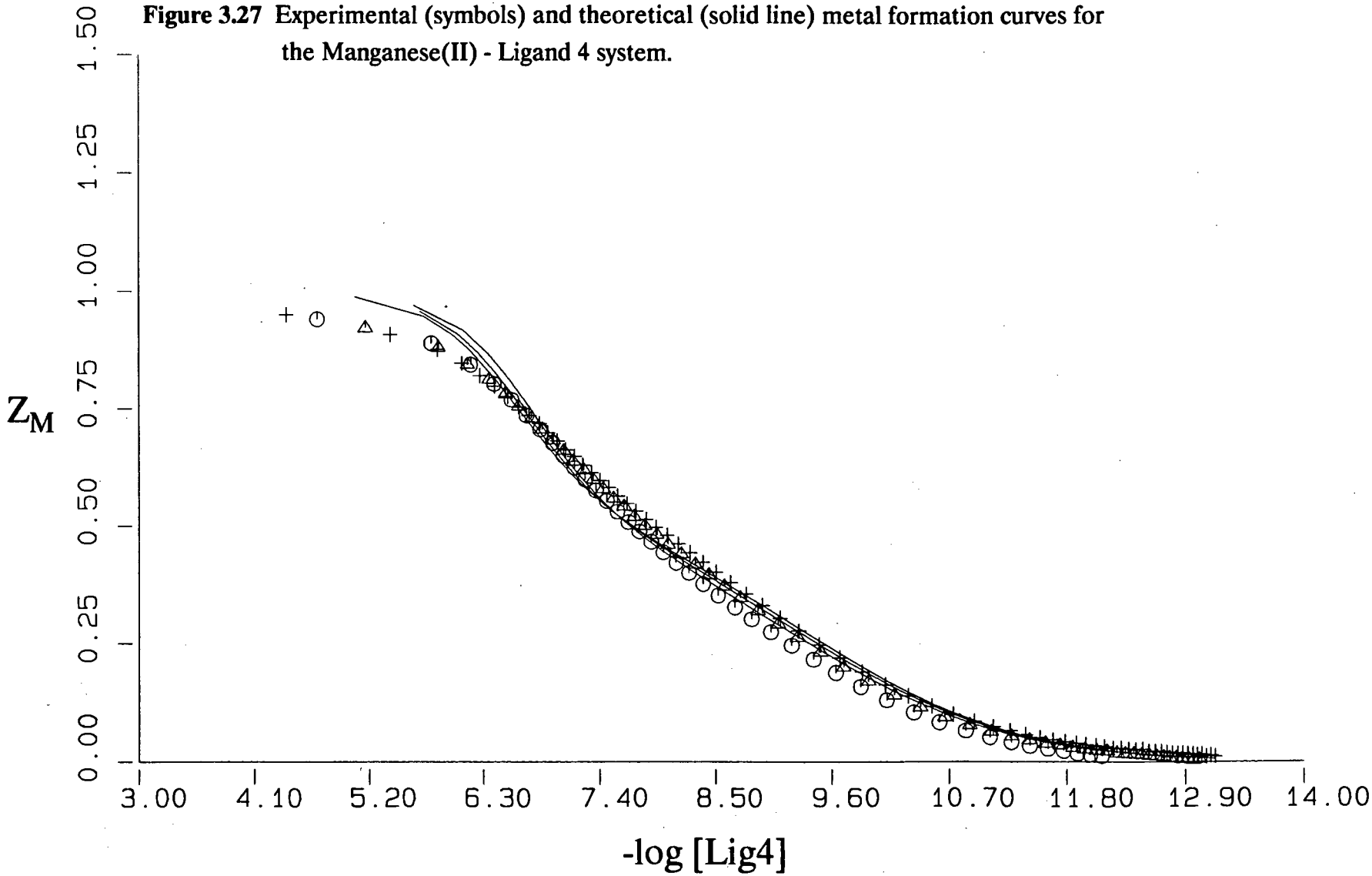


Figure 3.27 Experimental (symbols) and theoretical (solid line) metal formation curves for the Manganese(II) - Ligand 4 system.

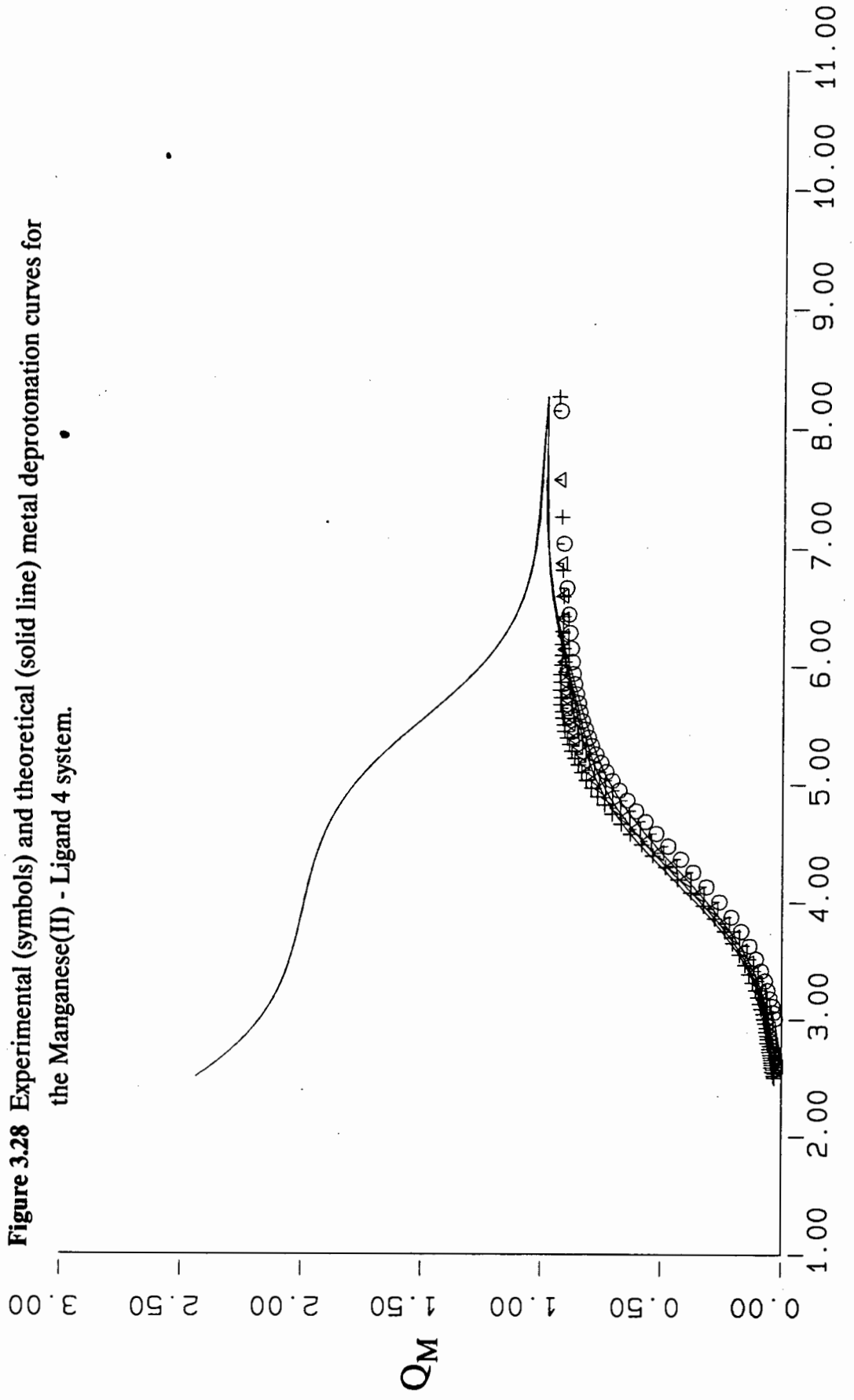


Figure 3.28 Experimental (symbols) and theoretical (solid line) metal deprotonation curves for the Manganese(II) - Ligand 4 system.

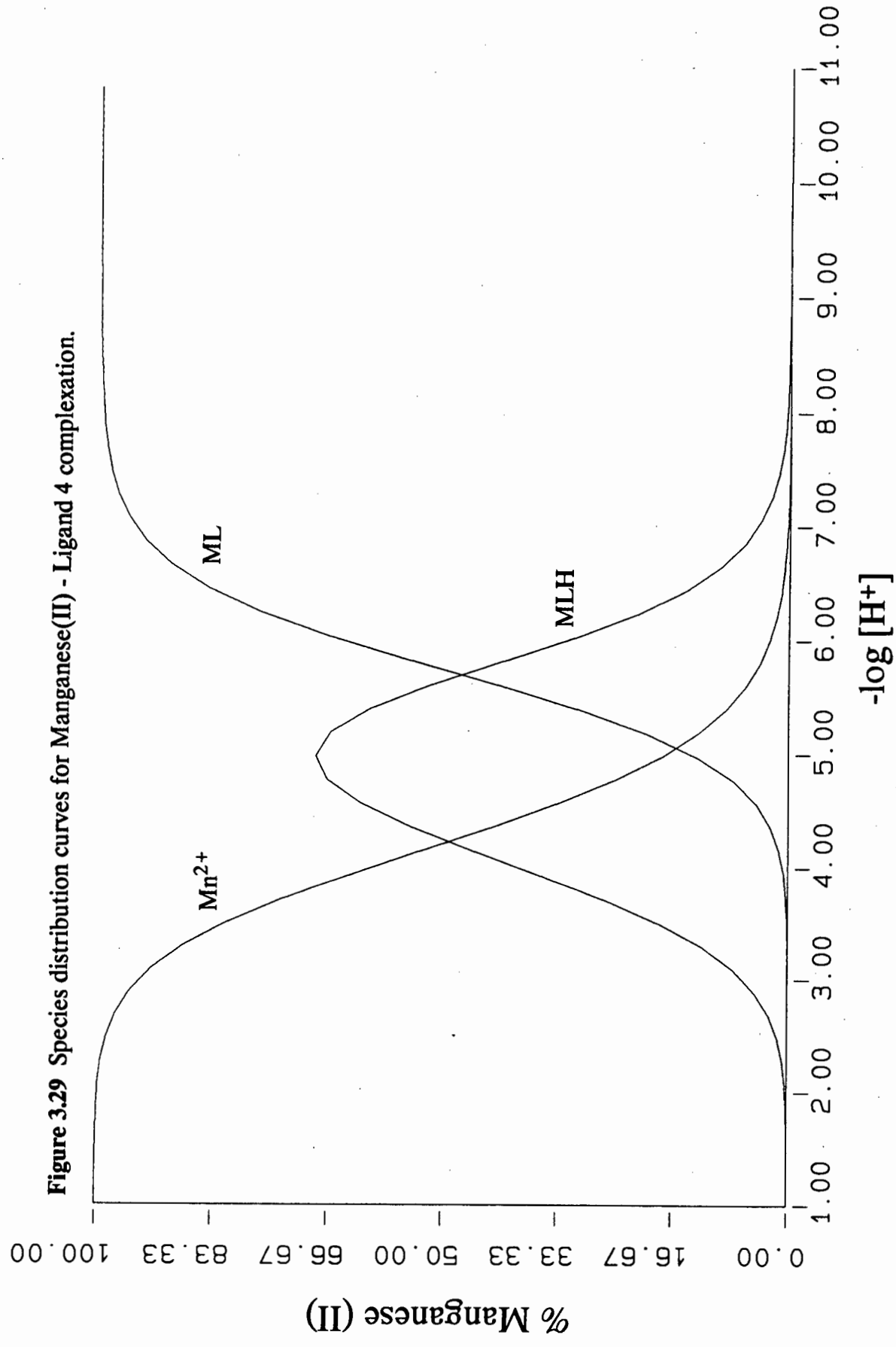


Figure 3.29 Species distribution curves for Manganese(II) - Ligand 4 complexation.

3.5.12 IRON(II) - LIGAND 4 - H^+ COMPLEXATION

The experimental metal formation curves presented in figure 3.30, show a slight tendency to level off at Z_M = 1 before showing the characteristic back - fanning pattern of the hydroxy species indicting that an ML and MLOH species may be present. The metal deprotonation curves shown in figure 3.31 suggest that an MLH and possibly even an MLH_2 species may be present in addition to the two previously mentioned complexes. Stability constants for the three species, MLH, ML and MLOH were estimated from the BETA task and then refined using the OBJT task resulting in an R - factor of 0.017. Addition of an ML_2 species to the model reduced the R - factor to 0.0097 and its validity as an important component of the model was confirmed by an ERR% calculation which showed that the ML_2 species was complexed to some 50% of the metal at high pH in the ligand : metal titrations of 2 : 1 and greater. Refinement of a stability constant of 28.51 for an ML_2H_2 species further reduced the R - factor, R_f, to 0.007 and simultaneous refinement with the electrode intercept using the OBJE task yielded a final R_f of 0.00669.

The species MLH, ML_2H_2, ML, ML_2 and MLOH were accepted as the best model for the speciation of the Fe^{2+} - Lig4 system and their refined stability constants are presented in table 3.14. The match between the theoretical and experimental data is satisfactory although there is room for improvement at higher pH. The speciation curves are presented in figure 3.32 and clearly show that each of the species form a significant part of the model.

Stability constants were also refined for the MLH_2 and M_2L_3 complexes neither of which made any improvement to the R -factor or the fit between the experimental and theoretical data. From an ERR% calculation, it was established that the MLH_2 complex reached a maximum of 12% while the M_2L_3 complex complexed up to 20% of the metal ions. Hovever, the M_2L_3 complex could only be refined in the absence of the ML_2H_2 species which complexed up to 33% of the metal ions in some

titrations. The M_2L_3 complex which has an overall charge of -8, was discarded in favour of the ML_2H_2 species. The MLH_2 species was also discarded from the model.

Using the complexes MLH,ML and MLOH as a basis, the experimental data were repeatedly analysed in turn for the species M_2L, M_2L_2, ML_2H, $ML(OH)_2$, $ML_2(OH)$ and $ML_2(OH)_2$. The BETA task was unable to estimate constants for these complexes.

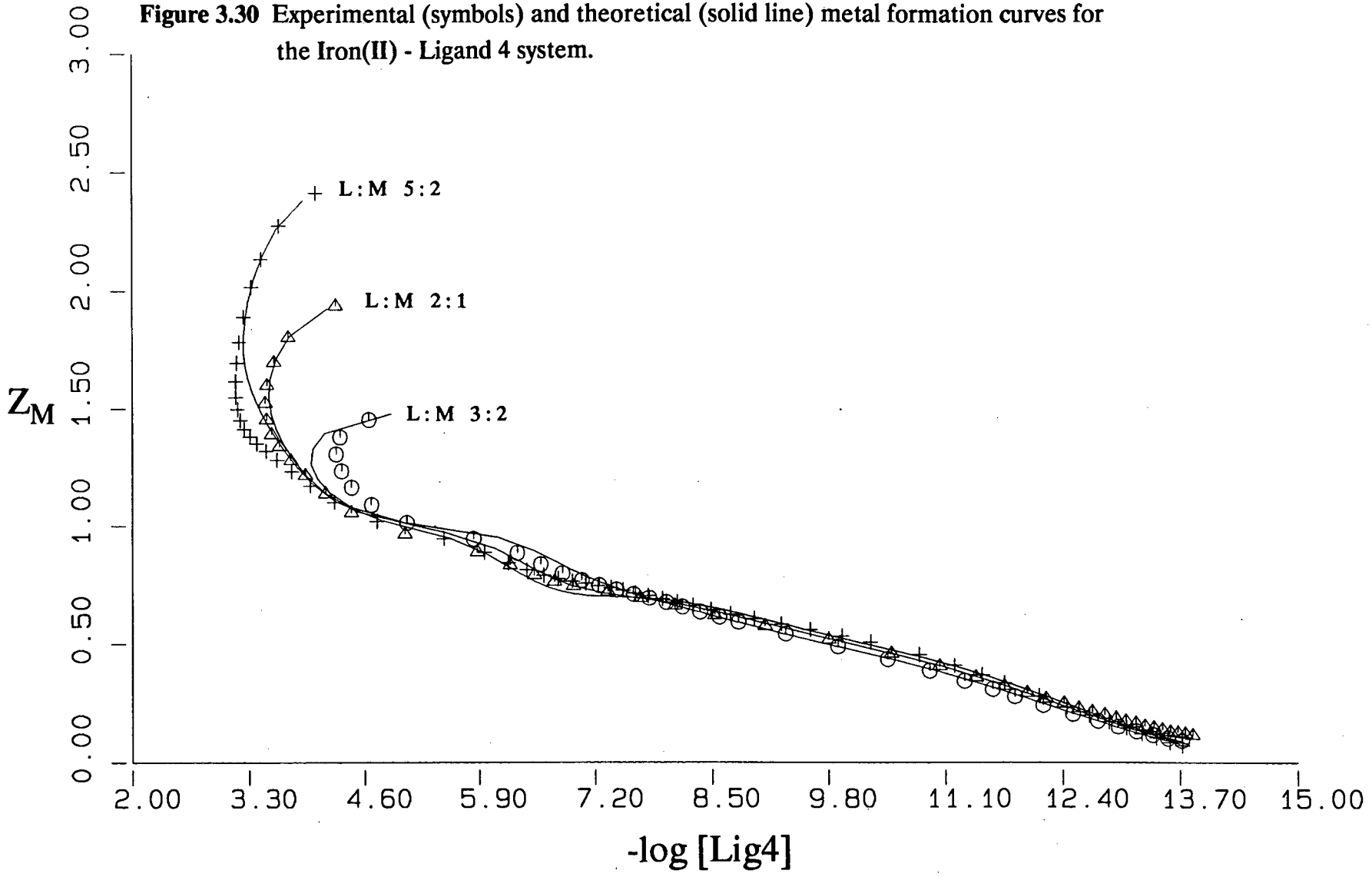
Table 3.14

Statistical analysis and logarithms of the overall stability constants, $\log\beta_{pqr}$, of iron(II) ions with Ligand 4, determined at 25 °C and 0.1 mol.dm^{-3} (Na^+)[Cl^-].

Complex	pqr	$\log\beta_{pqr}$	Std. dev.
MLH	111	15.27	0.0099
ML_2H_2	122	28.51	0.0145
ML	110	9.86	0.0130
ML_2	120	13.20	0.0177
MLOH	11-1	-0.97	0.0237

Objective Function:-	6.92×10^1
R-factor, R_f:-	0.00669
R-limit, R_l:-	0.00081
No of titrations:-	6
No of data points:-	508
[Ligand] range, mol.dm^{-3}:-	0.004282 - 0.005553
[Metal] range, mol.dm^{-3}:-	0.002223 - 0.002869
Ligand:Metal ratios:-	1:1, 3:2, 2:1, 5:2
pH range:-	2.0 - 11.0

Figure 3.30 Experimental (symbols) and theoretical (solid line) metal formation curves for the Iron(II) - Ligand 4 system.



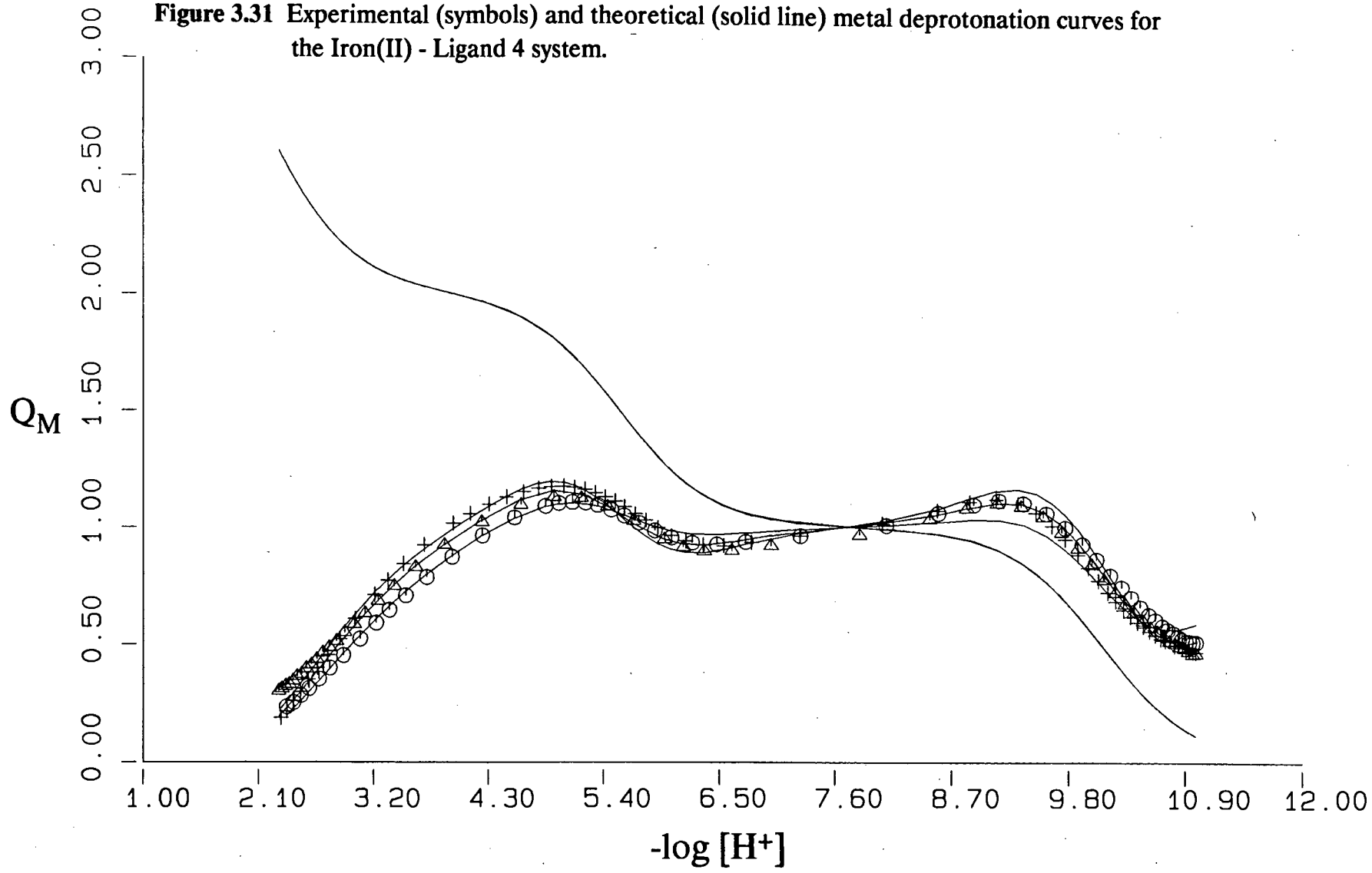
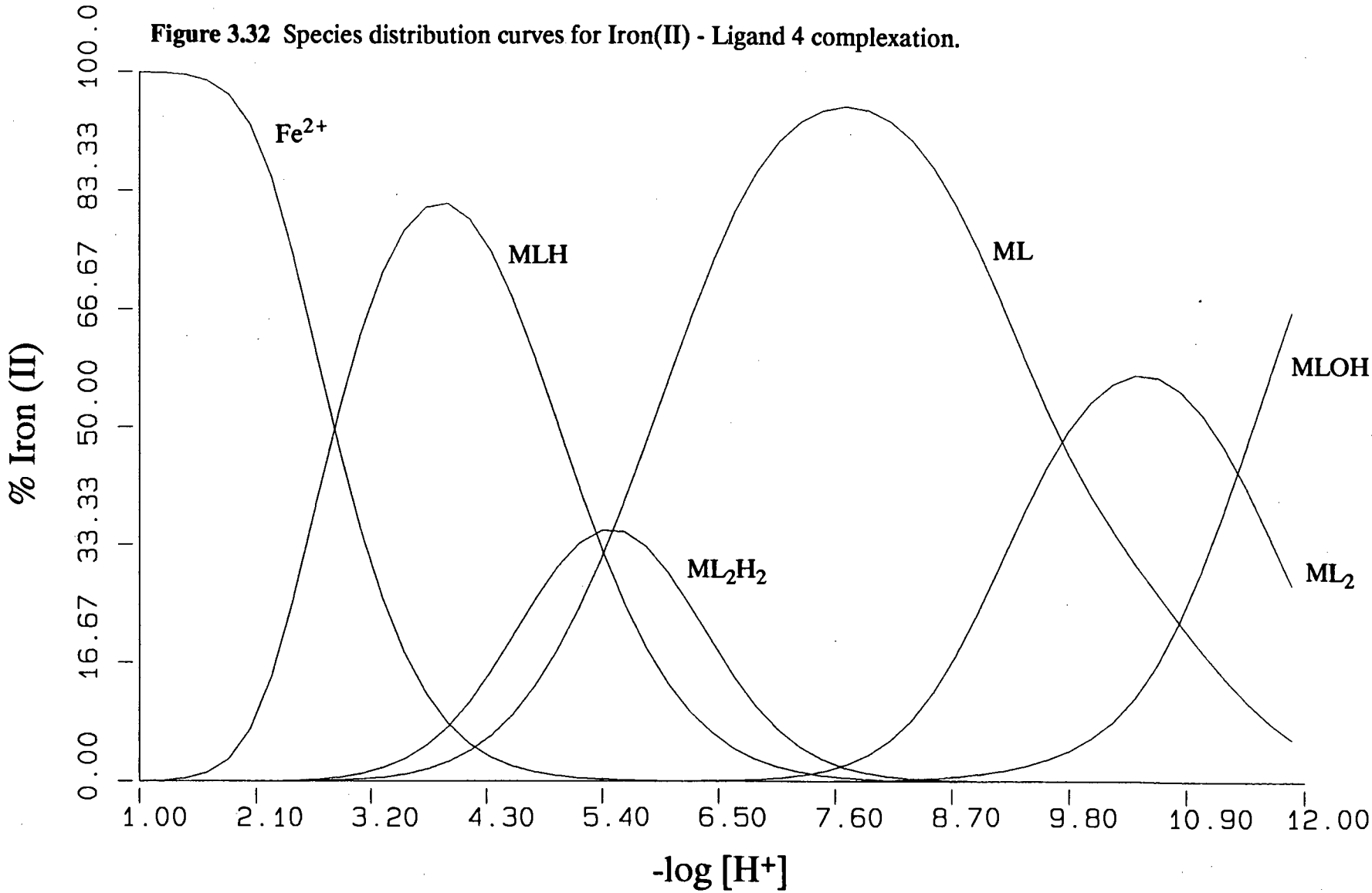


Figure 3.31 Experimental (symbols) and theoretical (solid line) metal deprotonation curves for the Iron(II) - Ligand 4 system.

Figure 3.32 Species distribution curves for Iron(II) - Ligand 4 complexation.



3.5.13 COBALT(II) - LIGAND 4 - H^+ COMPLEXATION

The Co^{2+} - Lig4 system was initially investigated in the pH range of 2 to 11. Although a constant of -1.36 was refined for an MLOH species, an ERR% calculation confirmed that it consisted of at most 10% of the total metal ion concentration and the theoretical curves fitted the experimental curves rather poorly at pH values greater than 7.5. The presence of an ML_2 and an $ML(OH)_2$ complex was investigated but these were not found. Having established the presence of the ML and MLH complexes from the experimental metal formation (figure 3.33) and metal deprotonation curves (figure 3.34), all experimental data points above the pH of 7.50 were discarded to ensure that the best possible constants could be refined for the remaining data set. Attempts to estimate the stability constants for the complexes, MLH_2, M_2L and M_2LH using the BETA task were unsuccessful except for the M_2L complex which subsequently gave a refined value of 15.05. An ERR% calculation revealed that this complex only consisted of 8% of the total metal and it was discarded from the model.

Refined constants as well as the statistical analysis for the present system are shown in figure 3.15. The species distribution diagram indicating the two well defined species, ML and MLH, is presented in figure 3.35

Table 3.15

Statistical analysis and logarithms of the overall stability constants, $\log\beta_{pqr}$, of cobalt(II) ions with Ligand 4, determined at 25 °C and 0.1 mol.dm^{-3} (Na^+)[Cl^-].

Complex	pqr	$\log\beta_{pqr}$	Std. dev.
MLH	111	15.88	0.0044
ML	110	10.82	0.0075

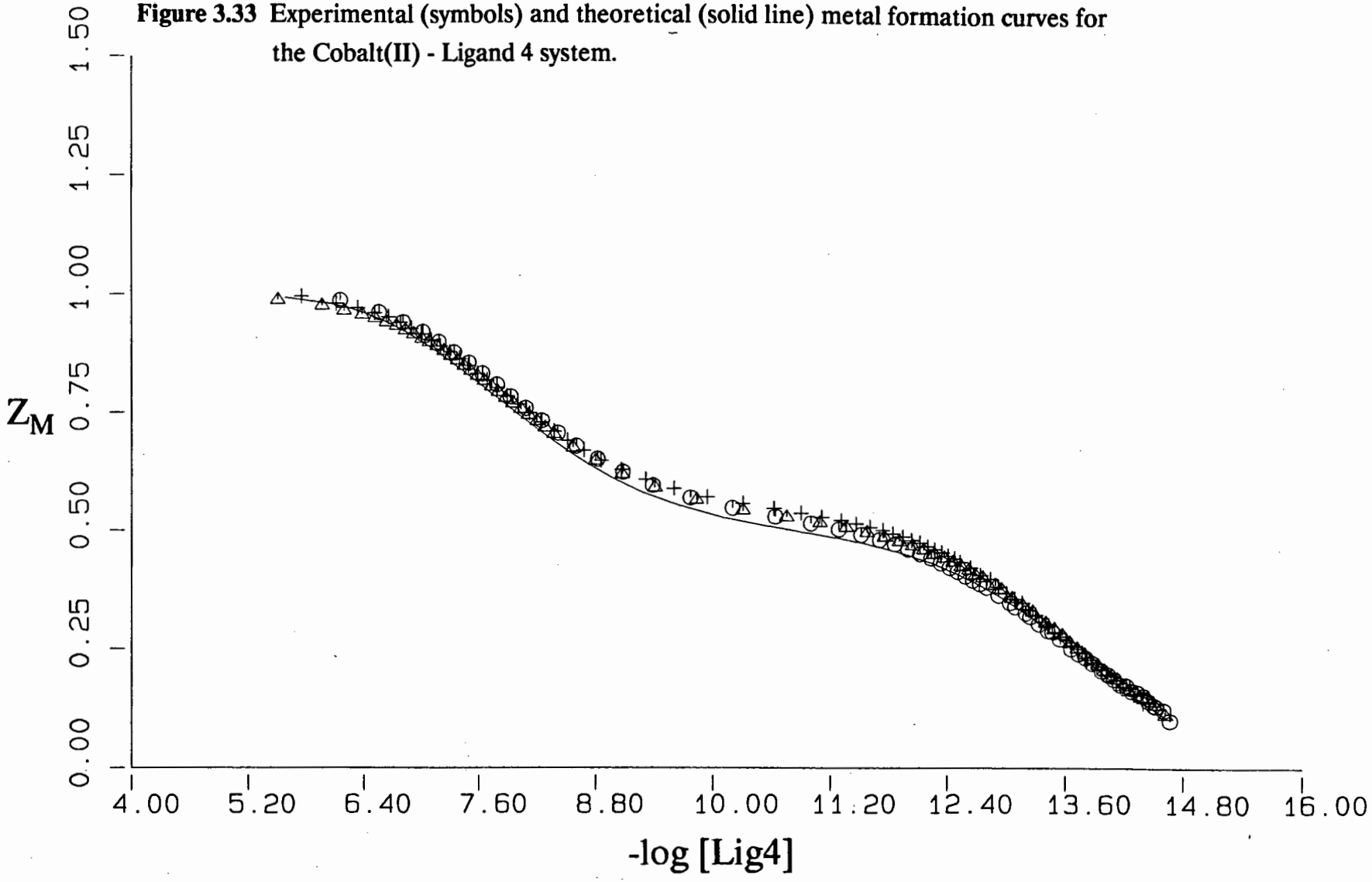
Objective Function:-	1.35×10^1
R-factor, R_f:-	0.00266
R-limit, R_l:-	0.00073
No of titrations:-	6
No of data points:-	547
[Ligand] range, mol.dm^{-3}:-	0.004988 - 0.005994
[Metal] range, mol.dm^{-3}:-	0.001986 - 0.002483
Ligand:Metal ratios:-	1:1, 2:1, 5:2, 3:1
pH range:-	2.5 - 9.0

Literature Data

Constant determined using paper electrophoresis at 20 °C and I = 0.1 mol.dm^{-3} KNO_3 [Maj80].

Complex	pqr	$\log\beta_{pqr}$	Std. dev.
MLH	111	16.46	-

Figure 3.33 Experimental (symbols) and theoretical (solid line) metal formation curves for the Cobalt(II) - Ligand 4 system.



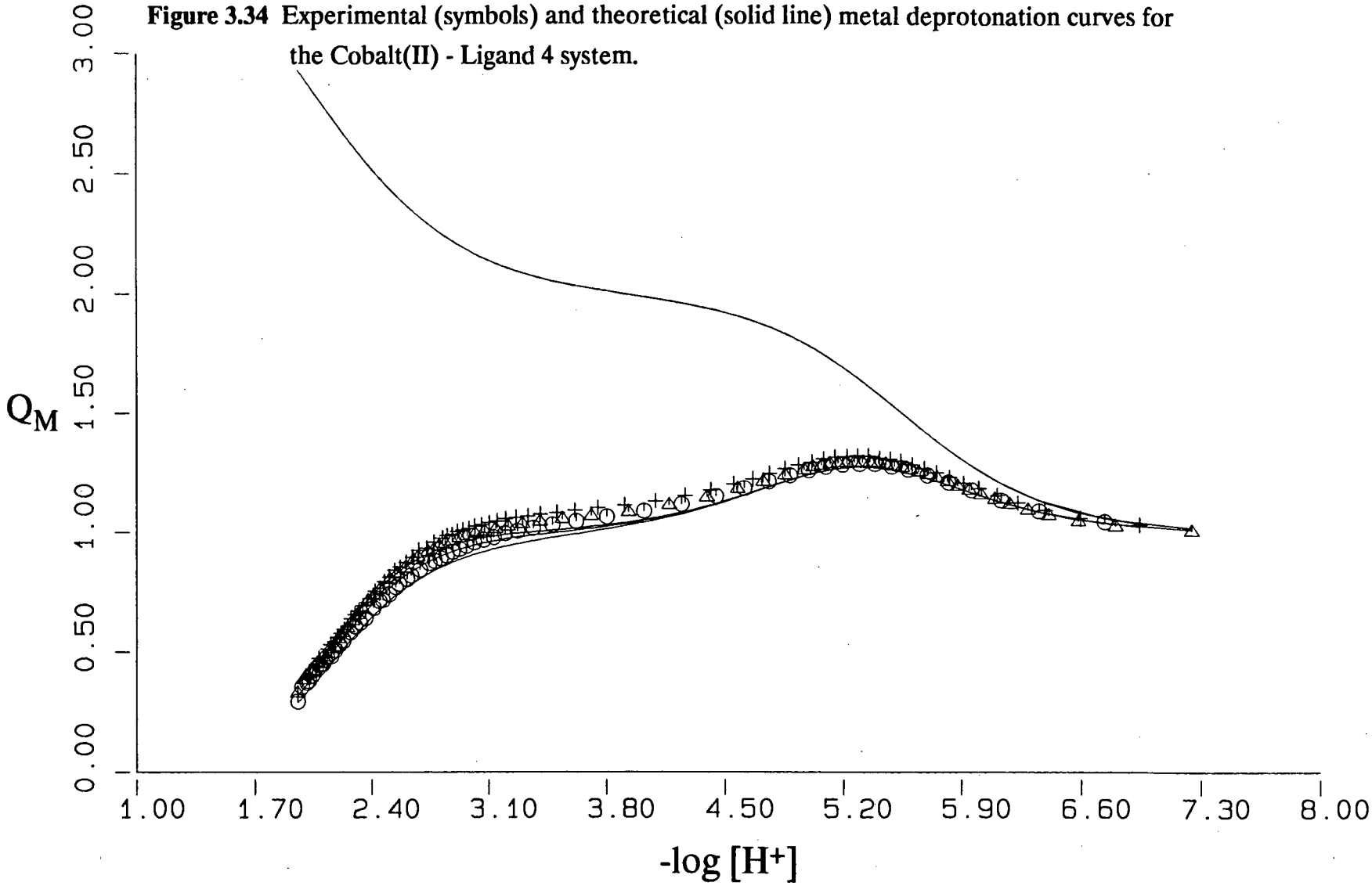


Figure 3.34 Experimental (symbols) and theoretical (solid line) metal deprotonation curves for the Cobalt(II) - Ligand 4 system.

Figure 3.35 Species distribution curves for Cobalt(II) - Ligand 4 complexation.

3.5.14 ZINC(II) - LIGAND 4 - H^+ COMPLEXATION

The experimental metal formation and metal deprotonation curves for the Zn^{2+} - Lig4 system are presented in figures 3.36 and 3.37 respectively. Interpretion of these curves following the standard procedure led to the choice of complexes of MLH, ML and MLOH. Refinement of these complexes using OBJT resulted in an R - factor of 0.015. A $\log\beta_{pqr}$ of 17.18 was refined for an MLH_2 species but this led to no improvement of the R -factor or the fit between experimental and theoretical data. This species was also complexed to less than 10% of the total metal ion concentration as calculated by the ERR% task. The MLH_2 species was subsequently discarded from the model. Stability constants were also refined for the species M_2L and M_2LH but only in the absence of the MLH species. The latter species not only gave a better R - factor, but was also the more likely species in view of the ligand : metal ratio of the titrations. The data set was further examined for the species $ML(OH)_2$, ML_2 and ML_2H none of which was found.

The species MLH, ML and MLOH were thus chosen as that constituting the model and refinement of the stability constants using OBJE with weighting resulted in an R - factor of 0.00608. Refinement of the stability constants with any of the other parameters led to correlation. The results of the system under discussion are presented in table 3.16 and the distribution of species is shown in figure 3.38. Each of these species form the major complex in one of three pH regions.

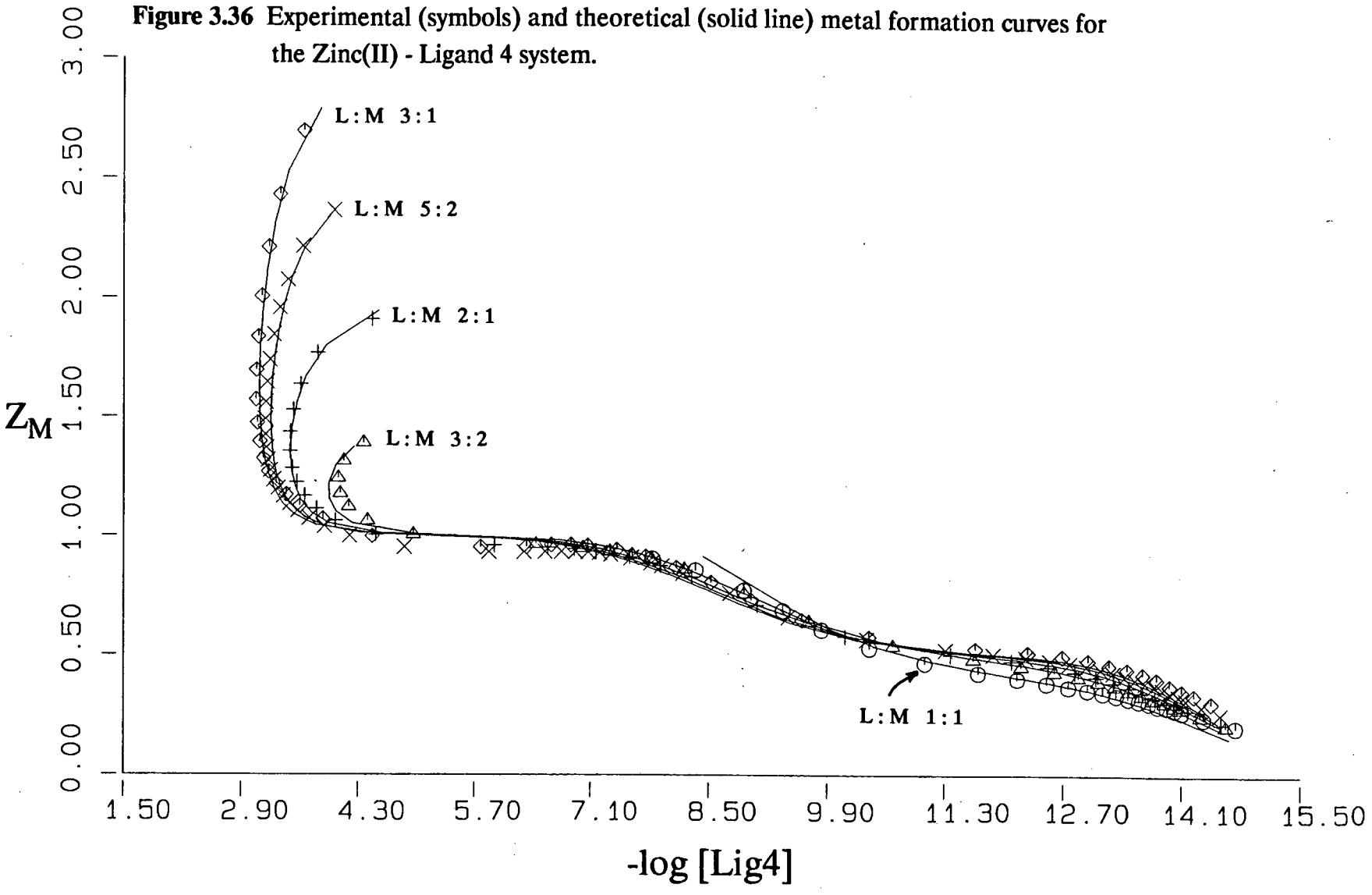
Table 3.16

Statistical analysis and logarithms of the overall stability constants, $\log\beta_{pqr}$, of zinc(II) ions with Ligand 4, determined at 25 °C and 0.1 mol.dm^{-3} (Na^+)[Cl^-].

Complex	pqr	$\log\beta_{pqr}$	Std. dev.
MLH	111	16.28	0.0062
ML	110	11.55	0.0068
MLOH	11-1	1.23	0.0079

Objective Function:-	6.69×10^1
R-factor, R_f:-	0.00608
R-limit, R_l:-	0.00074
No of titrations:-	9
No of data points:-	877
[Ligand] range, mol.dm^{-3}:-	0.004967 - 0.007450
[Metal] range, mol.dm^{-3}:-	0.002519 - 0.005038
Ligand:Metal ratios:-	1:1, 3:2, 2:1, 5:2, 3:1
pH range:-	2.0 - 11.0

Figure 3.36 Experimental (symbols) and theoretical (solid line) metal formation curves for the Zinc(II) - Ligand 4 system.



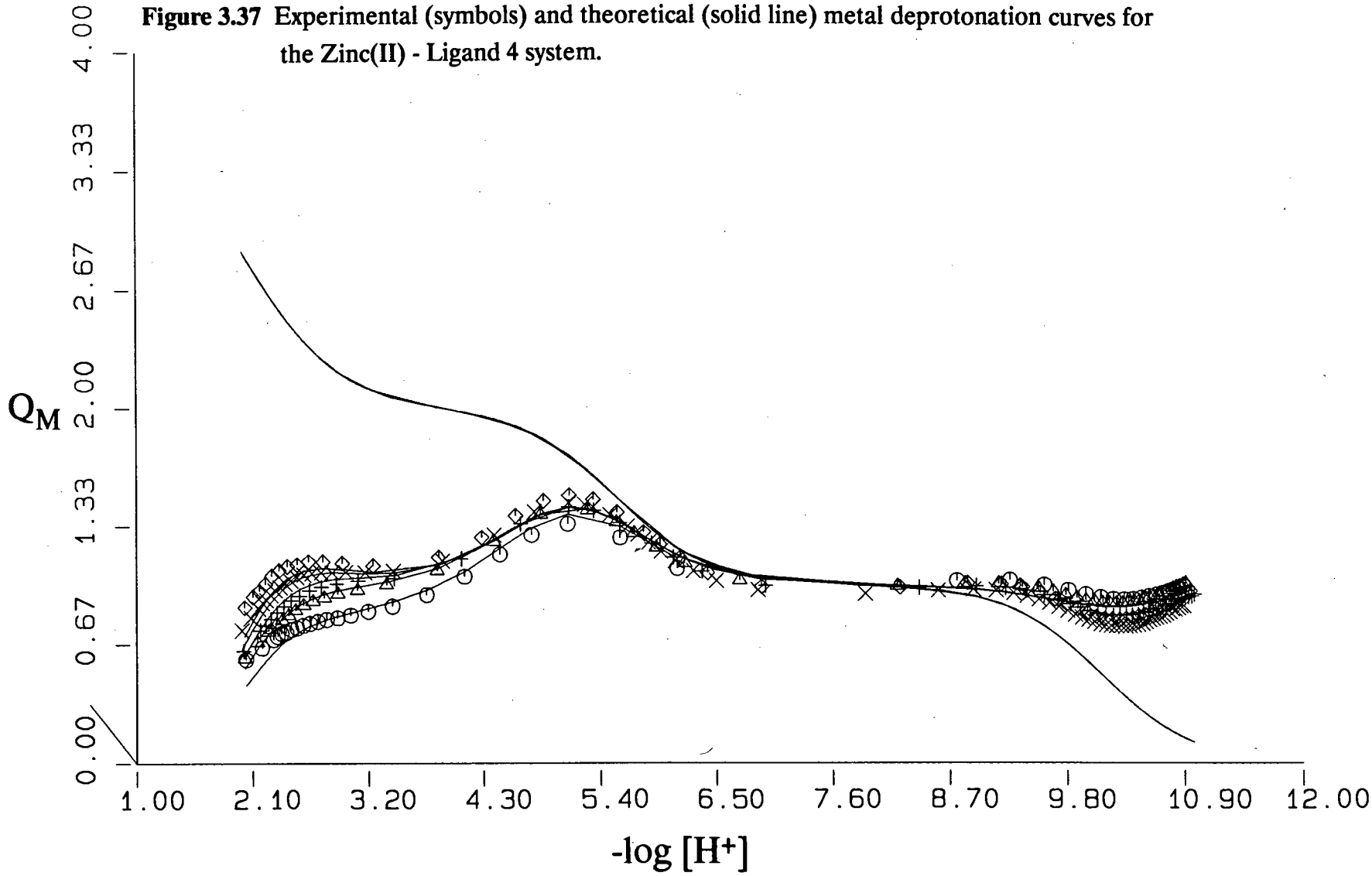
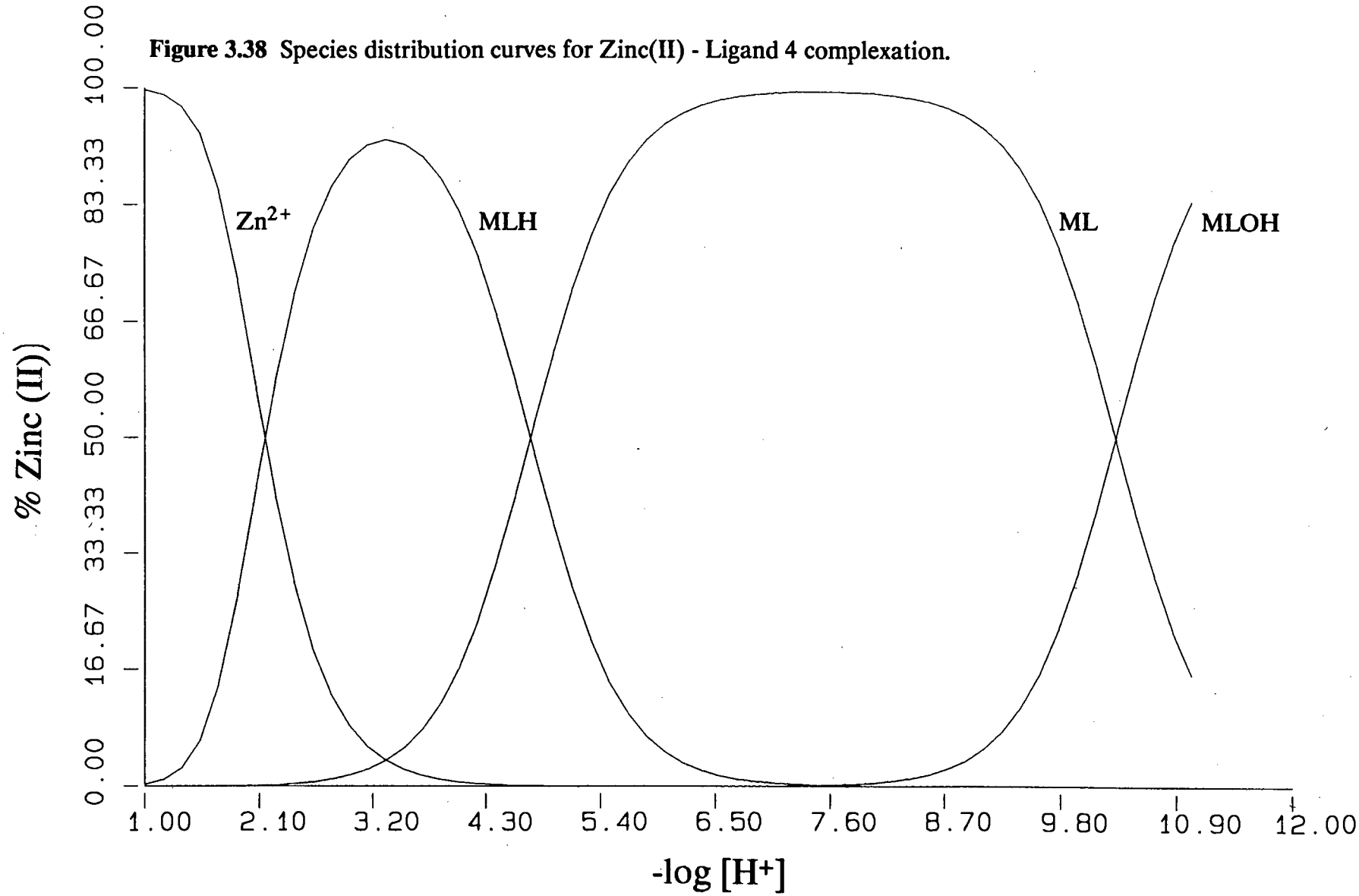


Figure 3.37 Experimental (symbols) and theoretical (solid line) metal deprotonation curves for the Zinc(II) - Ligand 4 system.

Figure 3.38 Species distribution curves for Zinc(II) - Ligand 4 complexation.



3.5.15 COPPER(II) - LIGAND 4 - H^+ COMPLEXATION

The experimental metal formation and metal deprotonation curves for the Cu^{2+} - Lig4 system are presented in figures 3.39 and 3.40 respectively. The characteristic pattern of the curves suggested that the species MLH, ML and MLOH were present in solution. Stability constants for the above complexes were estimated using the BETA task of ESTA. However, refining these constants using either of the optimization tasks, led to the following stability constants and standard deviations with correlation between the stability constants of the complexes; $\log\beta_{111}$ 18.37 (0.1092), $\log\beta_{110}$ 13.69 (0.1105) and $\log\beta_{11\text{-}1}$ 3.78 (0.1131). The reported constants were obtained using the OBJE task.

The phenomenon of correlation arises when metal - ligand complexation is high at low pH values resulting in few complex forming experimental points thus preventing the accurate determination of log K_1 for the formation of the first species. Since $\log\beta_n$ is the sum of the the logarithms of all species K_i (for i = 1 to n), it is essential that all the $\log K_i$ values be known. Although the stability constants are refined with correlation, one can determine logK for two of the three species formed, ie.

$$\log K_{MLH} = [MLH] / [ML][H] = 4.48,$$
$$\text{and } \log K_{ML} = [ML] / [MLOH][H] = 9.91$$

By fixing $\log\beta_{MLH}$ = 20.00 say, one can refine stability constants for the other two species without correlation. The numerical values of the stability constants $\log\beta_{ML}$ and $\log\beta_{MLOH}$, in the above case were 15.32 and 5.41 respectively. These results indicate that the logK values for the above reactions effectively remained unchanged.

It appeared as if the stability constants were sliding along a scale and fixing any one of the three constants, enabled one to refine the other two without correlation. It was then decided to use a competing ligand in order to accurately determine at least one of the stability constants of the present system. The principle of using a competing ligand is best illustrated by the following reactions,

$$Cu^{2+} - Lig4 + Lig^{comp} \rightleftharpoons Cu^{2+} - Lig^{comp} + Lig4 \text{ and}$$

$$Cu^{2+} - Lig^{comp} + Lig4 \rightleftharpoons Cu^{2+} - Lig4 + Lig^{comp}$$

Either of these reactions would ensure the presence of some complex - forming points for the system under investigation thus enabling one to accurately determine at least one of the stability constants. In the present context, complex - forming points are experimental data points obtained in a region where the concentrations of the individual components are measurable. In the Cu^{2+} - ligand 4 system all of the metal ions are bound by ligand molecules at low pH and this therefore results in the phenomenon of correlation.

An ideal competing ligand is one whose stability constant is of the same order of magnitude as that of the metal - Ligand system which has to be determined. In the above instance, we do not know the stability constant of the Cu^{2+} - Lig4 complex precisely but the value of 13.69 refined with correlation is more or less what one would expect for the system. This estimation is based on the stability constants of ligand4 with various other metal ions. The advantage of finding a ligand with a similar stability constant, enables one to use them both in similar concentration ranges. The choice of ligand should preferably be one which is commercially available in a pure form and whose aqueous equilibria have been established with

the metal ion of concern. It would also be advantageous if the denticity of the ligand, and its speciation were such that the formation of mixed ligand complexes would be unlikely.

Using literature constants, a number of speciation plots for the copper(II) - Ligand4 - Competing Ligand system were determined in order to assist with the choice of competing ligand. Among those ligands examined were IDA, EDDA (Ethylenediamine diacetic acid) and 4 - Nitrocatechol. 4 - Nitrocatechol showed promise as a competing ligand since its ML_2 species completely displaced Ligand4 at high pH at a Cu^{2+} : Lig4 : Lig^{comp} ratio of 1 : 1 : 2. In principle, this would enable one to refine the stability constants for the MLH and ML species of the Cu^{2+} - Lig4 system.

Since the above results were theoretical, and based on an estimated constant for the Cu^{2+} - Lig4 ML species, only experiment would show if 4 -Nitrocatechol were indeed a suitable competing ligand. Two preliminary titrations at ratios of 1 : 1 : 1 and 1 : 1 : 2 for Cu^{2+} : Lig4 : Lig^{comp} were performed. Using literature values as constants for the protonation and copper(II) complexation of 4 - Nitrocatechol, stability constants were refined without correlation for the MLH and ML species of the Cu^{2+} - Lig4 system.

It was decided to use 4 - Nitrocatechol as a competing ligand to assist in establishing the aqueous equilibria of the Cu^{2+} - Lig4 system. It was also decided that the protonation and copper(II) complexation constants for 4 - Nitrocatechol would be determined under our experimental conditions of temperature, ionic strength and choice of background electrolyte. These constants would then be fixed in the computation of Cu^{2+} -Lig4 constants from titration data using a competing ligand.

Figure 3.39 Experimental metal formation curves for the Copper(II) - Ligand 4 system.

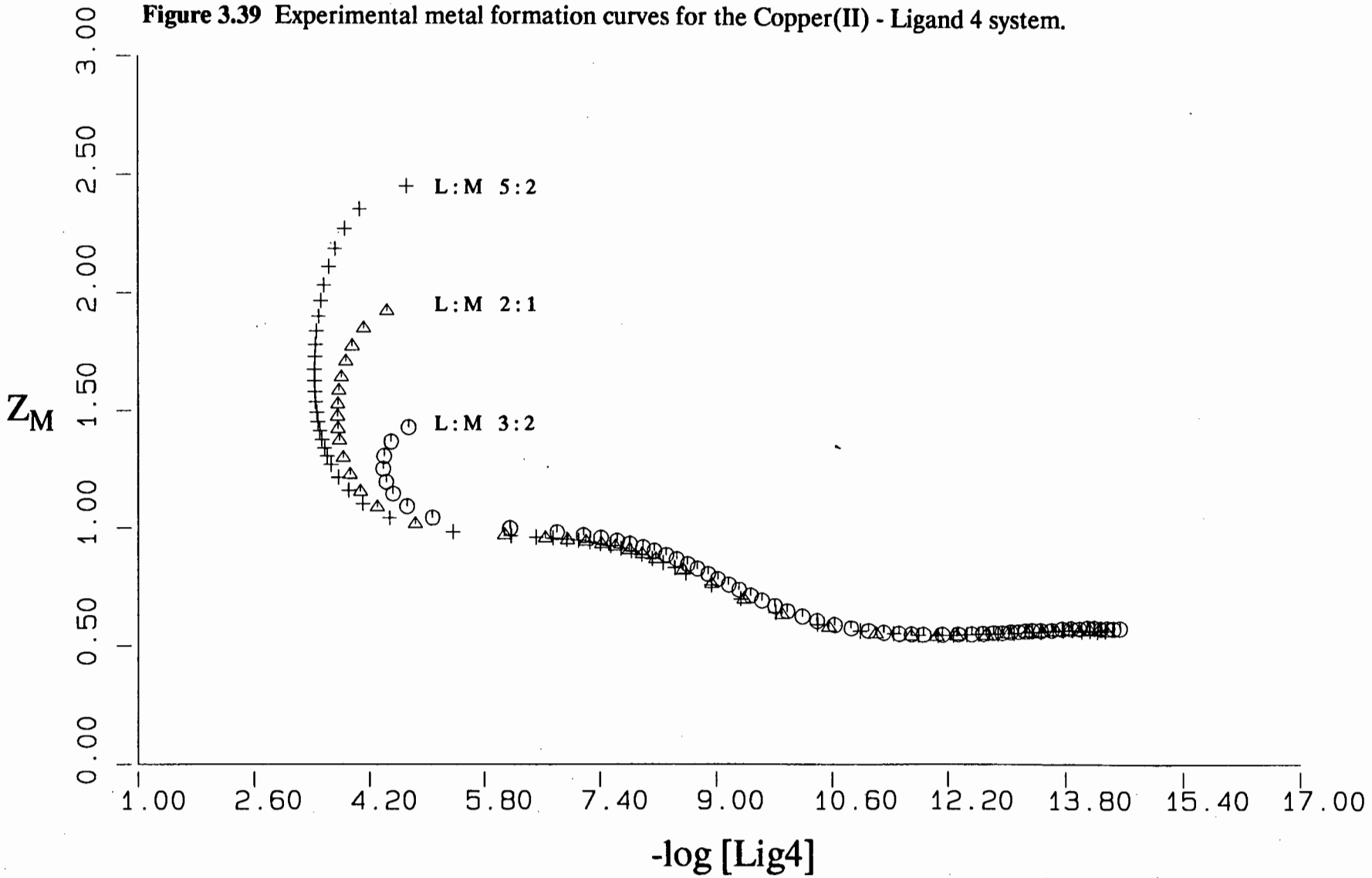
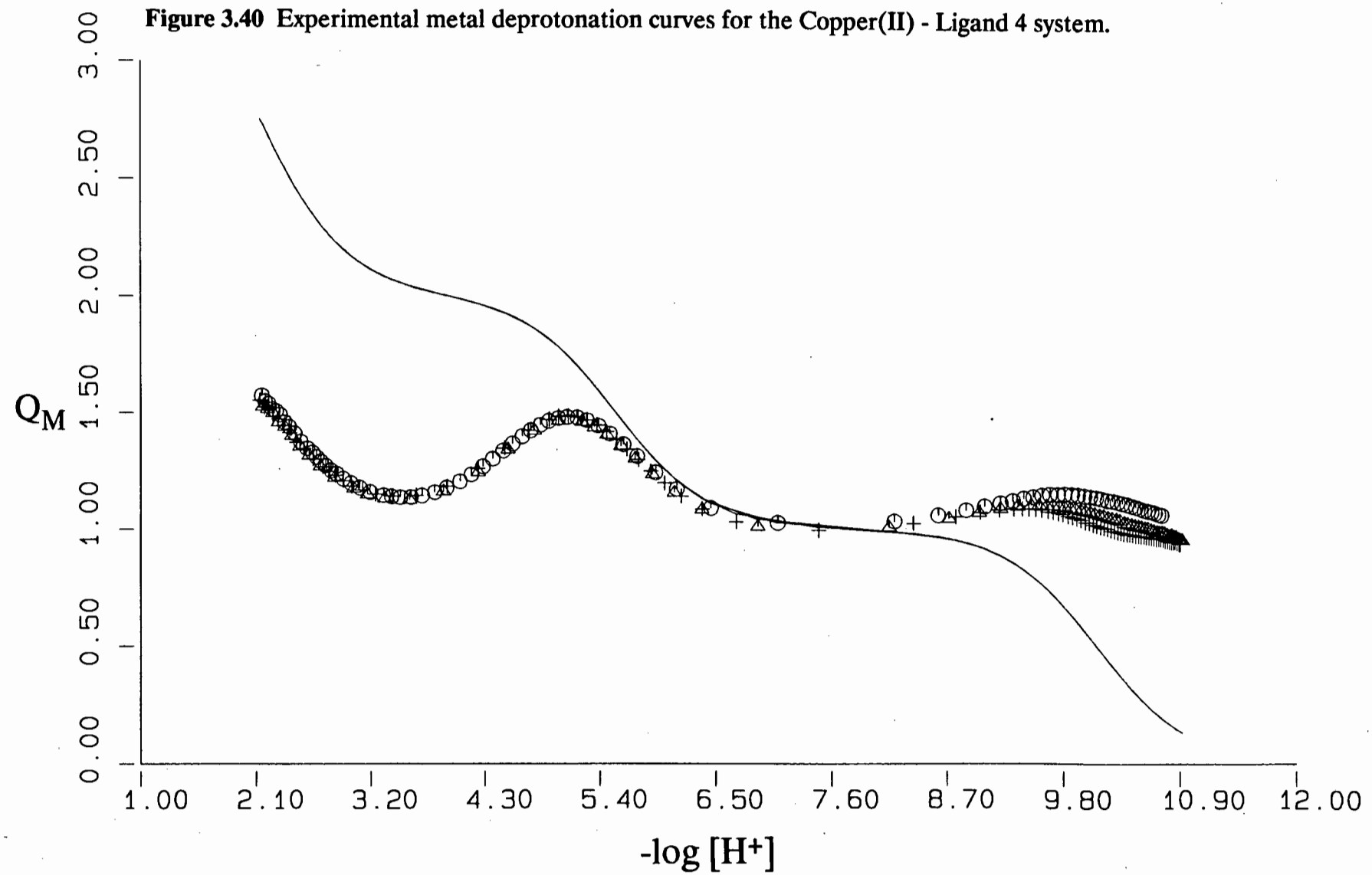


Figure 3.40 Experimental metal deprotonation curves for the Copper(II) - Ligand 4 system.



3.5.16 4 - NITROCATECHOL PROTONATION

The experimental proton formation curves of 4 - Nitrocatechol are presented in figure 3.41 and the refined protonation constants together with the literature values [Hak84] are presented in table 3.17. There is a difference of 0.31 log units between the first protonation constant determined in this study and that reported in the literature. However, all titrations were reproducible in the pH range studied and the experimental and theoretical curves fit well with a satisfactory R - factor and objective function. The speciation curves are presented in figure 3.42

3.5.17 COPPER(II) 4 - NITROCATECHOL - H^+ COMPLEXATION

The experimental metal formation and metal deprotonation curves of the copper(II) - 4 - Nitrocatechol system are presented in figures 3.43 and 3.44. Interpretation of both sets of curves clearly indicates the presence of an ML and ML_2 species. This is in accordance with those complexes reported in the literature [Hak84] and presented in table 3.18 together with the experimentally determined values of this study. The system was also examined for the species MLH, ML_2H, ML_2H_2, ML(OH), $ML(OH)_2$, $ML_2(OH)$ and $ML_2(OH)_2$. Although there is no experimental evidence for most of these species, they are all chemically possible.

The speciation curves are presented in figure 3.45 and this confirms the high degree of stability of the ML_2 complex which forms from a pH of 4 onwards and eventually complexes all of the ligand at a L :M ratio of 2 :1.. An ML_2 complex is likely to consist of two ligand molecules occupying the four equatorial sites on the central metal ion. It is therefore unlikely that any mixed ligand complexes would form if 4 - Nitrocatechol were to be used in the presence of a tetradentate ligand such as ligand 4.

Table 3.17

Statistical analysis and logarithms of the stepwise, $logK_n$, and overall, $log\beta_{01r}$, protonation constants of 4-Nitrocatechol , determined at 25 °C and 0.1 mol.dm^{-3} (Na^+)[Cl^-].

Complex	pqr	$logK_n$	$log\beta_{01r}$	Std. dev.
LH	011	10.54	10.54	0.0019
LH_2	012	6.63	17.17	0.0027

Objective Function:-	1.25×10^1
R-factor, R_f:-	0.00399
R-limit, R_l:-	0.00113
No of titrations:-	4
No of data points:-	196
[Ligand] range, mol.dm^{-3}:-	0.0039887 - 0.0055647
pH range:-	3.1 - 11.1

Literature Data

Constants determined potentiometrically at 25 °C and I = 0.1 mol.dm^{-3} KCl [Hak84].

Complex	pqr	$logK_n$	$log\beta_{01r}$	Std. dev.
LH	011	10.85	10.85	0.05
LH_2	012	6.69	17.54	0.03

Figure 3.41 Experimental (symbols) and theoretical (solid line) proton formation curves for 4 - Nitrocatechol.

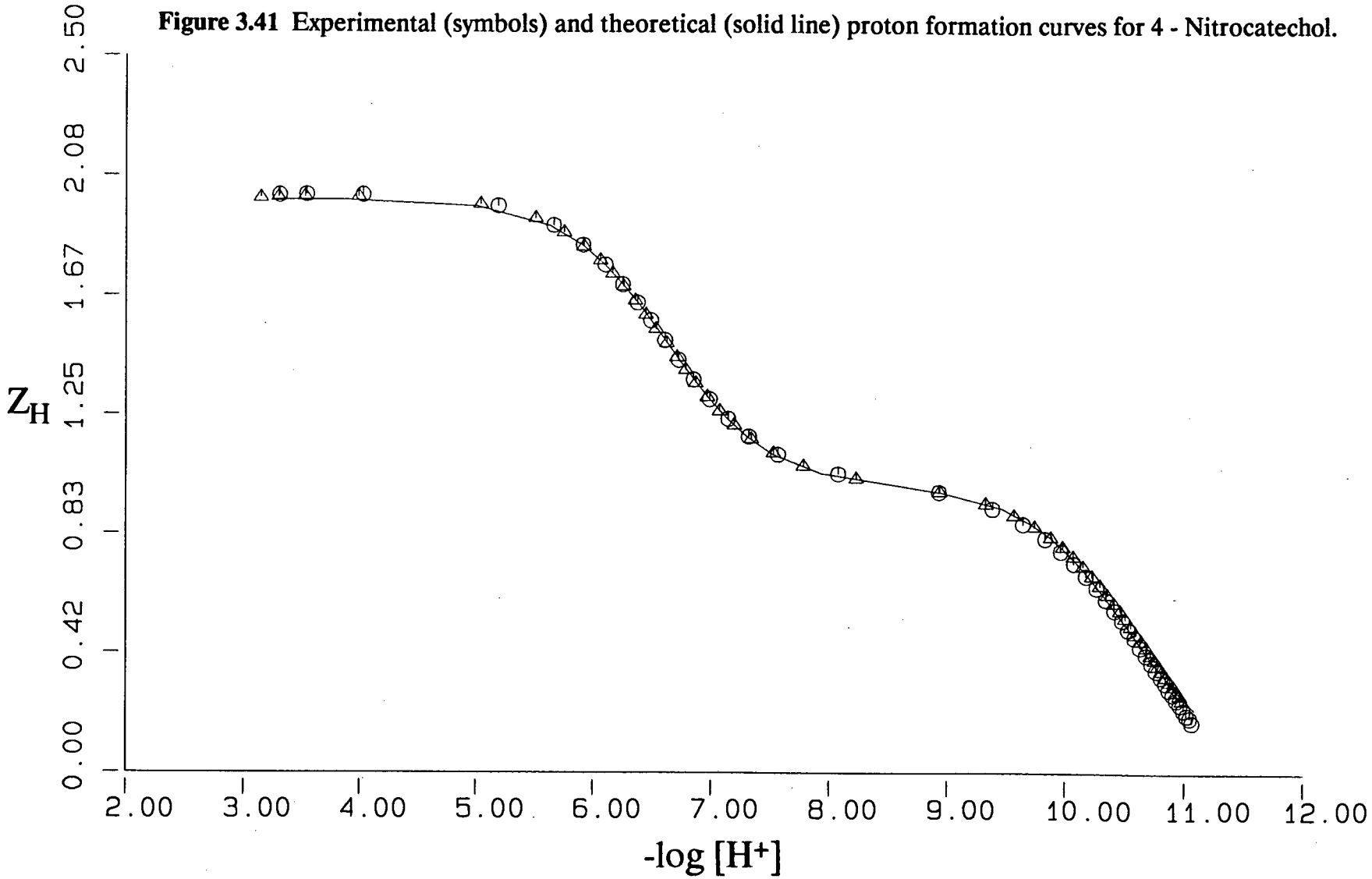


Figure 3.42 Species distribution curves for 4 - Nitrocatechol protonation.

Table 3.18

Statistical analysis and logarithms of the overall stability constants, $\log\beta_{pqr}$, of copper(II) ions with 4-Nitrocatechol, determined at 25 °C and 0.1 mol.dm^{-3} (Na^+)[Cl^-].

Complex	pqr	$\log\beta_{pqr}$	Std. dev.
ML	110	11.37	0.0016
ML_2	120	20.41	0.0041

Objective Function:-	3.87 X 10^0
R-factor, R_f:-	0.00421
R-limit, R_l:-	0.00217
No of titrations:-	4
No of data points:-	290
[Ligand] range, mol.dm^{-3}:-	0.0033005 - 0.0066010
[Metal] range, mol.dm^{-3}:-	0.0033602
Ligand:Metal ratios:-	1:1, 2:1
pH range:-	3.3 - 6.5

Literature Data

Constants determined potentiometrically at 25 °C and I = 0.1 mol.dm^{-3} KCl [Hak84].

Complex	pqr	$\log\beta_{pqr}$	Std. dev.
ML	110	11.69	0.02
ML_2	120	21.00	0.10

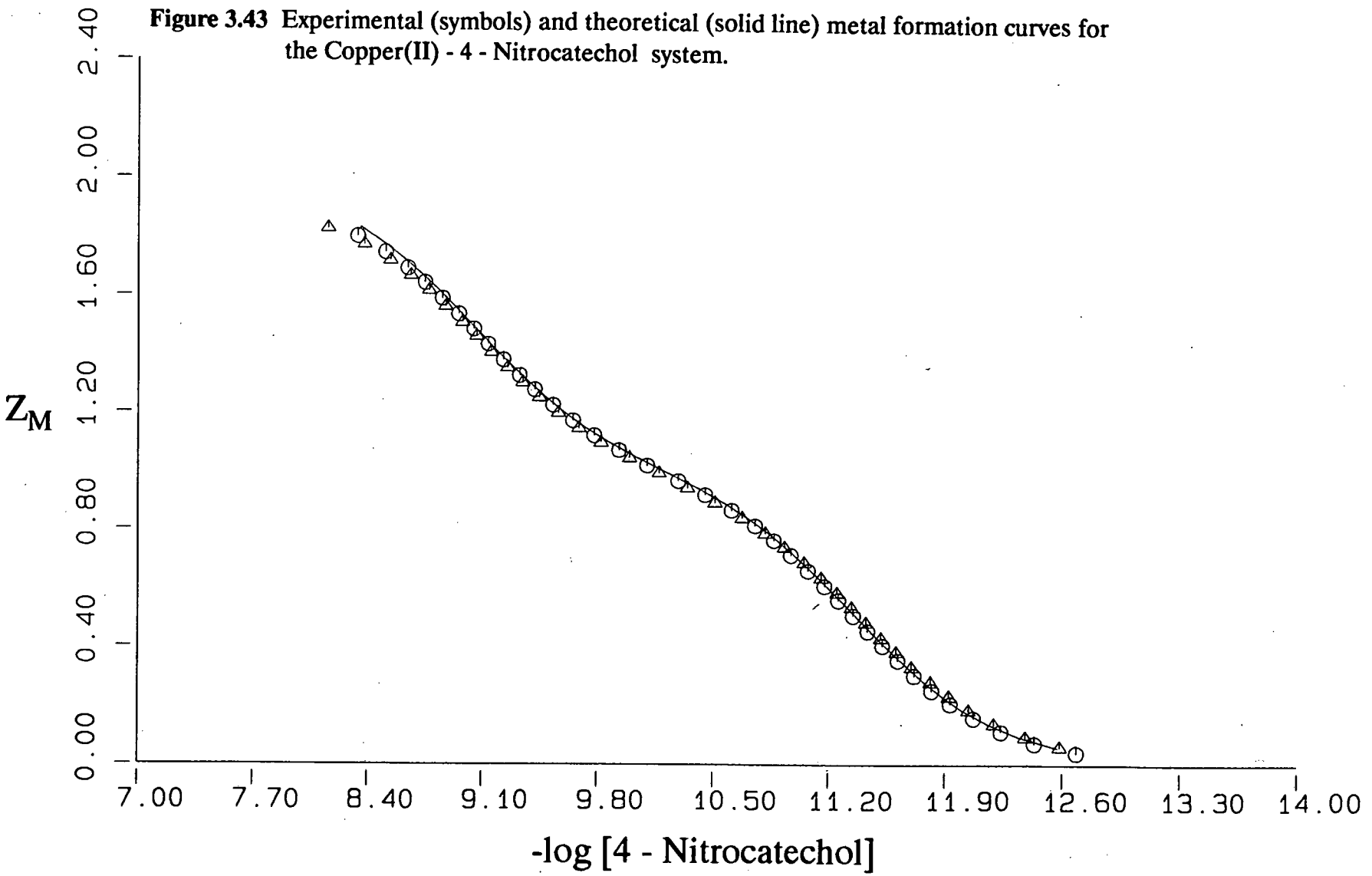


Figure 3.43 Experimental (symbols) and theoretical (solid line) metal formation curves for the Copper(II) - 4 - Nitrocatechol system.

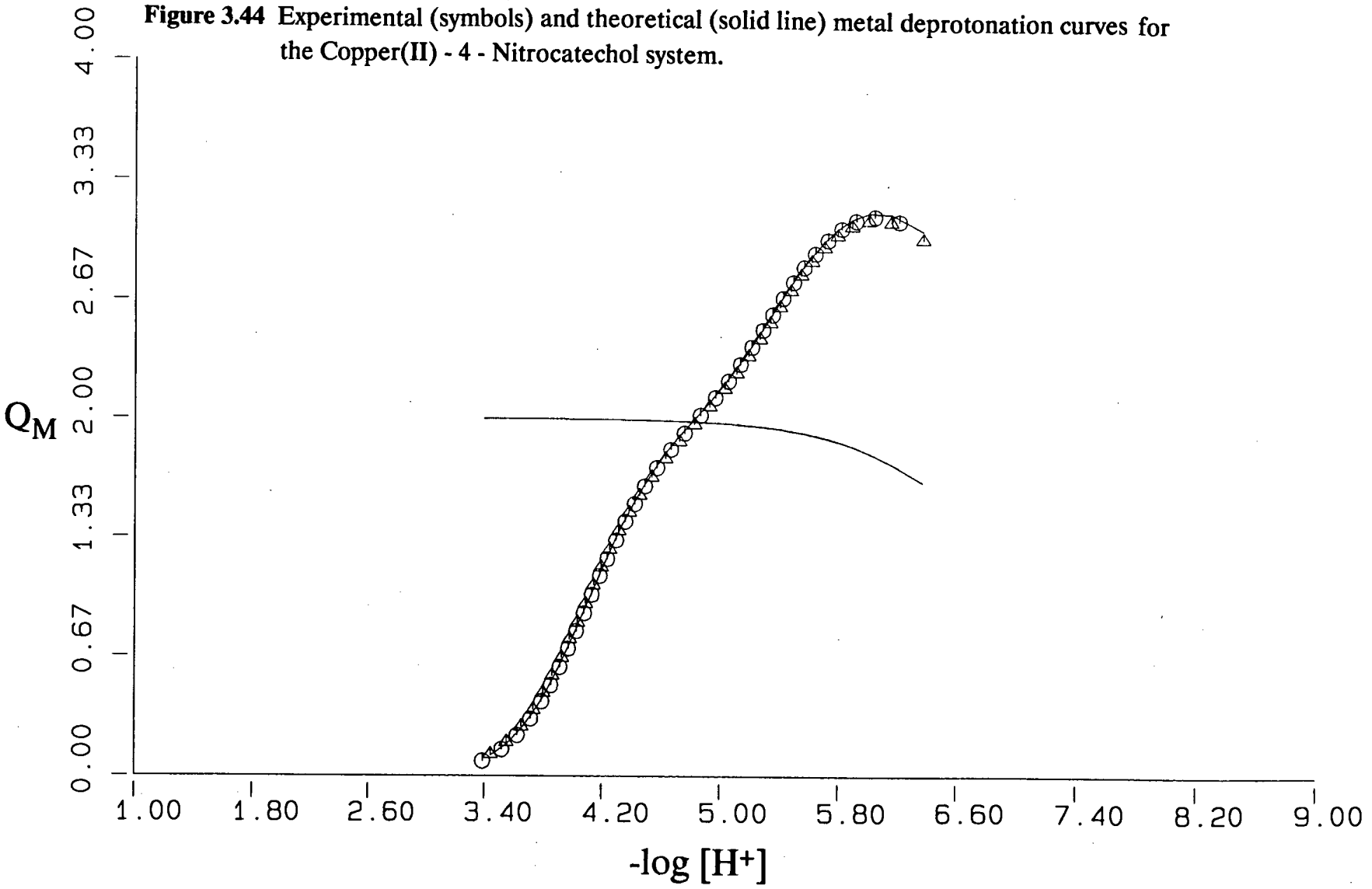
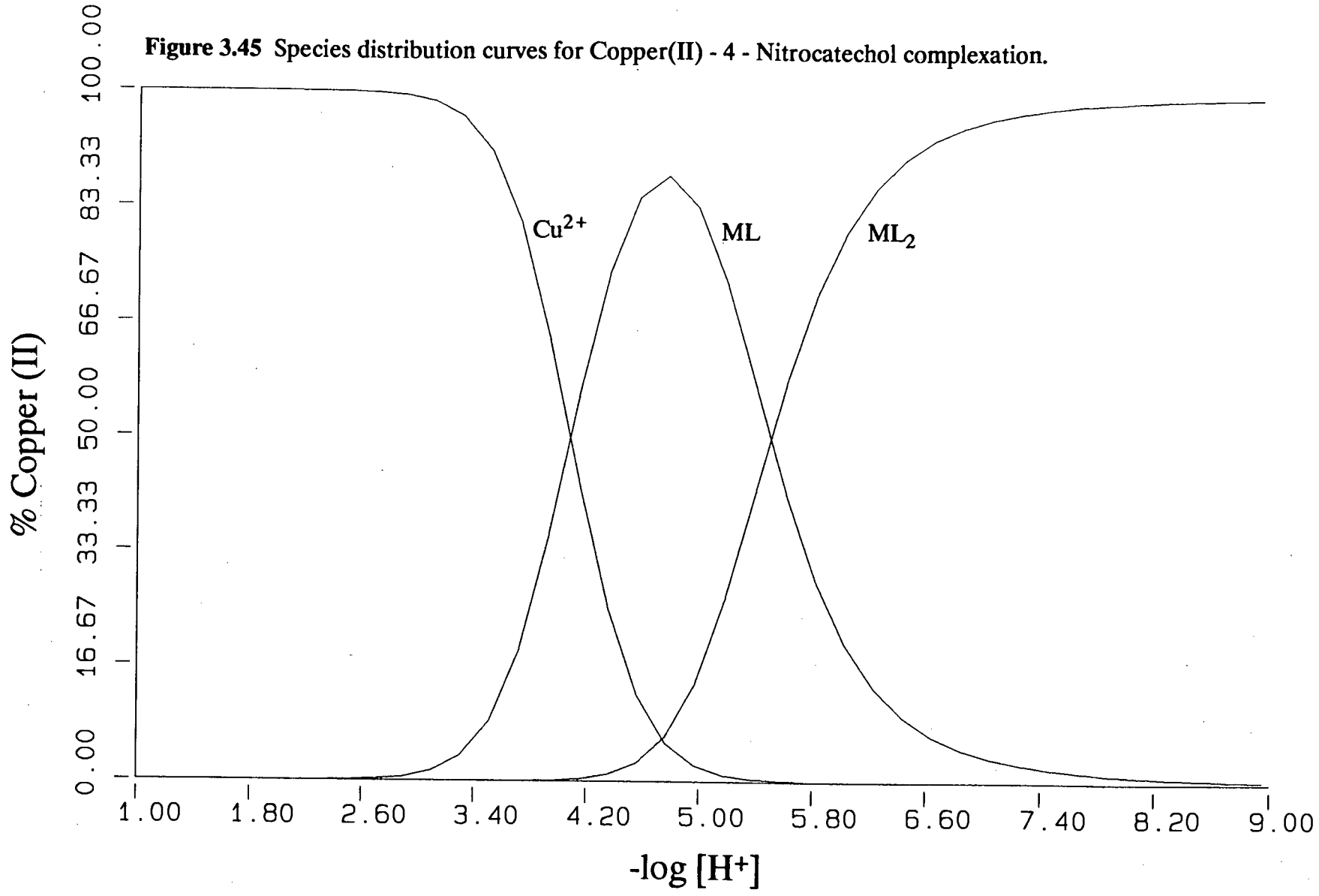


Figure 3.44 Experimental (symbols) and theoretical (solid line) metal deprotonation curves for the Copper(II) - 4 - Nitrocatechol system.

Figure 3.45 Species distribution curves for Copper(II) - 4 - Nitrocatechol complexation.



3.5.18 COPPER(II) - LIGAND 4 - 4 - NITROCATECHOL - H^+ COMPLEXATION

Potentiometric titrations of the above system were performed at the following ratios for Cu^{2+} : L4 : 4NC ; 1 : 1 : 1, 1 : 1 : 1.5, 1 : 1 : 2, 1 : 1 : 2.5 and 1 : 1 : 3. The chosen ratios would ensure that the ML_2 species for Cu^{2+} - 4NC, would dominate the speciation of the system at high pH thereby displacing most of the Ligand 4 molecules from the Cu^{2+} ions and enabling one to refine stability constants for the ML and MLH species of the Cu^{2+} - Lig4 system.

Stability constants for the above-mentioned species were refined without correlation and are presented in table 3.19. Protonation constants for Ligand 4 and 4 - Nitrocatechol as well as the copper(II) complexation constants for 4 - Nitrocatechol were fixed in this refinement process. From the stability constants for the ML and MLH species which are 14.08 and 18.77, K_{MLH} for the quotient

$$[MLH] / [ML] [H] = 10^{4.69}$$

This is in excellent agreement with the logK of 4.68 for the same reaction in the absence of the competing ligand. This not only gives one confidence in the refined constants but also lends support to the precision of the proton and copper(II) complexation constants of 4 - Nitrocatechol used in the above refinement.

The ML and MLH constants of copper(II) - Ligand 4 were refined from 7 titrations and 970 data points. The R - factor of 0.00547 and the objective function of 5.09 x 10^1 are both satisfactory considering the fact that there are four components in solution (Cu^{2+}, Lig4, 4NC and H^+ ions).

The original copper(II) - Ligand 4 titration data set of 7 titrations and 753 points was now used to refine a stability constant for the MLOH species resulting in a stability constant of 4.17 with an R - factor of 0.00320. The known constants for the ML and MLH species were fixed in this refinement. The results and statistical analysis are presented in table 3.20.

Additional species such as MLH_2, ML_2, ML_2H, ML_2H_2, M_2L and $ML(OH)_2$ were sought in the Cu^{2+} - Lig4 system, but none of these were found and the model of MLH, ML and MLOH was thus chosen.

The speciation curves for the Cu^{2+} - Lig4 - 4NC system at concentration ratios of 1 : 1 : 1 and 1 : 1 : 2 are presented in figures 3.46 and 3.47 respectively. From figure 3.46, one observes the presence of the Cu^{2+} - Lig4 MLOH species. However, this complex does not form in the presence of higher concentrations of 4 - Nitrocatechol where the Cu^{2+} - $(4NC)_2$ complex dominates the species distribution at high pH. This effectively ensures that a high concentration (if not all) of Ligand 4 is substituted at the Cu^{2+} metal binding sites resulting in the complex forming (complex breaking) experimental points required for the refinement of complexes without correlation.

The experimental and theoretical metal formation and metal deprotonation curves of the Cu^{2+} - Lig4 system are presented in figures 3.48 and 3.49 respectively. The fit between experimental and calculated data is good which again gives confidence in the model and stability constants reported. The speciation curves of the Cu^{2+} - Lig4 are presented in figure 3.50 and the most striking feature is the high percentage of Cu^{2+} ions, (100%), bound to Ligand 4 at a pH of 2. This of course was the root cause of the problem resulting in few (or no) complex forming experimental data

points, thus making it difficult to accurately refine a stability constant for the first species formed in solution.

In conclusion, it can be said that the method of using a competing ligand worked well and is dependent on a good choice of competing ligand. The principle of using a competing ligand is easy to grasp since the process of studying the aqueous equilibria of any metal - ligand system involves the competition between water molecules and the ligand for the available sites on the metal ion. Thus, any metal - ligand system can be regarded as a competing ligand system.

Table 3.19

Statistical analysis and logarithms of the overall stability constants, $\log\beta_{pqr}$, of copper(II) ions with Ligand 4, determined in the presence of a competing ligand, 4-Nitrocatechol at 25 °C and 0.1 mol.dm^{-3} (Na^+)[Cl^-].

Complex	pqr	$\log\beta_{pqr}$	Std. dev.
MLH	111	18.77	0.0131
ML	110	14.08	0.0084

Objective Function:-	5.09 X 10^1
R-factor, R_f:-	0.00541
R-limit, R_l:-	0.00076
No of titrations:-	7
No of data points:-	970
[Ligand4] range, mol.dm^{-3}:-	0.002515
[4NC] range, mol.dm^{-3}:-	0.003838 - 0.007698
[Metal] range, mol.dm^{-3}:-	0.002520
Cu^{2+}:Lig4:4NC ratios:-	1:1:1, 1:1:1.5, 1:1:2, 1:1:2.5, 1:1:3
pH range:-	1.8 - 11.0

Table 3.20

Statistical analysis and logarithm of the overall stability constant, $\log\beta_{11\text{-}1}$, of copper(II) ions with Ligand 4, determined at 25 °C and 0.1 mol.dm^{-3} (Na^+)[Cl^-].

Complex	pqr	$\log\beta_{pqr}$	Std. dev.
MLOH	11-1	4.17	0.0029

Objective Function:-	1.50×10^1
R-factor, R_f:-	0.00320
R-limit, R_l:-	0.00083
No of titrations:-	7
No of data points:-	753
[Ligand] range, mol.dm^{-3}:-	0.002493 - 0.004543
[Metal] range, mol.dm^{-3}:-	0.001832 - 0.002520
Ligand:Metal ratios:-	1:1, 3:2, 2:1, 5:2
pH range:-	2.0 - 11.0

Figure 3.46 Species distribution curves for Copper(II) - Ligand 4 - 4 - Nitrocatechol complexation.

Figure 3.47 Species distribution curves for Copper(II) - Ligand 4 - 4 - Nitrocatechol complexation.

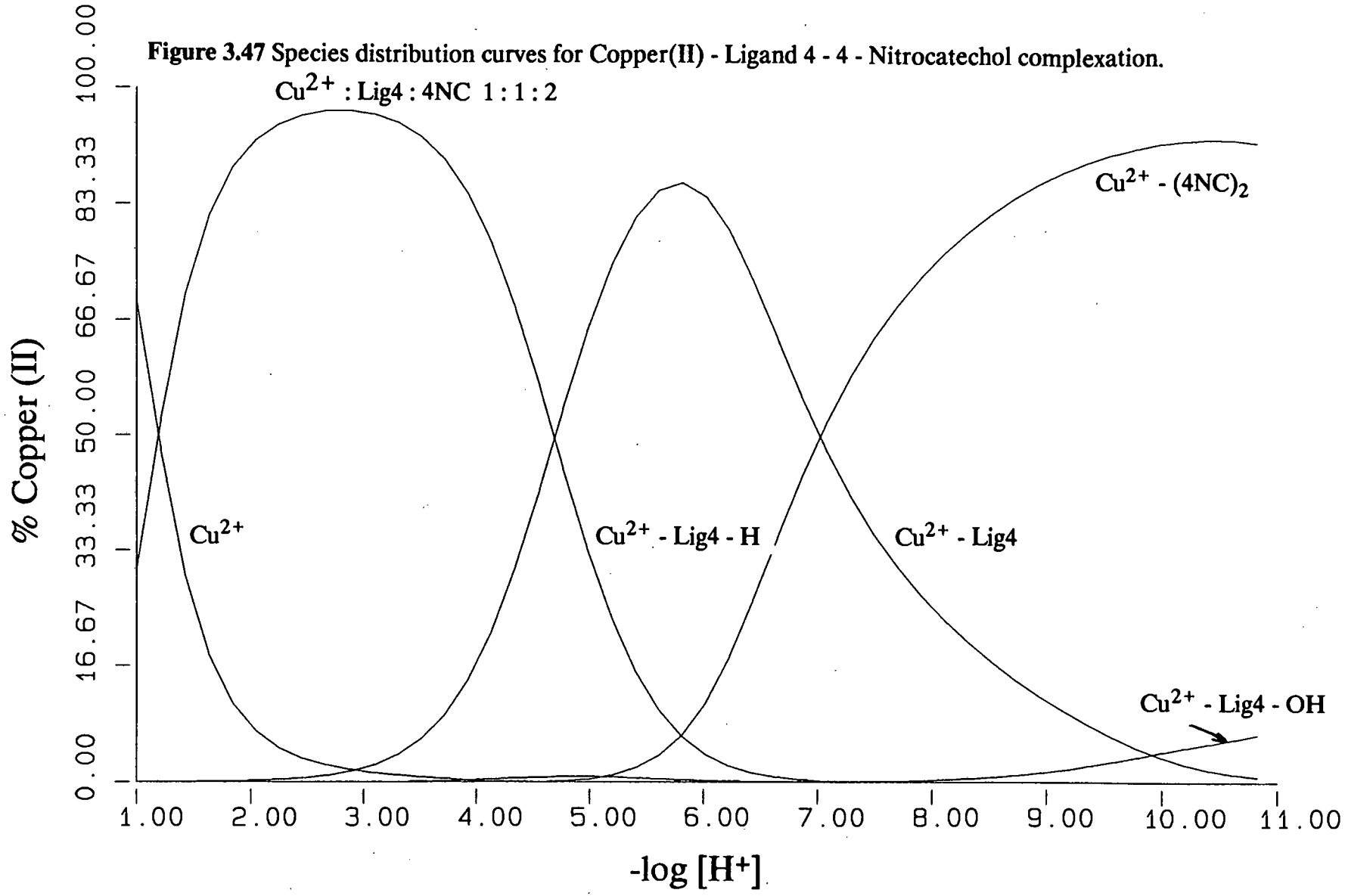


Figure 3.48 Experimental (symbols) and theoretical (solid line) metal formation curves for the Copper(II) - Ligand 4 system.

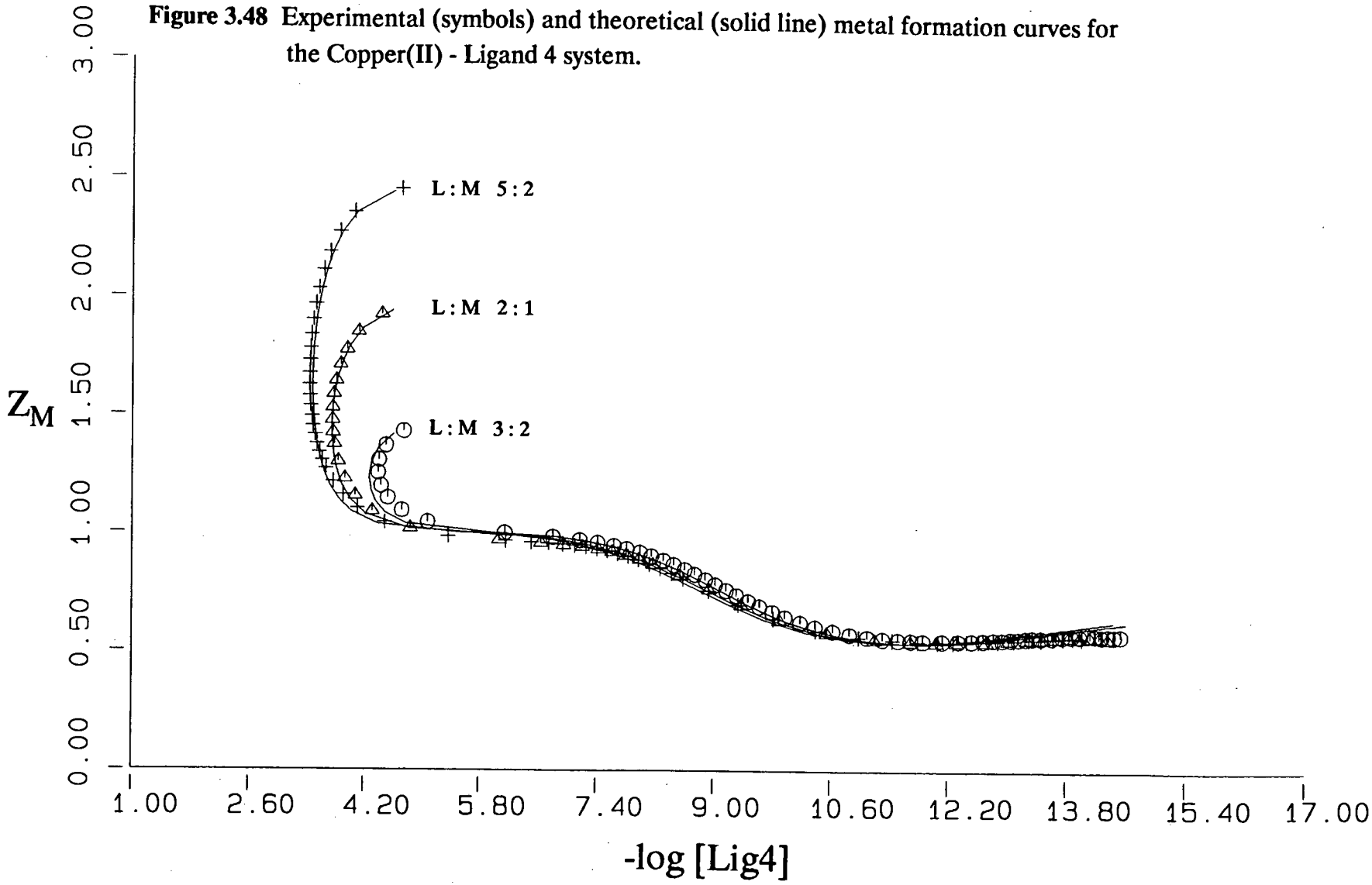


Figure 3.49 Experimental (symbols) and theoretical (solid line) metal deprotonation curves for the Copper(II) - Ligand 4 system.

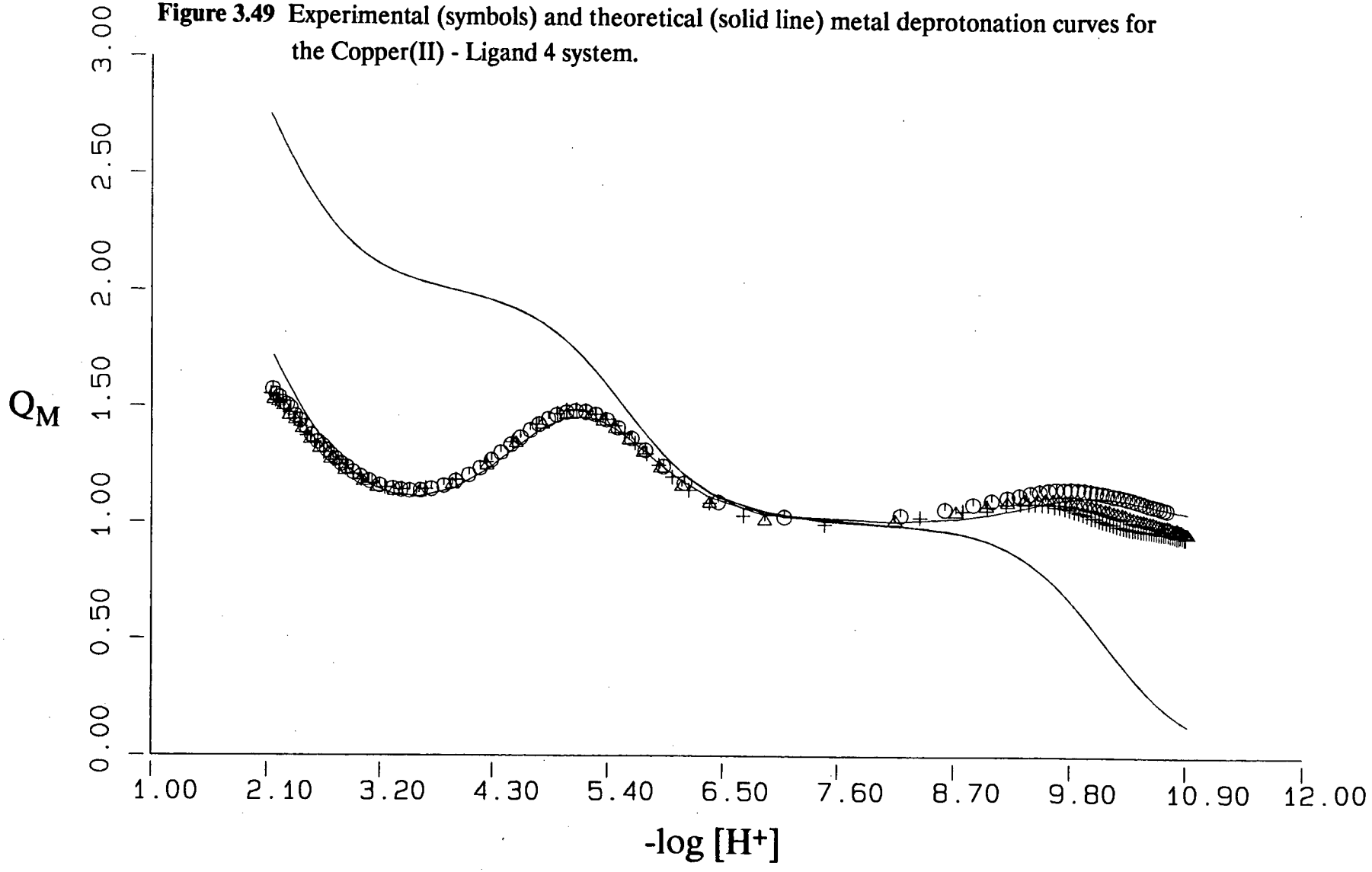
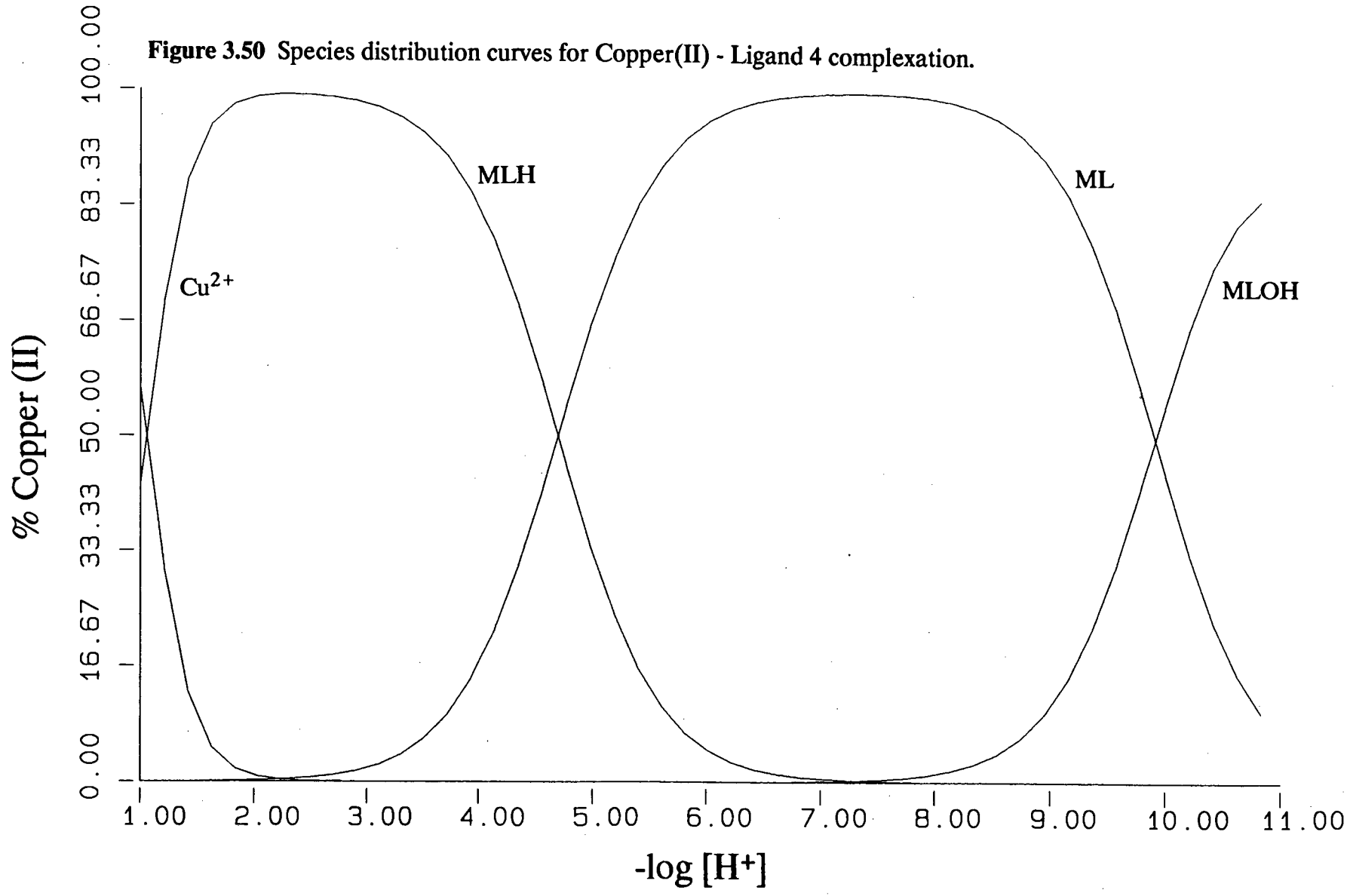


Figure 3.50 Species distribution curves for Copper(II) - Ligand 4 complexation.



3.5.19 COPPER(II) - LIGAND 3 - H^+ COMPLEXATION

Titrations in this system were performed at the ligand : metal ratios of 1 : 2, 1 : 1, 3 : 2, 2 : 1 and 3 : 1. The experimental metal formation and metal deprotonation curves which are presented in figures 3.51 and 3.52 respectively both exhibit the high degree of complex formation at low pH. Not surpisingly, the species MLH_2, MLH, ML and MLOH were refined with correlation. The logarithms of the respective stability constants were 24.70, 20.91, 15.54 and 4.89. 4 - Nitrocatechol is not suitable for use as a competing ligand in this system as the Cu^{2+} - Lig3 binding is even greater than that of Cu^{2+} - Lig4. This was confirmed by means of speciation calculations using the stability constants obtained with correlation. A ligand with a greater stability with Cu^{2+} ions had to be found for use as a competing ligand.

At this point in this study, it was decided to abandon the search for a competing ligand to solve the Cu^{2+} - Ligand 3 system as the computer modelling studies would involve Ligand 1 and Ligand 4 only.

Figure 3.51 Experimental metal formation curves for the Copper(II) - Ligand 3 system.

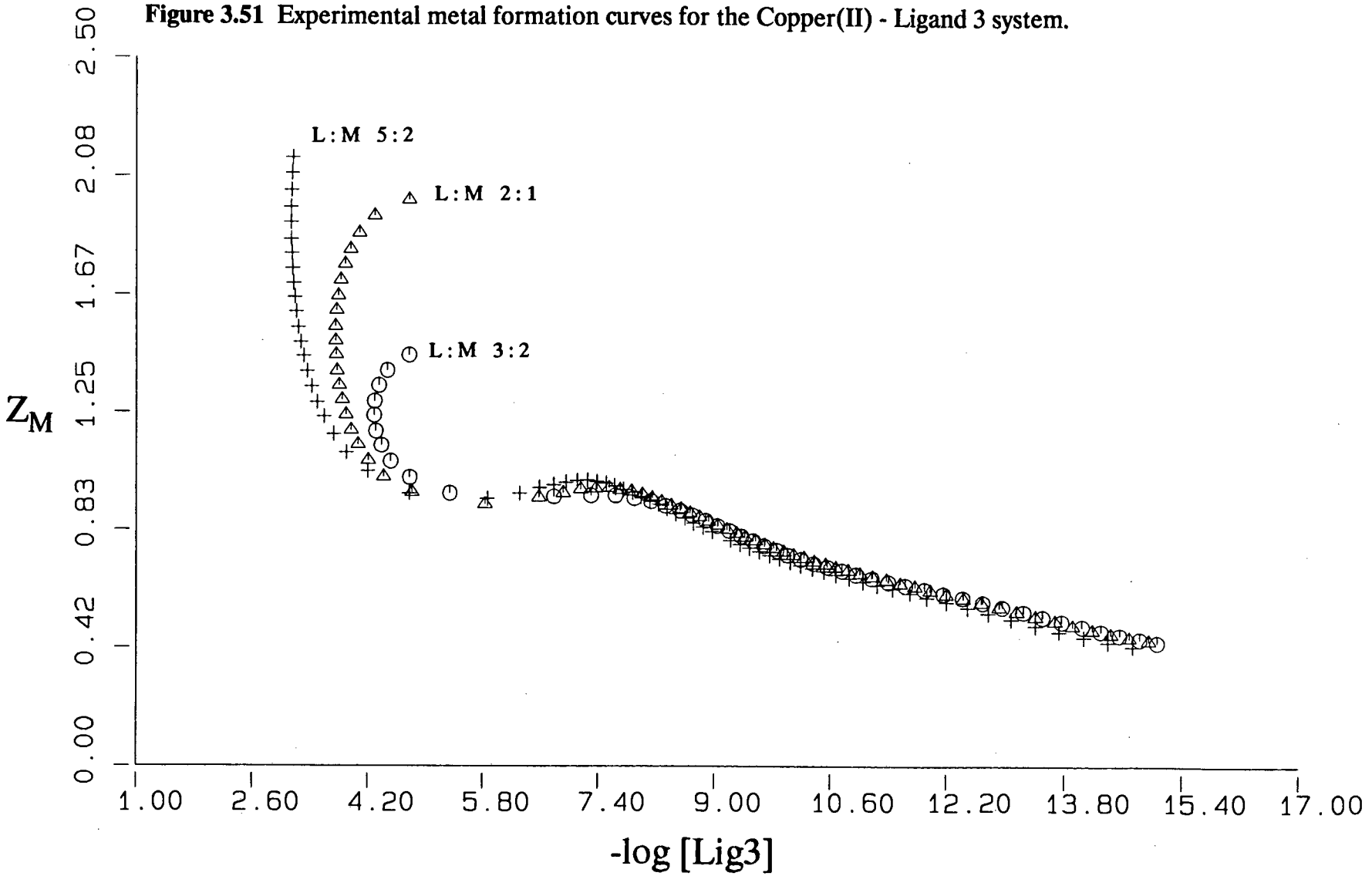
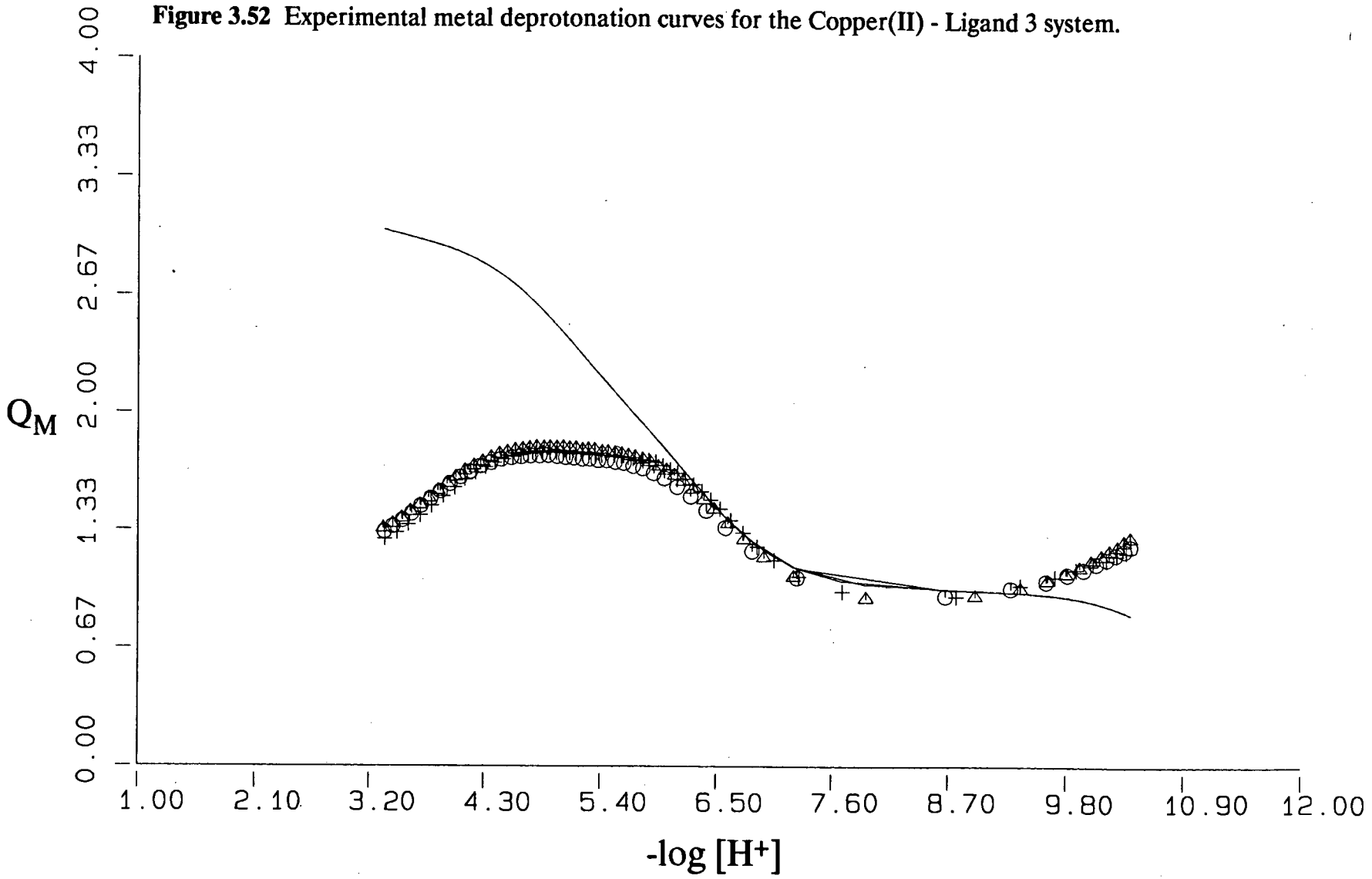


Figure 3.52 Experimental metal deprotonation curves for the Copper(II) - Ligand 3 system.



3.5.20 IRON(III) - LIGAND 4 - H^+ COMPLEXATION

The experimental metal formation and metal deprotonation curves of this system are presented in figures 3.53 and 3.54 respectively. The stability of the Iron(III) - Ligand 4 complex is so high that at the first experimental point at a pH of 2, the ML complex is fully formed. This can be seen in figure 3.53 where the first experimental point has a Z_M of 1. The metal deprotonation curves in figure 3.54 show that when the average number of protons on the ligand is three, the metal ion effectively displaces all three protons upon complexation.

Interpreting the metal formation curves, the ML species appears to be the dominant complex until a pH of about 6.5 whereafter the species ML_2, MLOH and $ML(OH)_2$ could possibly form. In attempting to refine any of these complexes, the ESTA2 OBJE and OBJT computations all terminated without convergence as a result of the high stability of the complex. Some thought was given to solving the system with a competing ligand but finding the correct ligand is a timeous process.

Owing to the importance of the stability constants of Iron(III) - Ligand 4 complexes, it was felt that some value, for the ML species at least, had to be estimated for the purposes of the computer modelling studies. This constant would fairly represent the complexation of Iron(III) - Ligand 4 in the modelling studies which would be determined at a pH of 6.5.

A graphical technique was employed whereby the $\log\beta_{110}$ for the ML species of Ligand 4 was plotted against that of a related ligand. ie. $\log\beta_{ML}$ vs $\log\beta_{ML'}$. The ligands considered were IDA, NTA, and Lig1.

This method has been shown to have an excellent correlation when plotting the stability constants of divalent and some trivalent metal ions of IDA and Lig1 against

Figure 3.53 Experimental metal formation curves for the Iron(III) - Ligand 4 system.

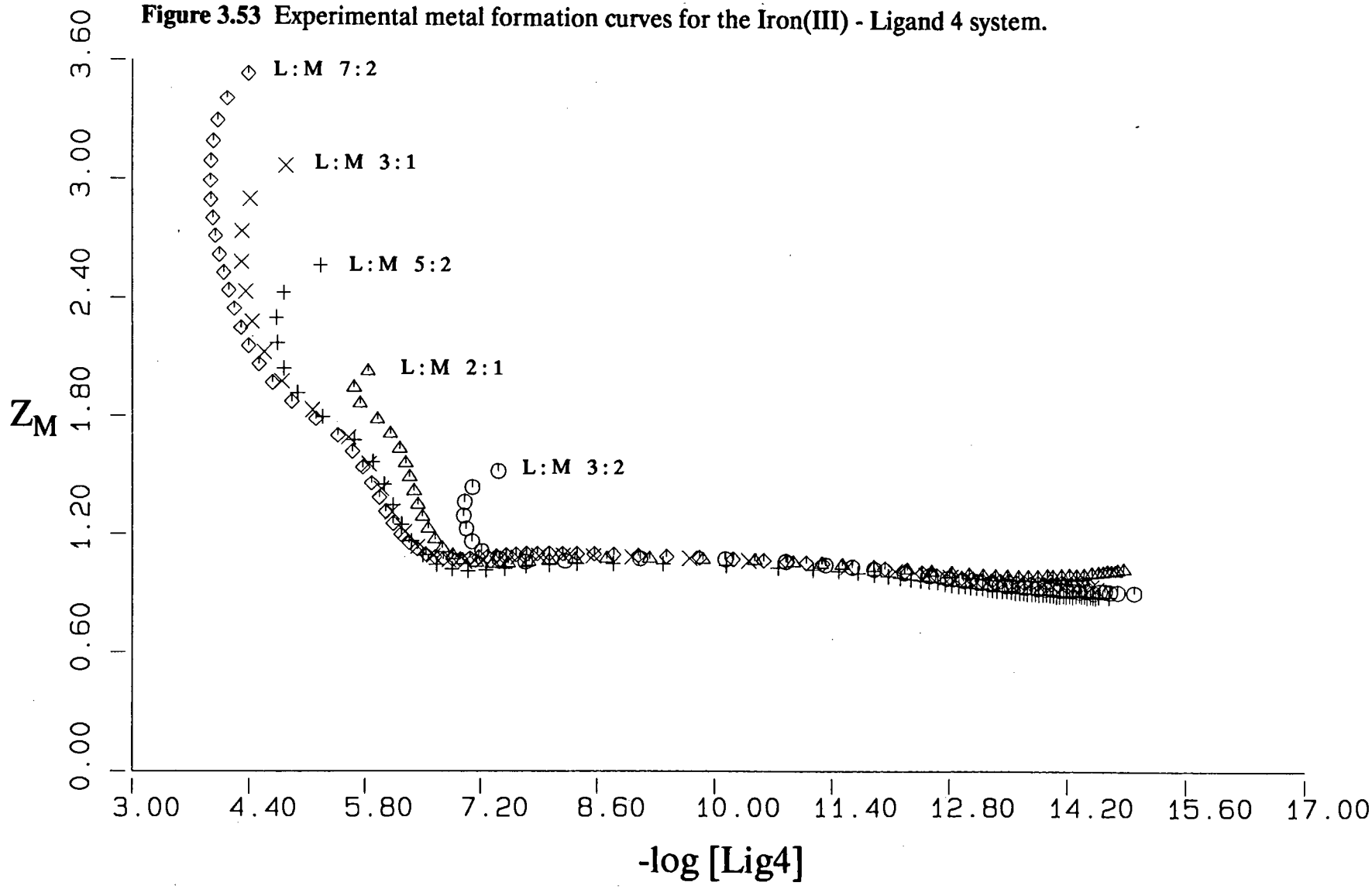
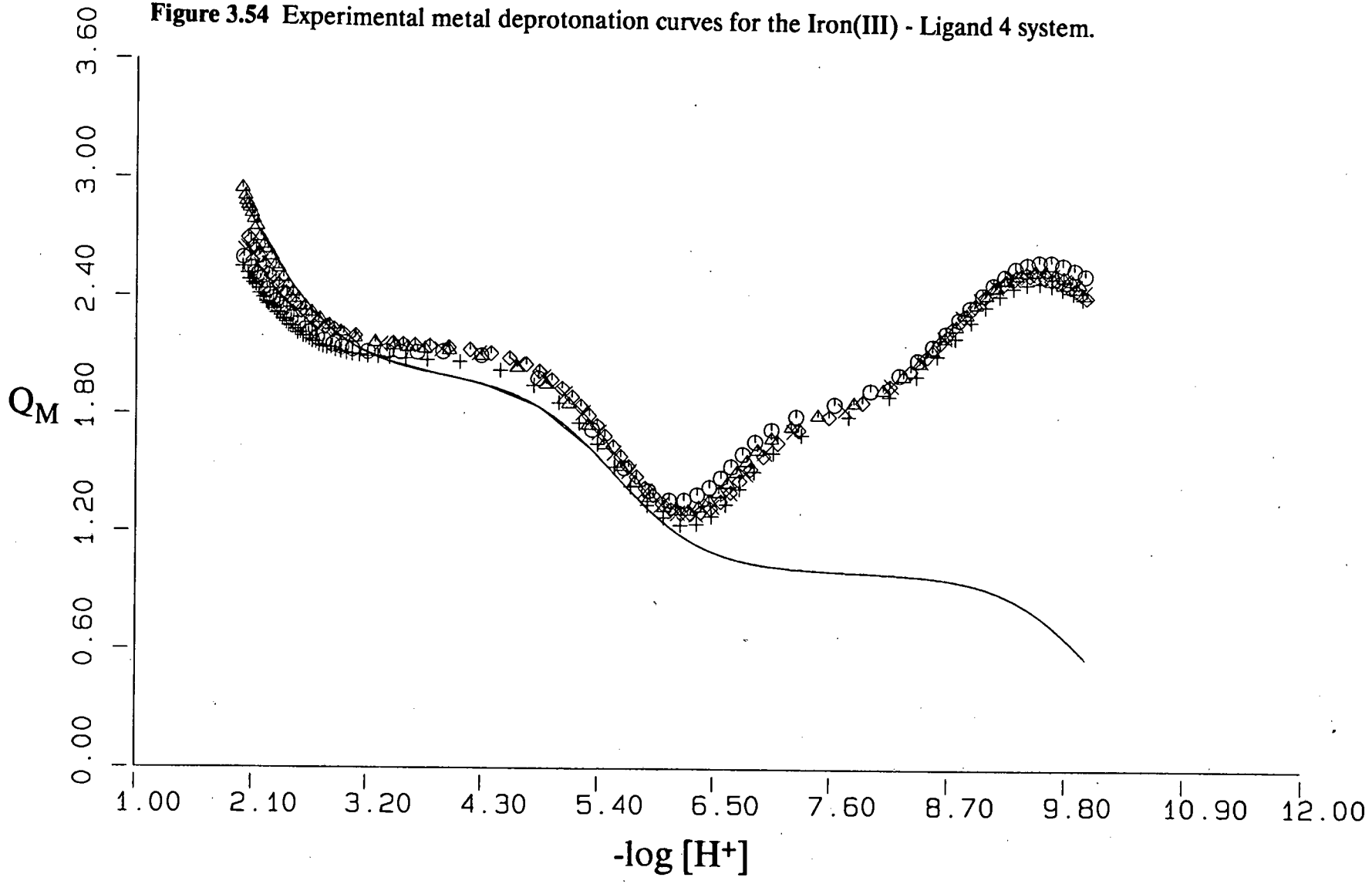


Figure 3.54 Experimental metal deprotonation curves for the Iron(III) - Ligand 4 system.



each other [Mot85]. The only stability constants of ligand 4 with trivalent metal ions that are available are those of Al^{3+} and Ga^{3+}. Stability constants of these two metal ions as well as that of Fe^{3+} have been determined with IDA [Mar74] and it was decided to estimate a stability constant for the Fe^{3+} - Lig4 ML species from a plot of $\log\beta_{ML}$ vs $\log\beta_{ML'}$ as depicted in figure 3.55. The estimated stability constant of the ML species of Fe^{3+} and Ligand 4 is 16.85. The logarithm of the reported stability constant for the Fe^{3+} - IDA complex is 10.72 at 25 °C and an ionic strength of 0.5 $mol.dm^{-3}$ [Mar74]. This value was corrected to an ionic strength of 0.1 $mol.dm^{-3}$ using the Davies equation resulting in a value of 9.43.

Another interesting technique for estimating the stability constants of metal - ligand complexes is the structure-reactivity relationship of Harris [Har83]. The basis of this hypothesis is that $\log K_{ML}$ can be calculated as the sum of fixed contributions for each type of donor atom, with a seperate term to account for the chelate effect of multidentate ligands. The only limitation is that it cannot account for strong inductive effects.

The equation formulated to determine stability constants is

$$\log K_{ML} = \sum_{i=1} n_i x_i + [r_5 + \sum_{i=2}^{n_5} (r_5 f_5^{i-1})] + [r_6 + \sum_{i=2}^{n_6} (r_6 f_6^{i-1})]$$

where x_i = functional group contribution of donor type i,

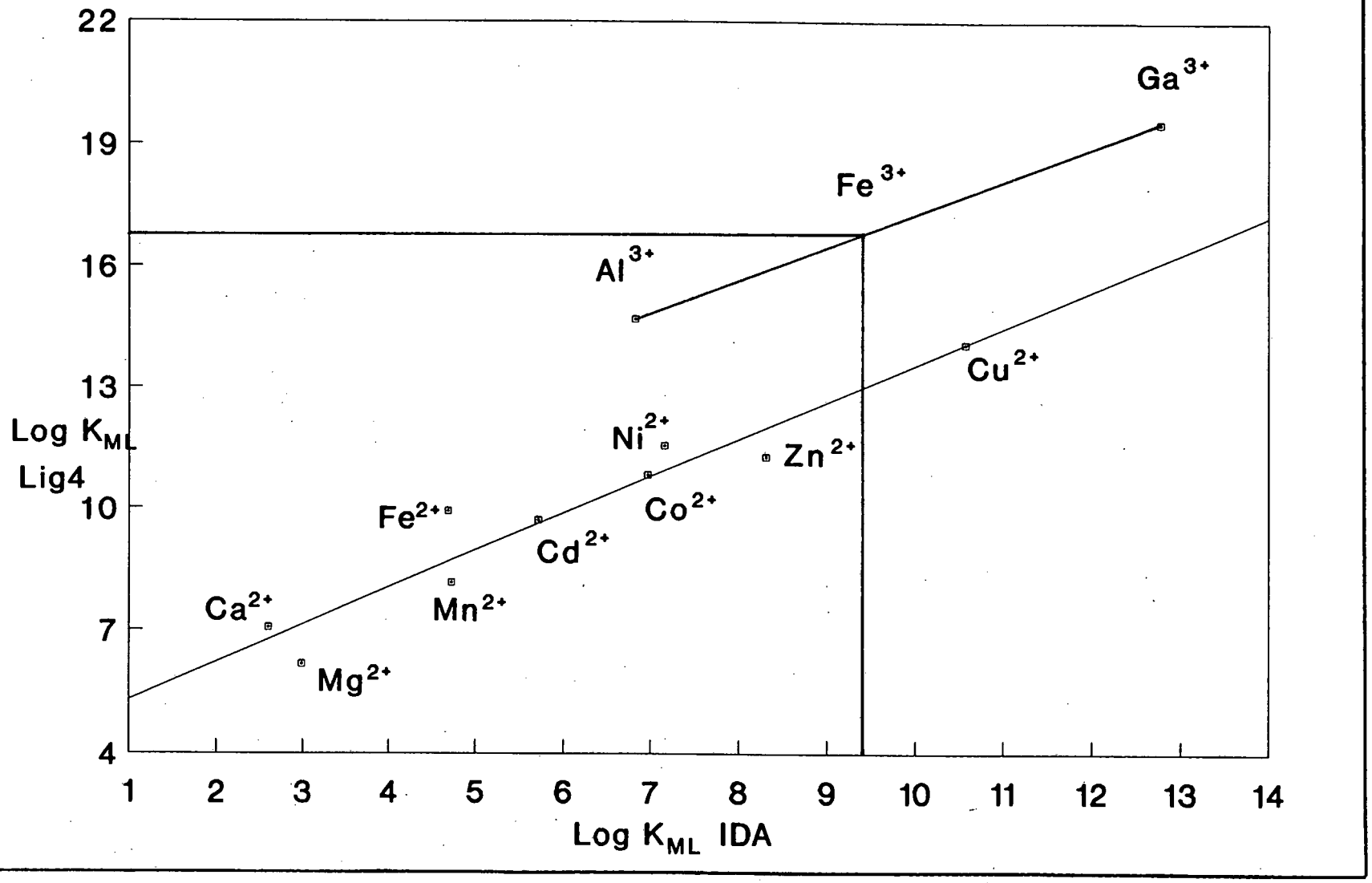
n_i = number of donor groups of type i,

n_x = number of x-membered chelate rings,

r_x = contribution of the initial x-membered chelate ring and

f_x = fractional contribution of successive x-membered rings.

Figure 3.55 Plot of log K_{ML} (Lig4) vs log K_{ML} (IDA)



In the equation, f_x is an adjustable parameter to account for the electrostatic repulsion between charged ligand donor groups and is a fraction of the preceding ring contribution. Functional group parameters, x_i, for carboxylate and amine functional groups among others have been reported for the metal ions Ni^{2+}, Cd^{2+}, Zn^{2+} and Fe^{3+}. Parameters for r_x and f_x (x = 5, 6), for the above metal ions and selected functional groups have also been reported [Har83]. The intention in formulating the equation was that the functional group parameters, x_i, would represent the contribution to $\log K_{ML}$ of each isolated metal-ligand bonding interaction. For example, the x_i value for amine groups with the Fe^{3+} ion should be close to the $\log\beta_{ML}$ for the Iron(III) - Ammonia system. For most of the metal ions and functional groups studied, this was in fact found to be the case and the residuals between the literature constants and x_i values are small [Har83].

This equation was applied in an attempt to calculate a stability constant for the ML species of the Fe^{3+} - Lig4 system. However, no x_i values have been reported for the phosphonate functional group with metal ions. Since a stability constant $\log\beta_{ML}$ for the Fe^{3+} - HPO_3^{2-} complex has not been reported, a value can be calculated from known stability constants of the Fe^{3+} ion and ligands consisting of a phosphonate group(s). For example, $\log\beta_{ML}$ for the Fe^{3+} - Lig1 complex is 16.09 [Mot85]. Since ligand 1 does not form any six-membered rings, the equation reduces to

$$\log K_{ML} = \sum_{i=1} n_i x_i + [r_5 + \sum_{i=2}^{n_5} (r_5 f_5^{i-1})]$$

Ligand 1 consists of one carboxylate, one amino and one phosphonate functional group. The reported parameters for the Fe^{3+} ion are x_i(carboxylate) = 3.44, x_i(amino) = 4.77, r_5 = 0.45 and f_5 = 1.0.

By substituting these values into the above equation, x_i(phosphonate) can be calculated.

$$16.09 = (1 \times 3.44) + (1 \times 4.77) + (1 \times x_i(\text{phosphonate})) + [0.45 + 0.45]$$

$$\text{therefore } x_i(\text{phosphonate}) = 6.98$$

Ligand 4 consists of two carboxylate, one amino and one phosphonate group. Using the calculated value of x_i(phosphonate) the calculated $\log\beta_{ML}$ for Fe^{3+} - Lig4 is

$$\log K_{ML} = (1 \times 6.98) + (2 \times 3.44) + (1 \times 4.77) + [0.45 + 0.45 + 0.45] = 19.98$$

Since so few stability constants for the Fe^{3+} ion and ligands containing phosphonate groups have been reported, it is difficult to establish just how representative the calculated x_i(phosphonate) of 6.98 really is. The same parameter for other reported functional groups and metal ions have been determined using many different metal-ligand systems. Consequently, there is uncertaintity in the calculated $\log\beta_{ML}$ for the Fe^{3+} - Lig4 constant.

There is indeed uncertaintity in the $\log\beta_{ML}$ for the same complex as determined graphically but the basis for its estimation is more sound and the value of 16.85 for the ML complex of the Fe^{3+} - Lig4 system was accepted and used in the modelling section of this study.

3.5.21 CADMIUM(II) - LIGAND 4 - H^+ COMPLEXATION

The cadmium(II) ion is also of interest in this study owing to its abundance in soil, and toxicity to plants if its bioavailability is increased. Due to a time factor it was not possible to study the aqueous equilibria of Cd^{2+} with Ligand 4 and it was decided to graphically estimate a stability constant for the ML species.

Figure 3.56 represents a plot of $\log K_{ML}$ (Lig4) vs $\log K_{ML'}$ (NTA) for divalent metal ions [Mar74]. An estimate for the $\log\beta_{ML}$ for the Cd^{2+} - Lig4 system is 10.35. This was obtained by using the logarithm of the Cd^{2+} - NTA constant of 9.78 reported at 25 ^oC and an ionic strength of 0.1 mol. dm^{-3}. Other ligands considered were IDA (figure 3.55) and Lig1 but the plot of $\log\beta_{ML}$ for Lig4 and NTA gave the best correlation for the divalent metal ions and was therefore chosen.

Figure 3.57 is a three dimensional plot of $\log\beta_{ML}$ for the ligands, IDA, Lig1, NTA and Lig4 with various divalent and two trivalent metal ions reported at 25 ^oC and an ionic strength of 0.1 mol. dm^{-3}. As discussed previously, the expected trend for the series of ligands is one of increasing stability in going from IDA to Lig4. The estimated stability constants of the Fe^{3+} - Lig4 and Cd^{2+} - Lig4 ML species generally fit in well with the trends shown for the ligands and selected metal ions.

Figure 3.56 Plot of log K_{ML} (Lig4) vs log K_{ML} (NTA)

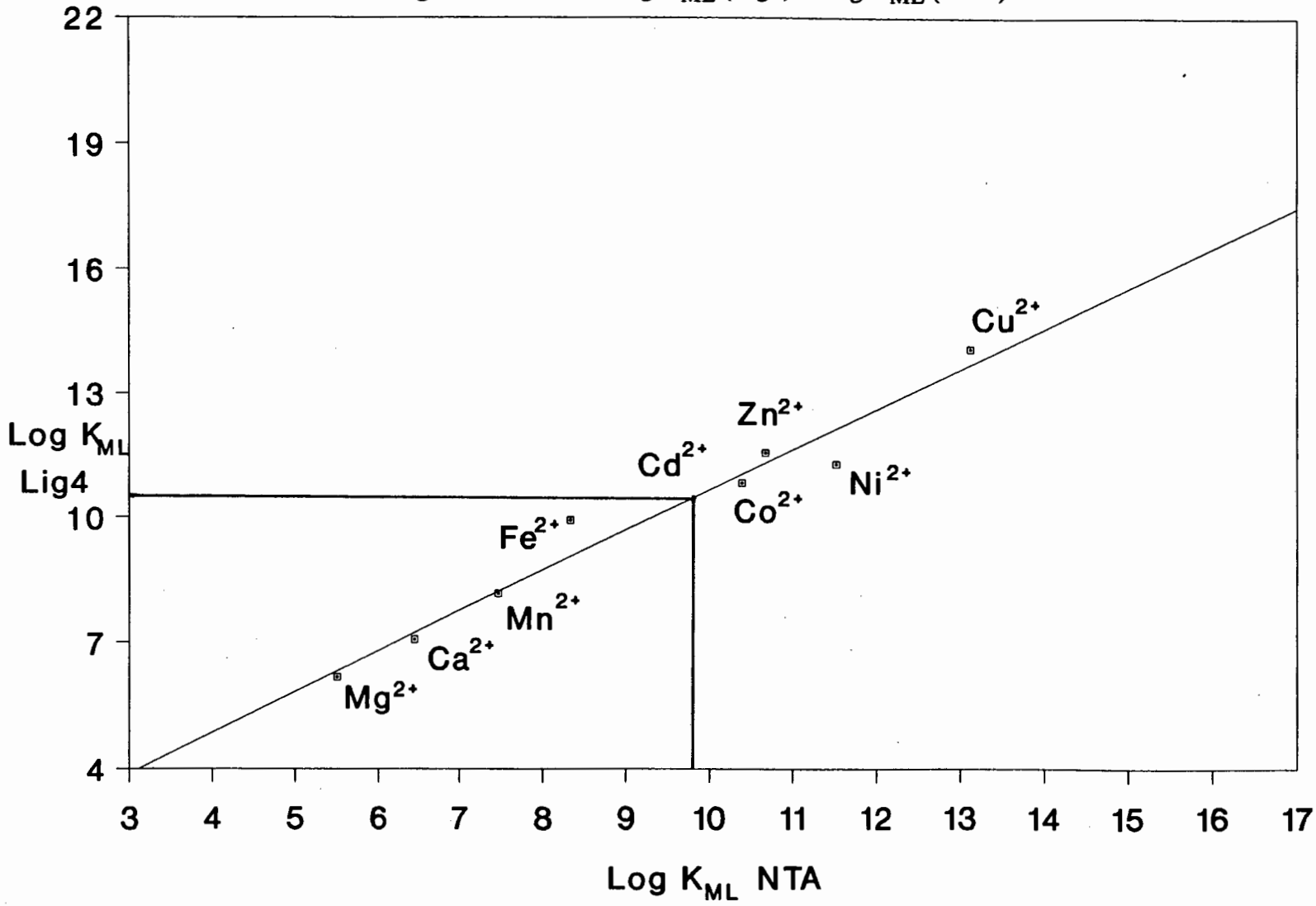
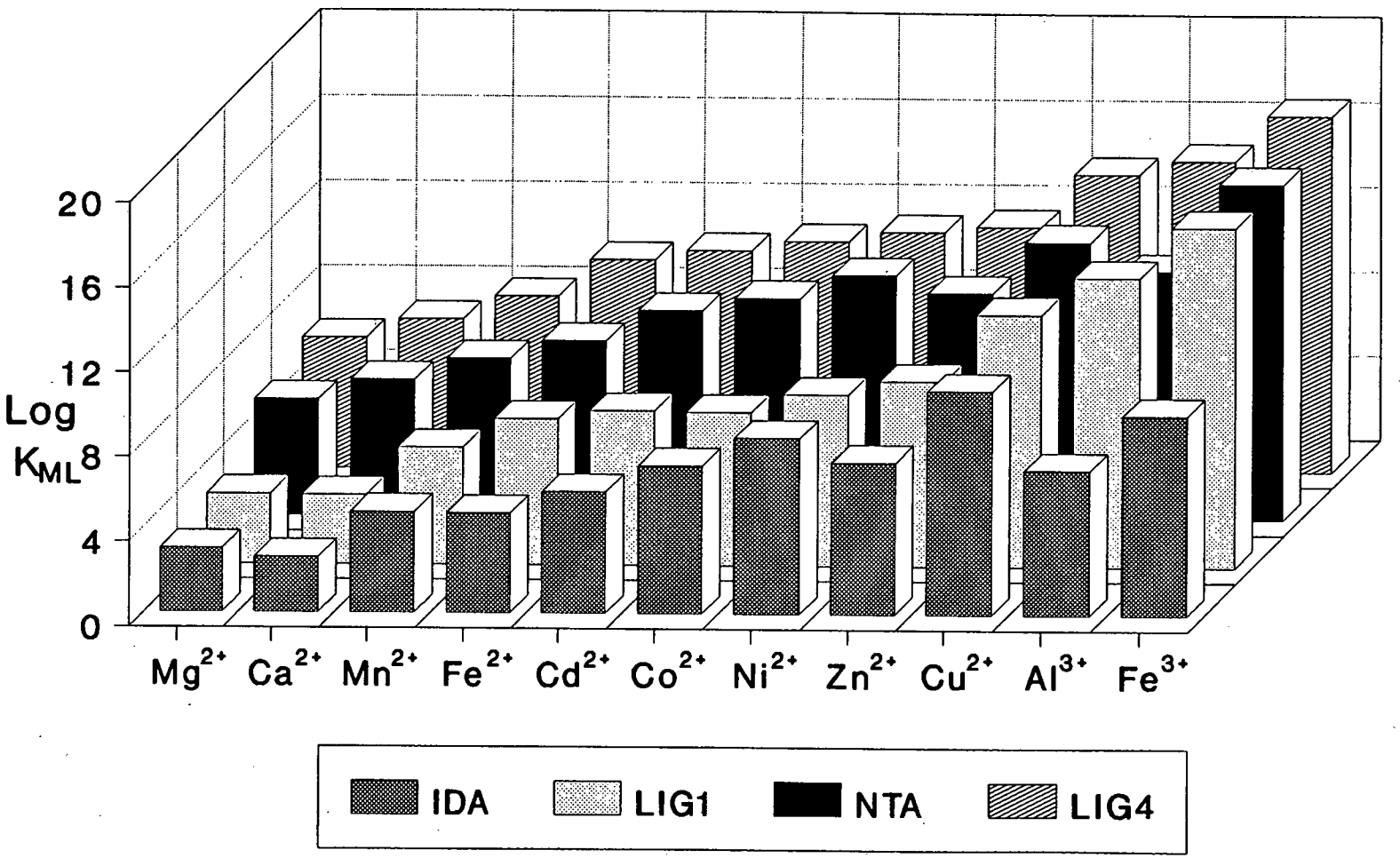


Figure 3.57 log K for the ML species of metal ions with IDA, Lig1, NTA and Lig4



3.6 PLAUSIBLE STRUCTURES OF COMPLEXES

Analysis of potentiometric data enables one to determine the stoichiometry of complexes in solution but provides no information on the stuctures of these complexes. In this study, Dreiding models have been built to examine the plausibility of various structures of the complexes determined in the potentiometric investigations. In this section, some of the most likely structures of the complexes formed between Ligands 1, 2, 3 and 4 with selected metal ions are presented.

3.6.1 NICKEL(II) - LIGAND 1 COMPLEXES

Ligand 1 consists of three functional groups and its metal ion complexes could thus include two stable 5 - membered chelate rings. The complexes found in the Ni^{2+} - Ligand 1 system from the potentiometric study are MLH, ML and ML_2. The logarithm of the calculated stability constant of the ML species formed between nickel(II) ions and Ligand 1 is 7.90 (table 3.7). Ligand 1 is chemically a combination of glycine (Gly) and aminomethylphosphonic acid (AMPA) and it is thus interesting to compare the stability constants of these compounds and ligand 1 with nickel(II) ions. From critical stability constant compilations, the logarithms of the Ni^{2+} - Gly and Ni^{2+} - AMPA complexes are 5.78 and 5.29 respectively (25 ^{o}C , I = 0.1). Since the logarithm of the Ni^{2+} - ligand 1 complex is 7.90, one can safely assume that the Ni(II) - Ligand 1 complex consists of two chelate rings as a result of the increased stability. Figure 3.58 thus represents a likely structure for the Ni(II) - Ligand 1 complex. The amino - carboxylate chelate ring and the amino - phosphonate chelate ring are both in the equatorial plane with the two charged functional groups trans to each other but it is also possible to have them at 90^{o} to each other.

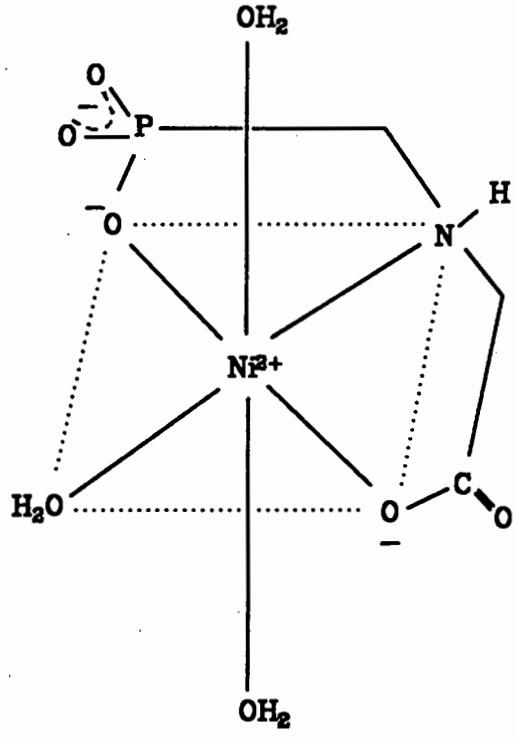


Figure 3.58 ML complex of the Ni^{2+} - Ligand 1 system

In the metal - ligand system under discussion, log K for the reaction,

$$ML + H \rightleftharpoons MLH$$

is 5.32, which is similar to the second protonation constant for ligand 1 (table 3.2). This constant of log K_2 = 5.42 corresponds to the dissociation of the proton on the phosphonate functional group. A likely structure for the MLH complex of the Ni(II) - Ligand 1 system is one where the proton is bound to the phosphonic acid functional group and simply dissociates at higher pH as depicted in figure 3.59.

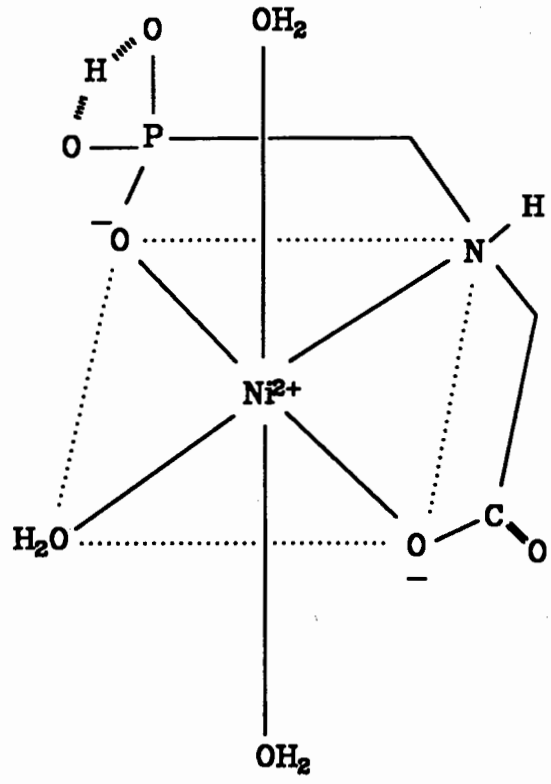


Figure 3.59 MLH complex of the Ni^{2+} - Ligand 1 system

A likely structure for the ML_2 complex is given in figure 3.60 where all six functional groups are bound to the metal ion with the two highly charged phosphonate groups at opposite ends of the complex. Each of the ligands is in a plane with the two planes at 90° to each other.

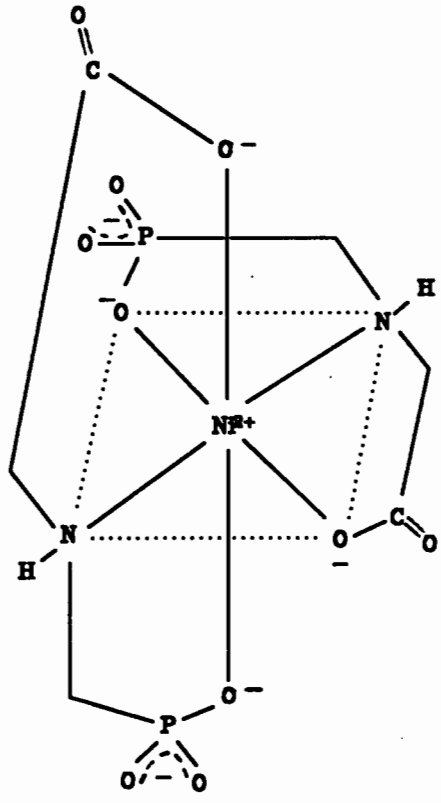


Figure 3.60 ML_2 complex of the Ni^{2+} - Ligand 1 system

3.6.2 NICKEL(II) - LIGAND 2 COMPLEXES

The only complex found in the Ni^{2+} - Ligand 2 system was the ML species. Ligand 2 has 5 functional groups and can in principle form metal ion complexes with up to four chelate rings. The structure presented in figure 3.61 shows the two amino and two carboxylate functional groups bound to the metal ion forming two 5 - membered and one 6 - membered ring. Figure 3.62 illustrates the more likely five coordinate complex which includes four stable 5 - membered rings. The high stability of this complex is reflected in its overall stability constant of $10^{12.24}$ which is higher than that of the Ligand 1, Ligand 3 and Ligand 4 complexes with Ni^{2+} ions.

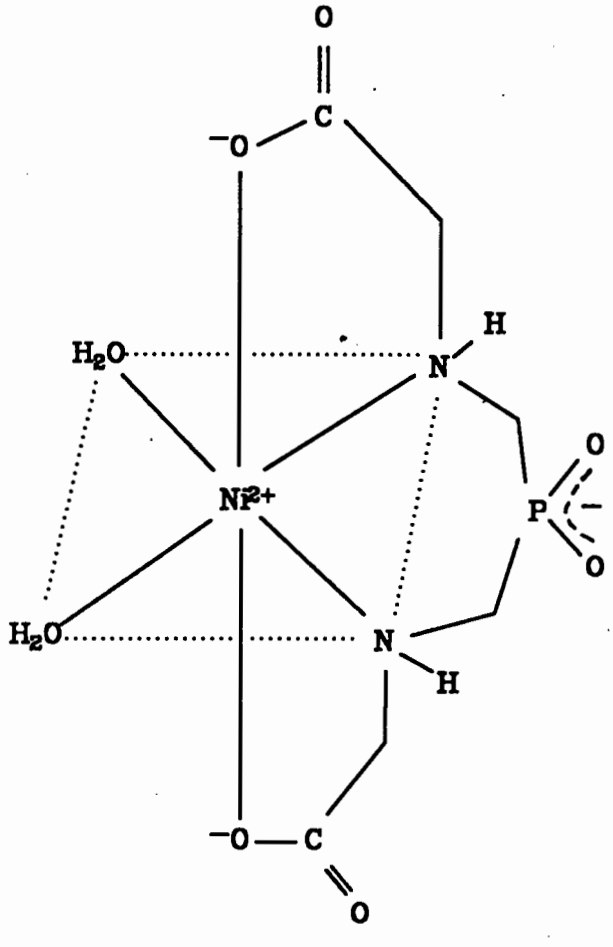


Figure 3.61 Possible ML complex of the Ni^{2+} - Ligand 2 system

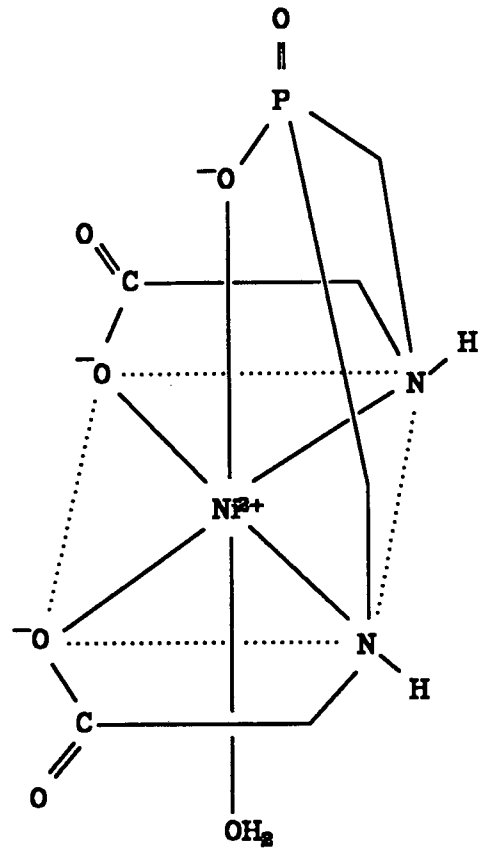


Figure 3.62 Likely ML complex of the Ni^{2+} - Ligand 2 system

3.6.3 NICKEL(II) - LIGAND 3 COMPLEXES

The species determined in the Nickel(II) - Ligand 3 system are ML, MLH and MLH_2. Ligand 3 consists of four functional groups and could form up to three 5 - membered rings. This is likely to be the case since the overall stability constant of the ML complex is greater than that of the Ni^{2+} - Ligand 1 ML species which forms two chelate rings and has a stability constant of 3 log units less. Figure 3.63 therefore represents a likely structure for the ML complex of the Ni^{2+} - Ligand 3 system.

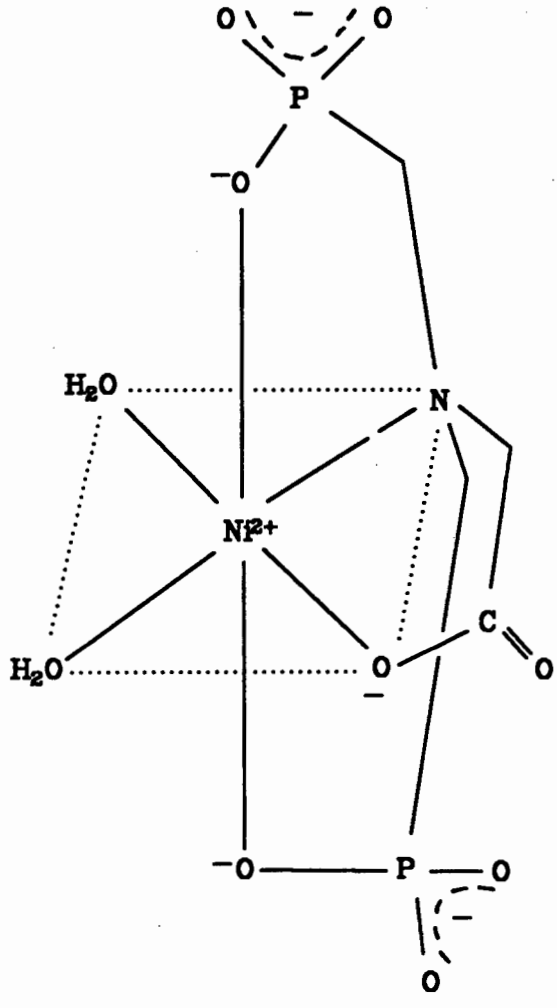


Figure 3.63 Likely ML complex of the Ni^{2+} - Ligand 3 system

The logarithms of the formation constants (logK) for the MLH and MLH_2 species of the present system are 6.25 and 4.82 respectively (table 3.9). This corresponds

well with the deprotonation of the phosphonic acid protons of Ligand 3 which have the constants $\log K_2$ = 6.40 and $\log K_3$ = 5.02 (table 3.4). It is therefore reasonable to assume that the protonated species MLH and MLH_2 have the same structure as that of the ML complex (figure 3.63) with the protons bound to the phosphonic acid functional groups. At higher pH, the protons dissociate resulting in the formation of the ML species.

3.6.4 LIGAND 4 - METAL ION COMPLEXES

Ligand 4 consists of one amino, one phosphonic acid and two carboxylic acid functional groups. It is thus tetra - coordinate and could form complexes with up to three 5 - membered chelate rings. Figure 3.64 represents a possible structure for the ML complex of Ligand 4 with selected metal ions. In the case of copper(II) ions, the axial bonds are elongated but the phosphonic acid functional group is still capable of binding to the metal ion in this position.

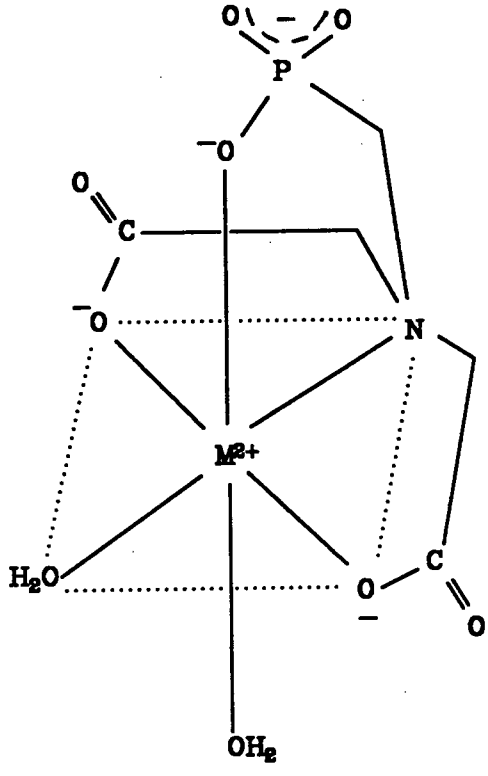


Figure 3.64 ML complex of Ligand 4 with selected metal ions

M^{2+} = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}

The logarithm of the formation constants for the reaction

$$ML + H \rightleftharpoons MLH$$

$logK_{MLH}$ for Ligand 4 and the metal ions under consideration, have been summarised in table 3.21.

Table 3.21

$logK_{MLH}$ for the Ligand 4 complexes of selected metal ions determined at 25 °C and I = 0.1 mol.dm^{-3}

Metal ion	$logK_{MLH}$
Mn^{2+}	5.69
Fe^{2+}	5.41
Co^{2+}	5.06
Ni^{2+}	5.46
Cu^{2+}	4.69
Zn^{2+}	4.73

All of the above constants are similar to the second protonation constant of Ligand 4 where $logK_2$ = 5.55 (table 3.5). A likely structure for the MLH complexes of Ligand 4 with the various divalent metal ions is presented in figure 3.65 where the proton is bound to the phosphonic acid functional group and dissociates at a pH of 5 to 6.

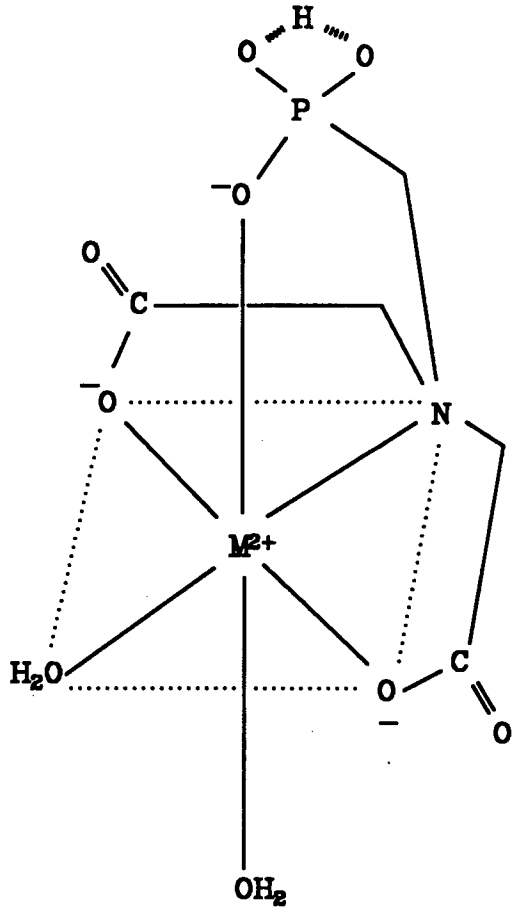


Figure 3.65 MLH complex of Ligand 4 with selected metal ions

M^{2+} = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}

An MLH_{-1} species was found for the metal ions Fe^{2+}, Cu^{2+} and Zn^{2+} in its speciation with Ligand 4. Hydroxy species result from a loss of a proton from one or more of the water molecules in the hydration sphere of the metal ion. Figure 3.66 represents a possible structure for this complex.

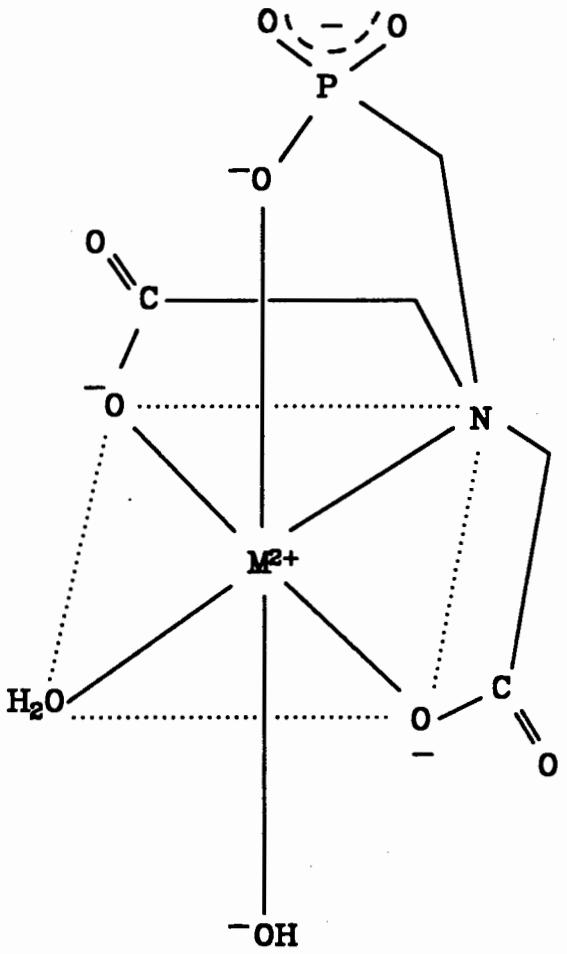


Figure 3.66 MLH_{-1} complex of Ligand 4 with selected metal ions

M^{2+} = Fe^{2+}, Cu^{2+} and Zn^{2+}

An ML_2 species was found for the Ni^{2+} and Fe^{2+} metal ions. As discussed previously, there is evidence showing the Ni^{2+} ion's preference for carboxylate functionality and since ligand 4 is tetradentate, a likely structure for the ML_2 species is one where the four carboxylate and two amino groups are bound to the metal ion

with the two highly charged phosphonate groups uncomplexed and at opposite ends of the complex. This structure is presented in figure 3.67 and is applicable to the Ni^{2+} ion as well as the Fe^{2+} ion. There are indeed many other possibilities for the structure of an ML_2 species including one where the two ligands are bidentate and tetradentate respectively.

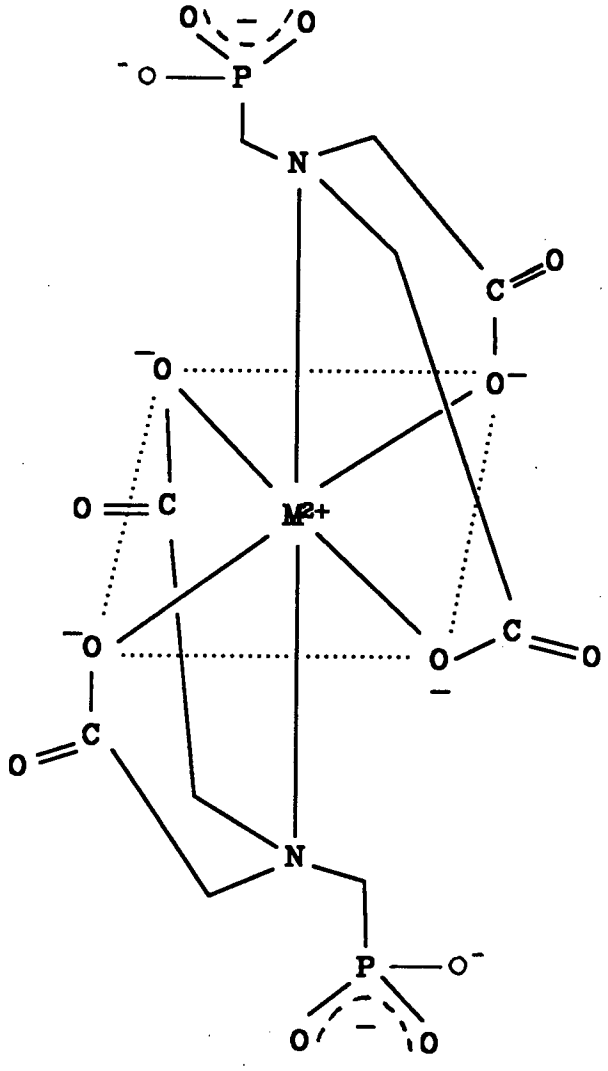


Figure 3.67 ML_2 complex of Ligand 4 with Fe^{2+} and Ni^{2+} ions

An ML_2H_2 complex was found in the speciation of Ligand 4 with Fe^{2+} ions. As with the ML_2 complex, there are many structural possibilities for this complex. Since no ML_2H complex was found in the potentiometric investigation, it is reasonable to assume that each ligand in the ML_2H_2 complex has one proton bound to it. A likely structure for the ML_2H_2 complex is one as depicted in figure 3.67 with each of the phosphonic acid groups in the monoprotonated form.

CHAPTER 4

^{1}H, ^{13}C and ^{31}P NUCLEAR MAGNETIC RESONANCE

CONSISTING OF

INTRODUCTION

EXPERIMENTAL

RESULTS AND DISCUSSION

4.1 INTRODUCTION

Nuclear magnetic resonance (NMR) spectroscopy is one of the most effective methods for the elucidation of chemical structures owing to its diverse range of applications. The general theory of NMR has been dealt with adequately in the literature [Gun80], [Ebs87], [Der87] and where necessary, only a brief outline relevant to this study is given.

Organic compounds dissolved in aqueous solution usually consist of two types of protons; the labile protons bound to the functional groups which exchange rapidly with the protons of water and other functional groups, and the non -labile protons bound to the alkyl and aromatic parts of the molecule. The resonance signals of labile protons coalesce with that of the water protons if a proton NMR study is conducted in aqueous solution. Nevertheless, the non - labile protons exhibit distinct chemical shifts for each of the non - equivalent types in the molecule.

If a base is added to a solution of an organic compound in acidic solution, the degree of protonation of each of the functional groups is affected resulting in the numerous microequilibria being re - established in solution. Since protons are likely to be dissociated from certain functional group sites, the resulting increase in electron density causes a shielding of the non - labile protons in the immediate vicinity of the functional group and changes the chemical shift of these protons.

One can assume that the chemical shift of a proton one bond length away from a functional group will be affected most by the change in the chemical environment of the functional group as a result of deprotonation.

The position of a proton signal at any pH is given by the equation

$$\delta = N_A \delta_A + N_B \delta_B \qquad \text{...eq. 4.1}$$

where N_A, N_B, δ_A and δ_B are the mole fractions (N) and the chemical shifts (δ) of the protonated (A) and non - protonated (B) forms of the ligand in solution [Kos73]. In following the change in chemical shift of a particular signal with varying pH, a point of inflection is obtained when the concentrations of protonated and non - protonated forms of the ligand in solution are equal. At this point, the chemical shift observed is

$$\delta = 1/2 (\delta_A + \delta_B) \qquad \text{...eq. 4.2}$$

It also follows from the dissociation equation

$$K_a = N_B . [H^+] / N_A \qquad \text{...eq 4.3}$$

that when $N_A = N_B$, the dissociation constant is equal to the hydrogen ion concentration ie. pK_a = pH. It is therefore possible and interesting to compare protonation constants determined potentiometrically with those determined from the pH - δ relationship.

Since variable acidity / basicity results in substantial changes in chemical shifts of non - labile protons, it is possible to establish the sequence of deprotonation of a given molecule on the basis of the pH - δ relationship.

Ligands **I**, **II**, **III** and **IV** belong to the family of mixed carboxylic - phosphonic amino acids, and can contain up to five acidic centres ($-CO_2H$, $-PO_3H_2$ and $-NH_2^+$).

$H_2O_3PCH_2NHCH_2CO_2H$ **(I)**

N - (Phosphonomethyl) glycine (Ligand 1) NDP = 3

$HO_2P(CH_2NHCH_2CO_2H)_2$ **(II)**

N,N'[Phosphinicobis(methylene)] bis glycine (Ligand 2) NDP = 3

$(H_2O_3PCH_2)_2NCH_2CO_2H$ **(III)**

N,N - bis(Phosphonomethyl) glycine (Ligand 3) NDP = 5

$H_2O_3PCH_2NH(CH_2CO_2H)_2$ **(IV)**

N - (Phosphonomethyl) iminodiacetic acid (Ligand 4) NDP = 4

Although the pK_a values for some of these substrates have been determined previously, little information is available on the sequence of the protonation equilibria in these multi - centred systems. Since the ionization constants for **I, II, III** and **IV** have been determined potentiometrically in this study, nuclear magnetic resonance spectroscopy was applied as the technique for establishing the order of deprotonation. NMR spectroscopy involving chemical shift measurements has been used in protonation studies with a wide variety of weak bases [Lil71], [Ola85], and offers a number of advantages over spectrophotometric techniques. The ligands under investigation are particularly well suited for NMR study, since the protonation equilibria can be probed by following the chemical shift changes in the ^{1}H, ^{13}C and ^{31}P spectra. The absence of Π - bonds in the molecular framework of the compounds studied should minimize the magnetic anisotropy contributions and the presence of formal charge(s) developed near the magnetic nuclei should lead to substantial shielding and deshielding effect(s) [Bec69]. Appleton et. al. [App84] succesfully applied NMR to the study of the acid - base equilibria of

aminoalkylphosphonic acids, and observed both large variations in the chemical shifts of the individual nuclei with pD, and well defined inflection points on the titration curves. The same group have studied the Pt^{2+} complexes of amino and iminophosphonic acids, and presented plots of δ_H, δ_C and δ_P against pD for **I**. The results were interpreted in terms of the sequential deprotonation of the individual acidic centres [App86]. In the NMR studies, the experimental measurements of **I** were repeated in order to confirm the applicability of this method to the related systems **II**, **III** and **IV**.

4.2 EXPERIMENTAL

Deuterium oxide (Merck, min 99.75%), sodium deuteroxide (Wilmad Glass, 40% in D_2O, min 99% D) and deuterium chloride (Nuclear Magnetic Resonance Ltd., 20% in D_2O, min. 99% D) were used to prepare solutions for the NMR measurements. Substrates **I**, **II**, **III** and **IV** were prepared in the concentration ranges of 0.03 to 0.10 moles.dm^{-3}. Solutions were prepared by dissolving the substrates in D_2O and titrating them with small quantities of sodium deuteroxide to give solutions at various pD values. Deuterium chloride was used to decrease the pD of the solution to a desired value in the event of a large increase in pD.

pD was measured by means of a Radiometer pH Meter 29 pH meter fitted with a Radiometer GK 2401C combination electrode, standardised against a Beckman pH 4.00 buffer solution. Hence, pD was given by pD = meter reading + 0.40 [Gla60].

The NMR (^{1}H, ^{13}C and ^{31}P) spectra were recorded on a Varian VXR-200 superconducting FT spectrometer at a probe temperature of 23 ^{o}C, using dioxane (^{1}H, ^{13}C) or trimethyl phosphate (^{31}P) as internal standards. Since the pK_a values of dioxane and trimethyl phosphate are of the order of −3 (minus 3) and −4 (minus 4)

respectivly [Lil71], any protonation of the standards in the pH range studied is negligible.

4.3 RESULTS AND DISCUSSION

The (^{1}H, ^{13}C, ^{31}P) nuclear magnetic resonance spectra of compounds **I** to **IV** all showed the presence of signals expected from their structures as sharp singlets or doublets due to the coupling of the ^{31}P nucleus. Since the NMR titrations were conducted in D_2O, only the signals of the methylene groups appeared in the proton magnetic resonance spectra. The effect of pD was measured using the signals of the CH_2 groups in the ^{1}H and ^{13}C spectra and the P atom in the case of the ^{31}P spectra all in the pD range of 1 to 13. Owing to the reduced sensitivity of the carboxylate carbon atoms in the ^{13}C NMR spectra, together with solubility limitations for some of the substrates, the signals of the carboxylic acid carbon atoms have not been included in the plots. Within the experimental pH range, significant changes in the chemical shifts were observed : 0.5 to 1.1 ppm for ^{1}H, 3.8 to 7.5 ppm for ^{13}C and 7 to 19 ppm for ^{31}P spectra.

The effect of pD on the chemical shifts of both methylene groups (^{1}H and ^{13}C atoms) and the phosphorus atom in **I** are presented in figure 4.1. The results obtained are in excellent agreement with those reported previously [App86] for this substrate. In the vicinity of the first pK_a value, (2.11), the chemical shift of the ^{1}H and ^{13}C nuclei of the phosphonomethyl CH_2 group and that of the ^{31}P nucleus remains constant whereas the ^{1}H and ^{13}C nuclei of the glycine methylene group undergo significant shielding and deshielding respectively. Deprotonation of acidic functions usually cause downfield shifts of the signals of neighbouring carbon atoms [Bre87] and these changes have been explained [Qui74] as a result of competition between the deshielding effect of a decrease in excitation energy and the shielding effect of an increase in electron density on deprotonation. The shielding of the ^{1}H nuclei on the first deprotonation is *ca* -0.4 ppm, whereas the shielding of the

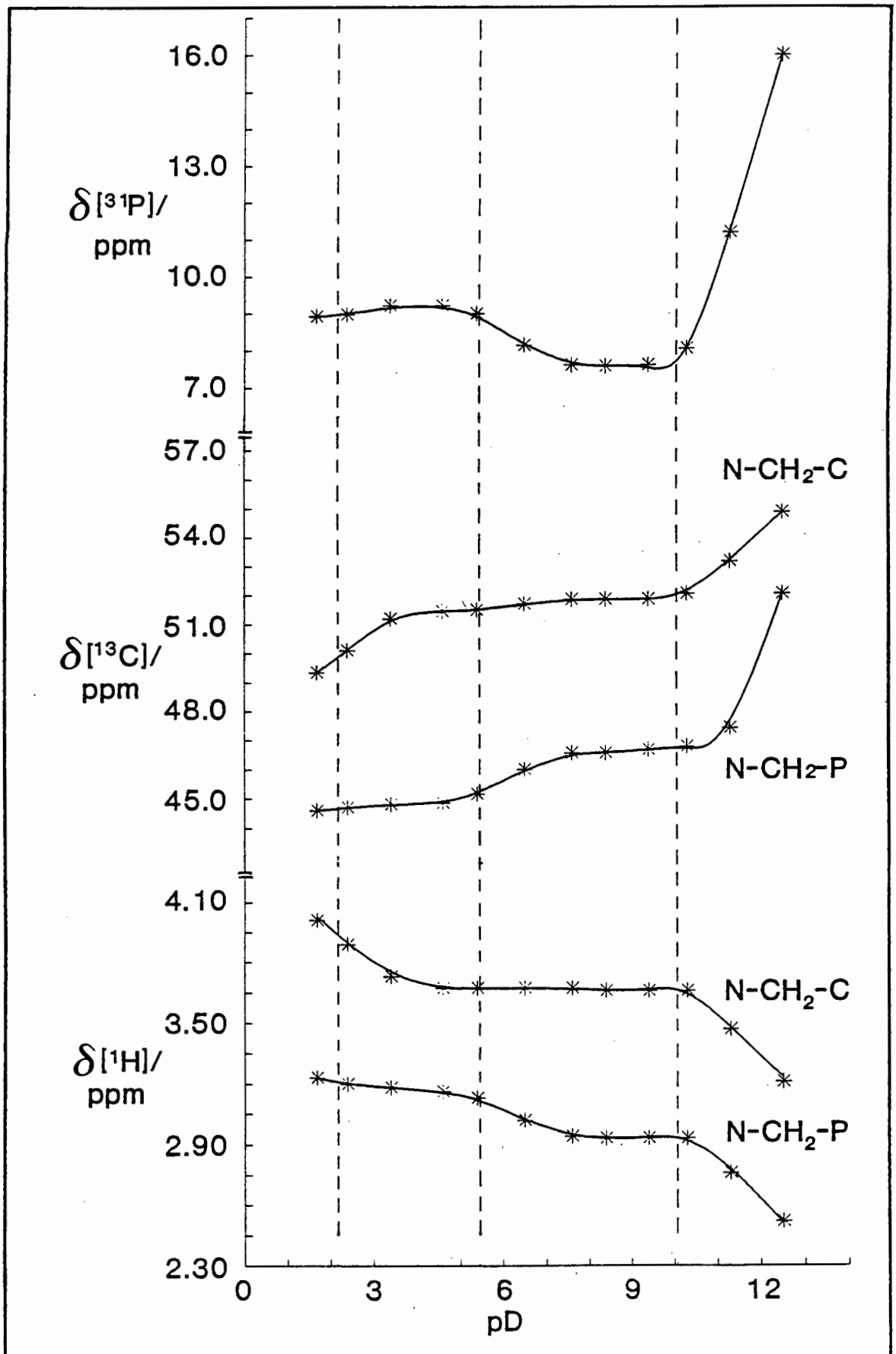


Figure 4.1 The effect of pD on the chemical shift of nuclei in **I**.

methylene carbon is *ca* +3 ppm. This is in agreement with the corresponding average values of -0.21 and +3.5 ppm observed for the a - methylene groups on ionisation of aliphatic carboxylic acids [Hag69]. The observed effects enable one to conclude that the first deprotonation of **I** occurs at the carboxylic acid end of the molecule.

At the second pK_a value (5.42) the singlets of the glycine CH_2 group do not change their chemical shift values, whereas the ^{1}H and ^{13}C nuclei of the CH_2P group are affected, giving rise to a *ca* -0.3ppm shielding and *ca* 2ppm deshielding, respectively. This result clearly indicates that the second deprotonation of **I** involves the phosphonic group, which is changing from the mono- to the dianionic form.

The third deprotonation of **I** (pK_a = 10.06) involves the nitrogen atom. ^{1}H nuclei of both methylene groups undergo significant shielding (-0.4 to -0.5 ppm) and both ^{13}C nuclei significant deshielding (+3.5 to +5.5 ppm). The latter shifts can be compared with an average value of *ca* +3 ppm reported for the α - carbon atom on deprotonation of primary alkyl ammonium ions [Lev80].

The effect of pH on the shielding parameters of the ^{31}P nucleus in **I** is more complex. Around the second pK_a value weak shielding (ca -1.5 ppm) was observed, whereas near the third ionisation strong deshielding (*ca* +8.5 ppm) of the ^{31}P nucleus was observed. Although the second deprotonation of orthophosphoric acid results in a ^{31}P low-field shift of *ca* 3 ppm [Hal72a], the presence of a highly positive active site in the vicinity of the phosphate group is known to change the effect of the signal position relative to pH [Gor84]. Although the second deprotonation of **I** involves the PO_3H^- group, the effect of the charge is neutralised by strong intramolecular hydrogen bonding of the adjacent NH_2^+ group. Only on the third deprotonation, is the phosphate group released from the effects of intramolecular

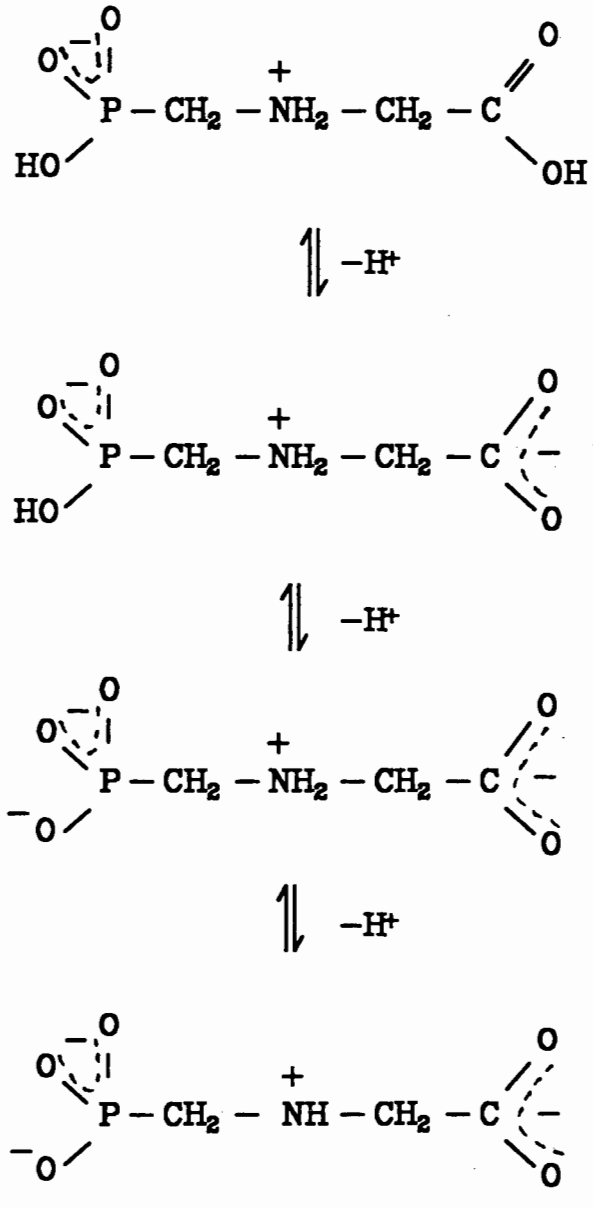


Figure 4.2 Deprotonation sequence of functional groups in **I**.

hydrogen bonding resulting in the strong shielding effect of the ^{31}P nucleus. The deprotonation behaviour of **I** represented in its zwitterionic form is presented in figure 4.2.

Due to the limited solubility of substrate **II**, no reliable ^{13}C data could be obtained over the whole pD range. Figure 4.3 shows the variations of ^{1}H and ^{31}P chemical shifts with pD for **II**.

As in **I**, the first ionisation (pK_a = 2.10) involves one of the carboxylic groups , since it is the glycine and not phosphinic , methylene protons which experience shielding effects of *ca* 0.2 ppm.

When approaching the second ionisation, (pK_a = 6.55), both types of methylene protons undergo shielding effects whereas the ^{31}P signal begins to move downfield. This behaviour is consistent with the second deprotonation occuring at one of the nitrogen atoms and affecting the chemical shifts of all the nuclei studied.

The third ionisation (pK_a = 9.00) involves the deprotonation of the second NH_2^+ group and results in further shielding of the methylene groups and also in a dramatic (*ca* 19 ppm) deshielding of the ^{31}P atom. This latter effect, which necessarily cannot involve the ionisation of the POH group, supports the proposal of strong deshielding of the phosphorus nucleus once the adjacent ammonium centre(s) have been fully deprotonated. The sequence of deprotonation for substrate **II** as interpreted from the above results is presented in figure 4.4.

Substrate **III** has five dissociable protons and the effects of pD on the chemical shifts of its methylene ^{1}H and ^{13}C nuclei and the ^{31}P atoms are presented in figure 4.5.

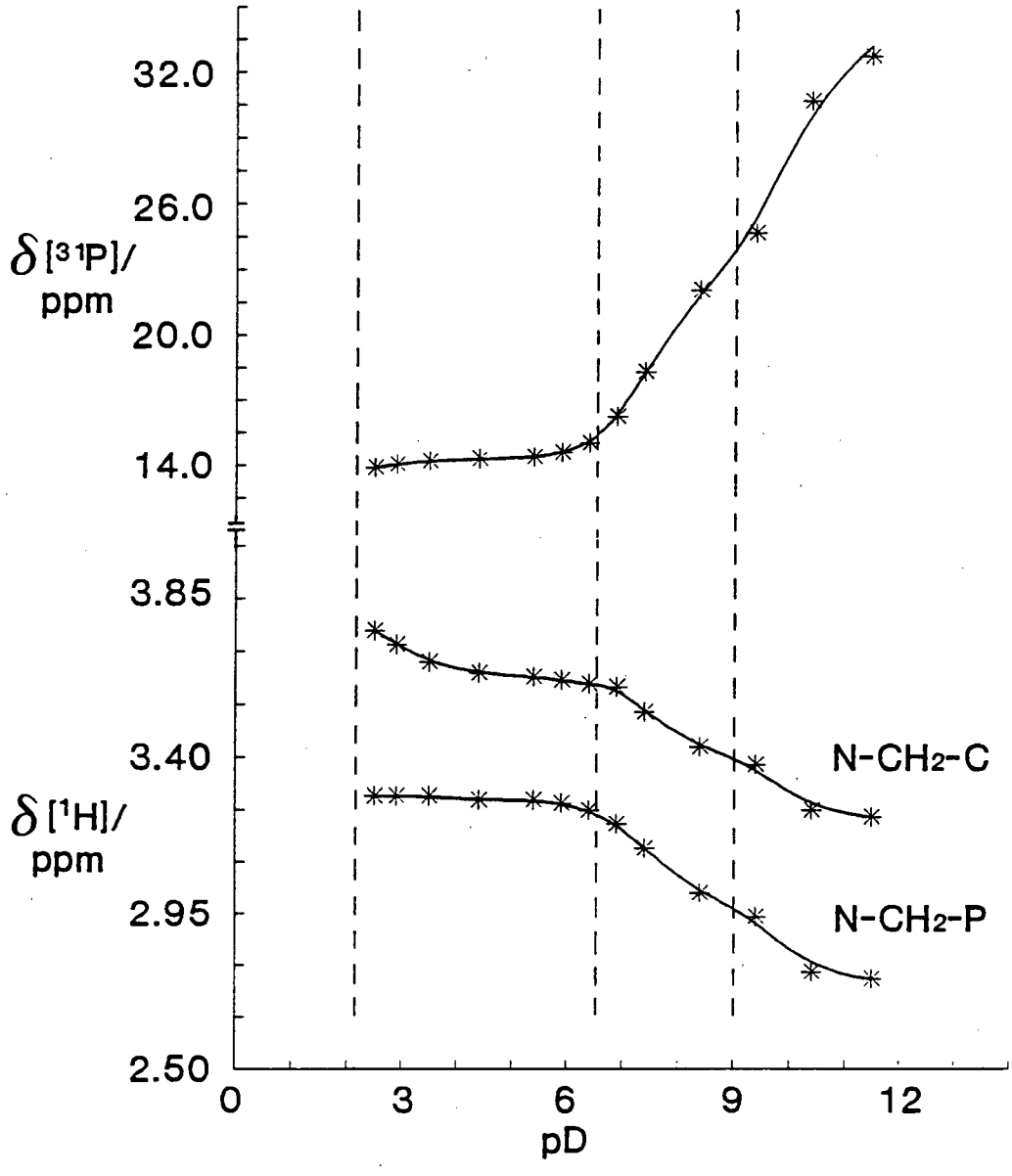


Figure 4.3 The effect of pD on the chemical shift of nuclei in **II**.

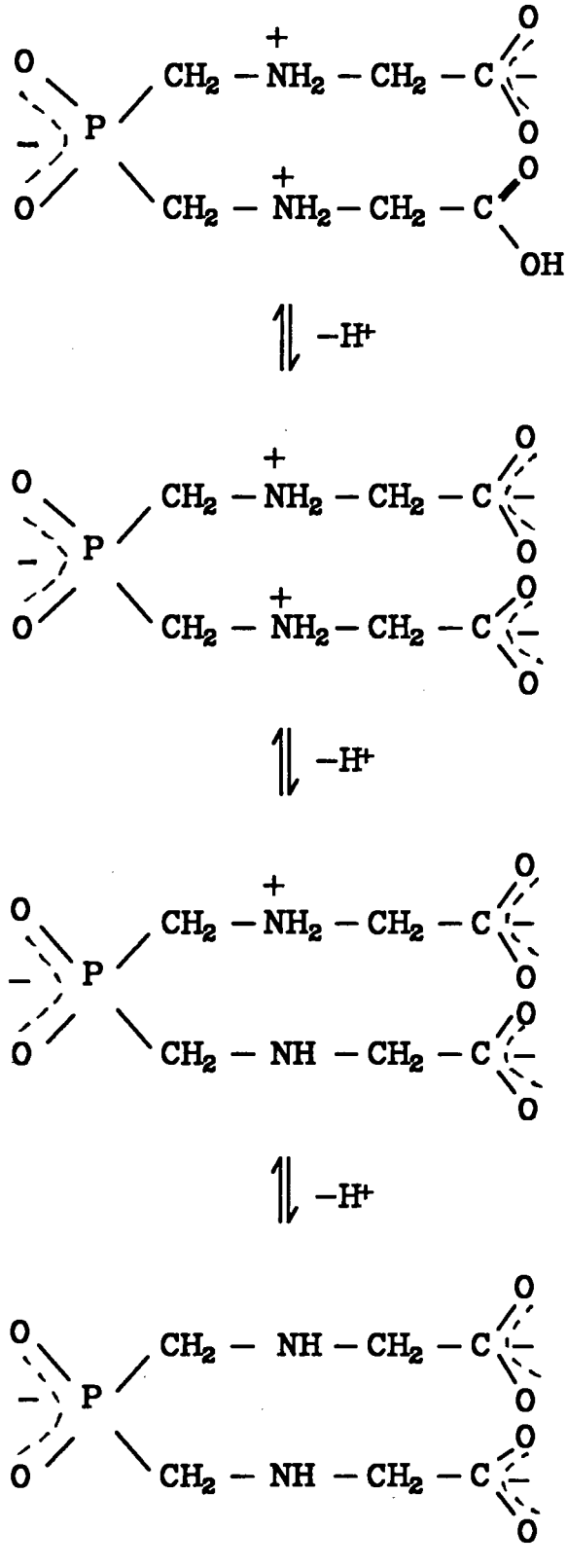


Figure 4.4 Deprotonation sequence of functional groups in **II**.

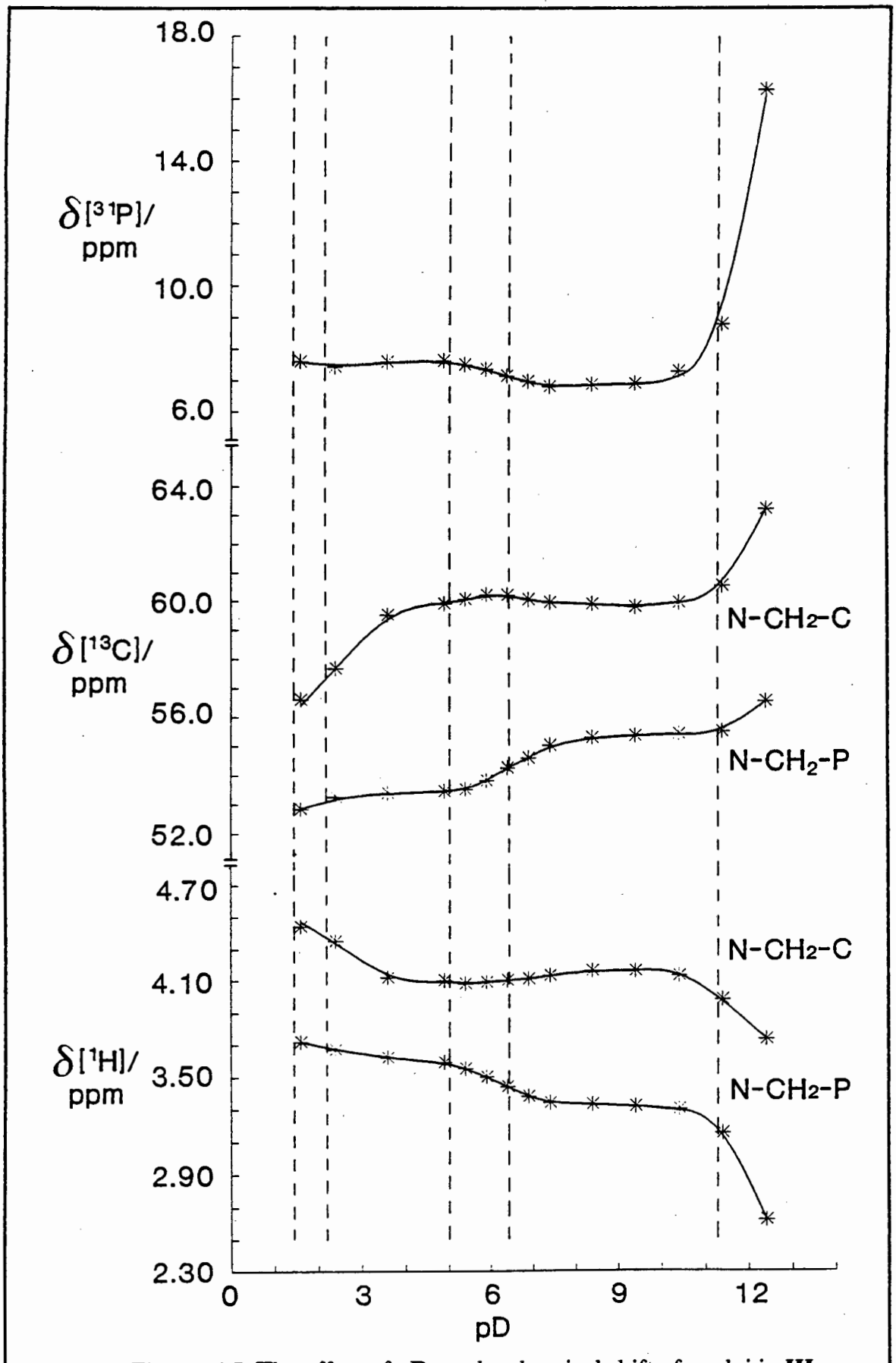


Figure 4.5 The effect of pD on the chemical shift of nuclei in **III**.

The first deprotonation (pK_a = 1.42) involves the non - ionised phosphonic group, resulting in weak shielding and deshielding of the ^{1}H and ^{13}C nuclei of the phosphonomethyl groups. The compensating effects of intramolecular hydrogen bonding result in this deprotonation having no noticible effect on the chemical shift of the ^{31}P nuclei. The second ionization (pK_a = 2.10) occurs at the carboxyl group, as can be seen from the effect on the chemical shift of the glycine methylene group in both the ^{1}H and ^{13}C spectra.

The next two ionizations (pK_a = 5.02 and 6.40) involve both phosphonic groups. The chemical shifts of the glycine moiety remain constant but the CH_2 atoms of the phosphonic part undergo further shielding and deshielding effects (-0.3 and +2.0 ppm) respectively. The least acidic hydrogen atom of the NH^+ group undergoes ionisation at pH 11.19, causing strong shielding (-0.4 and -0.7 ppm) for all methylene protons, deshielding (+3 and +1.5 ppm) for all methylene carbons and strong deshielding (+10 ppm) of the ^{31}P nuclei. The deprotonation sequence of **III** is presented in figure 4.6.

The limited solubility of substrate **IV** resulted in unreliable data for the chemical shifts of ^{13}C nuclei of the pD range of this study. Substrate **IV** is the strongest acid in the series of ligands under investigation and sufficient chemical shift data could not be obtained in the vicinity of the first deprotonation as presented in figure 4.7. The second deprotonation, although expected to be that of the carboxylic acid group, is also not unambiguous since all nuclei studied appear to be affected.

The effect of the third deprotonation is clear since the chemical shifts of the glycine methylene protons remain fairly constant whereas the CH_2P group shows a distinct point of inflection with the corresponding decrease (-0.26 ppm) in chemical shift. This point of inflection corresponds well with the pK_a of 5.55 determined

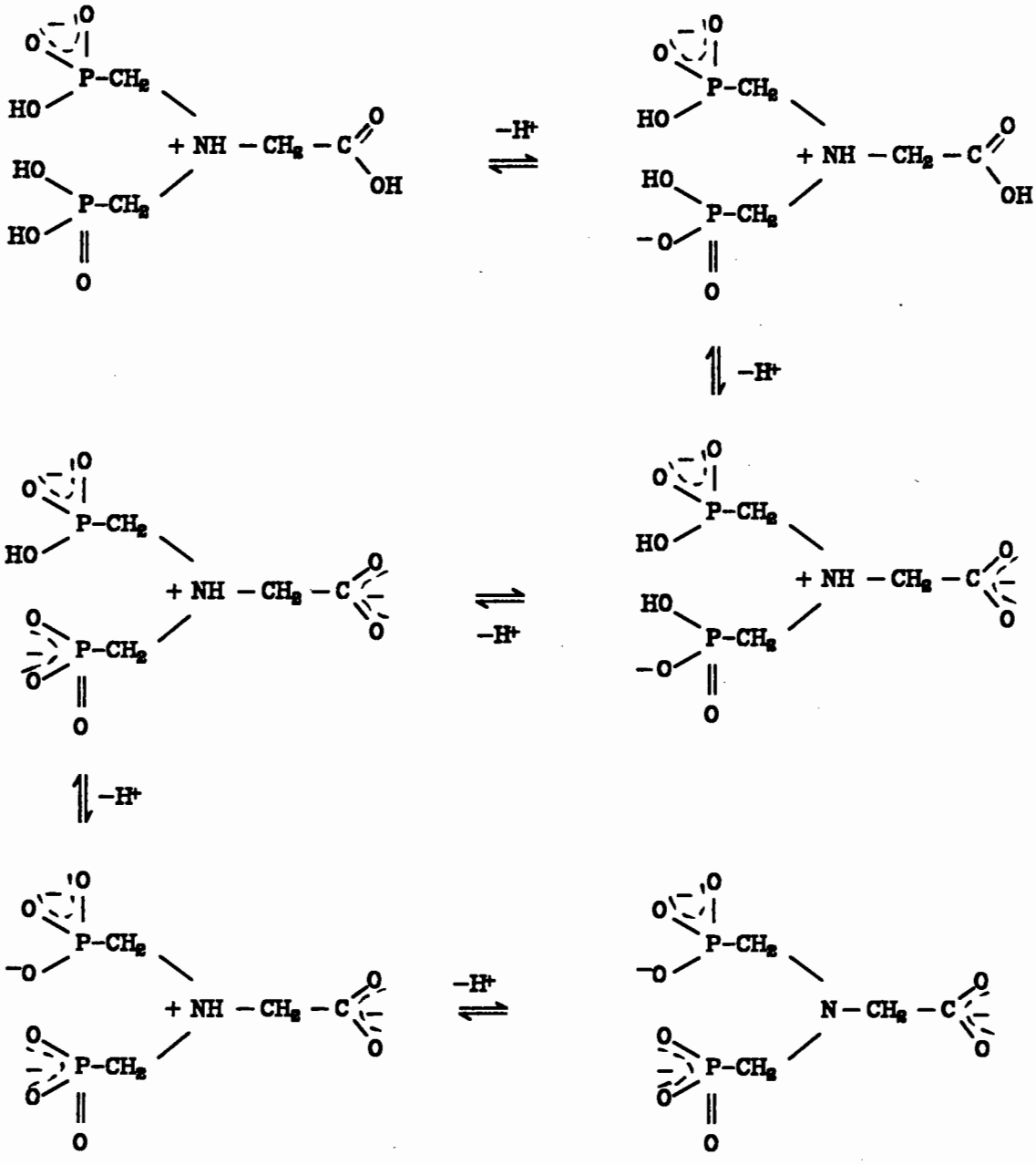


Figure 4.6 Deprotonation sequence of functional groups in **III**.

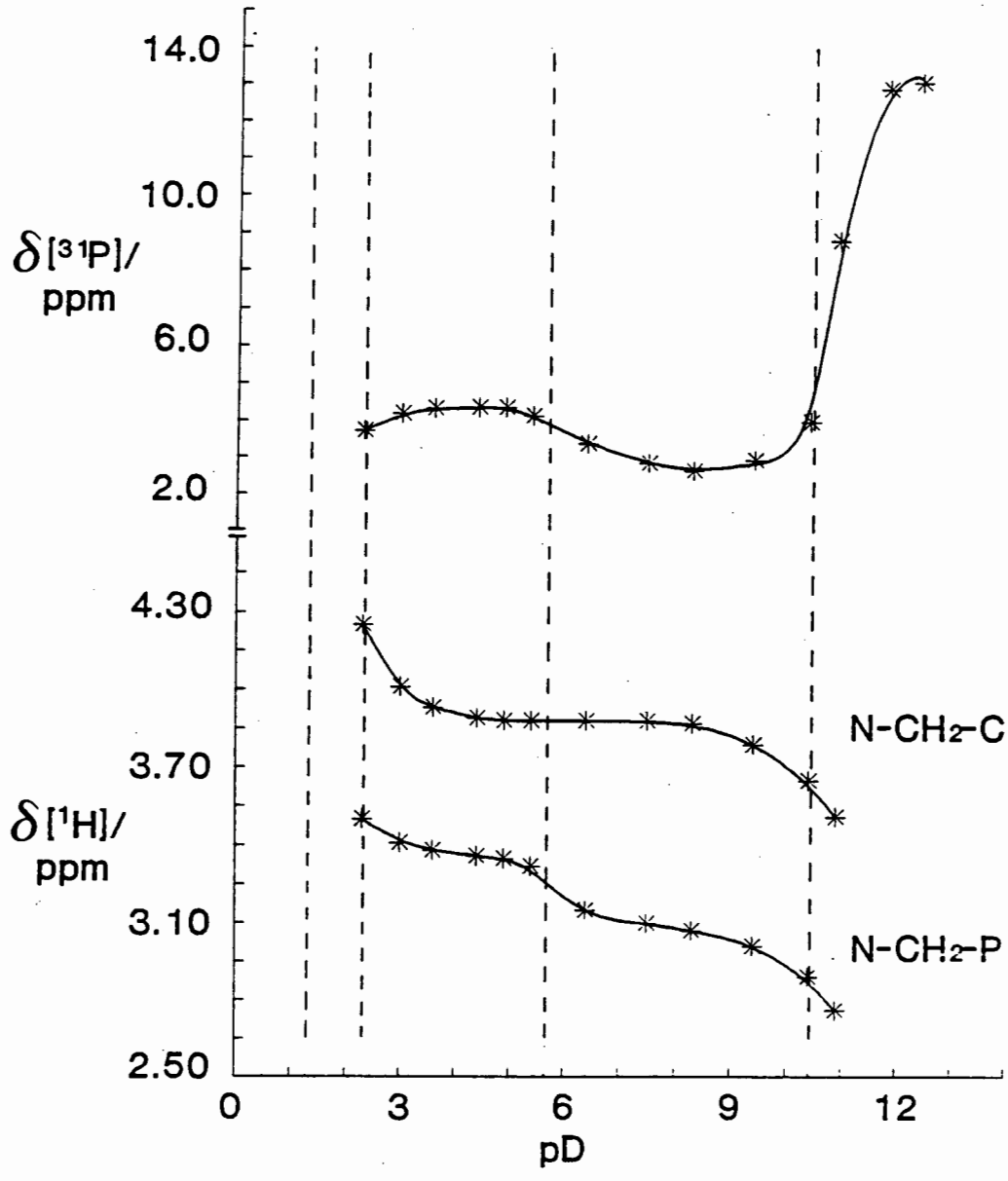


Figure 4.7 The effect of pD on the chemical shift of nuclei in **IV**.

potentiometrically for **IV**. This deprotonation corresponds to the ionization of the phosphonic acid moiety of **IV**.

The last deprotonation (pK_a = 10.11) affects the chemical shifts of all nuclei studied in the expected manner and consequently corresponds to the deprotonation of the nitrogen atom. The protonation behavior of **IV** is presented in figure 4.8.

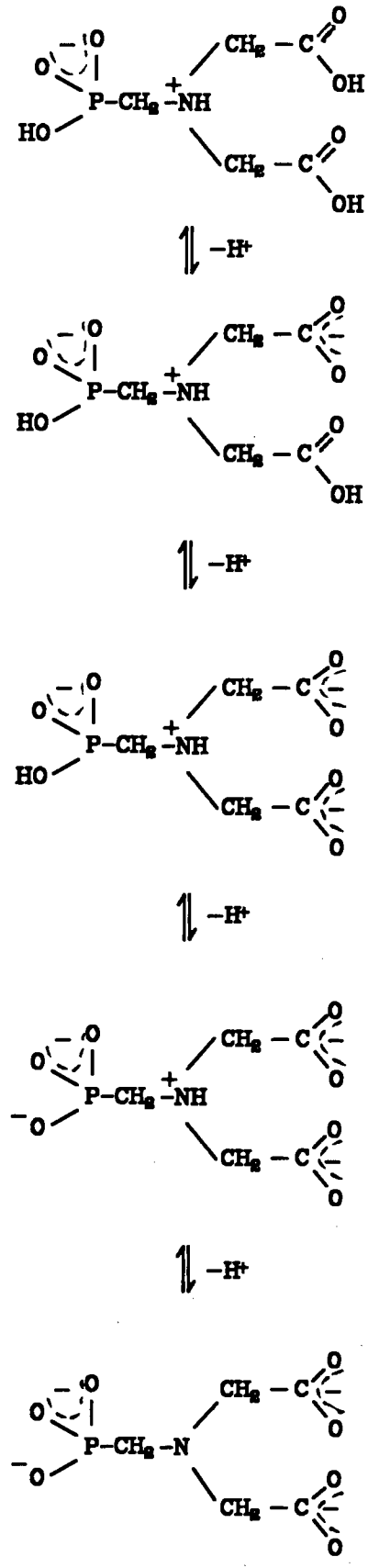


Figure 4.8 Deprotonation sequence of functional groups in **IV**.

CHAPTER 5

CHEMICAL MODELLING

CONSISTING OF

INTRODUCTION

THEORY

CONSTRUCTION OF A SOIL SOLUTION MODEL

RESULTS AND DISCUSSION

5.1 INTRODUCTION

Soil solutions are open natural water systems whose composition is determined as a result of many simultaneously occuring interactions between the various soluble organic, inorganic and metal ion species. Its composition is further influenced by dissolved gases and by the presence of mineral and organic solid phases through the processes of adsorption and desorption. The determination of the effects of contaminants, acid rain, pesticides and plant growth regulators, among other factors, to soil solution speciation are difficult to assess owing to the complexity of the system. Metal ions are non-biodegradable substances and their potential toxicity is controlled by their chemical forms in solution [Flo82].

Computerised chemical models can be used to determine the concentrations and physicochemical forms of species in solution and to predict the possible effects of changes in pH, concentration, redox eqilibria etc, on the equilibrium speciation of the system.

A mathematical model is an equation or set of equations which represents the behaviour of a system. A chemical model can thus be described as a theoretical construction which allows one to predict the thermodynamic properties of solutions. Any model is only as good as the assumptions upon which it is based and consequently it carries with it its own set of restrictions. Nordstrom et. al. cautions one of the temptation to use chemical models as ready-made interpretations of reality without a clear understanding of their weaknesses [Nor79]. Despite the fact that real systems are not at equilibrium, Sillén contends that an equilibrium model may be sufficiently similar to the real system to make a comparison interesting and a useful first approximation of the real system [Sil67].

The ion association theory is the basis of chemical modelling. The species distribution problem can be formulated in two thermodynamic ways, viz. the equilibrium constant approach and the Gibbs free energy approach. Both approaches are subject to the conditions of mass balance and chemical equilibrium.

Chemical equilibrium requires that the most stable arrangement for a given system be found as defined by the equilibrium constants for all mass action expressions of the system. Brinkley pioneered the formulation of the mathematics to this approach [Bri46], [Bri47]. Alternatively, a solution to the problem may be obtained by minimising the Gibbs free energy for all the components and defined species, the basic mathematics of which was first presented by White et. al. [Whi58]. The free energy approach is recommended for solving small systems with relatively few components, provided that the necessary data are available. Nordstrom et. al. predict that the Gibbs free energy method will be used more often to solve soil solution equilibria of complex systems once the necessary thermodynamic data have been compiled [Nor79].

By either thermodynamic approach, the problem can be stated numerically as one of finding a solution to a set of non-linear equations. It is more feasible to solve the simultaneous equations by an iterative method rather than in exact form. Newton-Raphson iteration is suited to the equilibrium constant approach and conversion assumes that the solution not only exists but that it is unique. Zeleznik and Gordon have reviewed both thermodynamic approaches to solving a speciation problem as well as the different numerical techniques that could be used in the computation [Zel68].

Owing to the complexity of soil solution speciation, most chemical models have adopted the chemical equilibrium approach. Among the many processes that control

soil solution speciation are chemical reactions between metal ions and soluble organic and inorganic components, plant processes such as absorption of nutrients and release of root exudates, kinetically controlled processes such as weathering, adsorption and desorption of soluble components by insoluble mineral and organic matter as well as applied chemicals such as pesticides and plant growth regulators.

A fundamental assumption made in the development of a soil solution model is that the system is at equilibrium, or sufficiently close to equilibrium, thus enabling one to use equilibrium constants to accurately reflect the concentrations of all the species defined in the model. Most modelling studies to date have only focussed on a subset of the various factors influencing soil solution speciation and certain speciation programs have been developed specifically for solving a defined problem. It is reasonable to assume that if more processes are included in a model, it represents the natural system better. However, this makes it more difficult to recognise those factors to which the model is most sensitive.

Perrin and Sayce developed the COMICS program for calculating the equilibrium speciation in a multi-metal, multi-ligand system from the pH of the solution, the total concentration of each component and the relevant equilibrium constants. The possible complexes included protonated, hydroxy, polynuclear and mixed ligand complexes [Per67]. HALTAFALL developed by Ingri et. al. can cope with all of the features of COMICS and in addition accounts for the possible effects of dissolved gases as well as the precipitation and dissolution of potential solids provided that the partial pressures and solubility products are available [Ing67]. Truesdell and Jones developed WATEQ which encompasses all of the features of COMICS and HALTAFALL and also determines the redox potential of solutions from redox couples [Tru74]. WATEQ2 is a revised version of WATEQ and has been expanded to include solubility equilibria for many more metals as well as the calculation of

redox potential from redox couples including polysulphides. The thermodynamic database has also been updated using critically evaluated values and new equilibrium constant compilations [Bal79]. Leggitt has used six programs, MINIQUAD, COMPLEX, EQUIL and COMICS, among others, to determine the equilibrium concentrations of multi-component systems and reported an order of efficiency for the programs under investigation [Leg77].

REDEQL developed by Morel and Morgan is a program based on the equilibrium constant approach and uses Newton-Raphson iteration to find a solution to the speciation problem as defined by the mass balance equations [Mor72]. REDEQL2 [McD73], MINEQL [Wes76] and GEOCHEM [Mat79] have all been developed with REDEQL as a basis. REDEQL2 and GEOCHEM allow for specialised capabilities such as adsoption/desorption, ion exchange and ionic strength calculation and correction.

Furrer et. al. have recently developed STEADYQL [Fur89] which differs from all previous algorithms in that it considers chemical processes for studying the composition and speciation of soil solutions in three different time frames. In the formulation of the model, fast reversible processes are described in terms of chemical equilibrium, slow processes by kinetic equations for which the steady state solution is found and very slow processes which are considered to be invariant in time for the solution of the system. This is particularly useful in view of the findings by Hering and Morel that the reaction between Cu(II) ions and ligands (natural and synthetic) is particularly slow in seawater with a high Ca(II) ion content [Her89]. Reactions of the above-mentioned type would normally be considered to be fast owing to the relatively high binding strength of the Cu(II) ion. STEADYQL has since been used successfully to predict changes in acidity of soil solutions [Fur90].

May and Murray are in the process of developing JESS (Joint Expert Speciation System) [May87]. JESS comprises a suite of programs for calculating the speciation of any system easily and efficiently.

The chemical speciation program MINEQL [Wes76] does not contain the adsorption and ion exchange subroutines of REDEQL2 and GEOCHEM and is a more compact program. MINEQL consists of about 500 lines of Fortran coding as opposed to REDEQL2's 2500 lines. In the present study of soil solutions we are examining the interactions between soluble metal ions, inorganic ions and natural and synthetic organic compounds (fulvic acids, plant root exudates and plant growth regulators). Equations that would account for the possible effects of dissolved gases (O_2, CO_2) and redox couples (Fe^{2+}/Fe^{3+}, caffeic acid/benzoquinone acrylic acid etc.) have been incorporated into the model as well as solubility products for a number of potential solids such as hydroxides, silicates and aluminosilicates.

MINEQL has been developed to accomodate all of the features under examination in our proposed model and since it is available in this laboratory, it is the logical choice of program for using in our studies. MINEQL accomodates as many potential solids as specified by the user and iterates on a set of solids until the correct set in equilibrium with the aqueous phase is found. Solids will only "precipitate" if at the end of a computation cycle, their solubility products are exceeded. Precipitated solids may "redissolve" in subsequent computations.

5.2 THEORY

The general theory pertaining to the modelling of chemical speciation has been adequately dealt with in the literature. The basis of the techniques presently used were formulated by Brinkley [Bri46], [Bri47] and White [Whi58]. The thermodynamic principles and algorithms, for solving systems of non-linear

equations, have been reviewed by Zeleznik and Gordon [Zel68], Morel and Morgan [Mor72] and Leggett [Leg77] amongst others. The chemical, mathematical and computational procedures as used in MINEQL are described in the user's manual [Wes76].

The basis of this study involved the construction of a soil solution model and examining the effect of selected organophosphorus plant growth regulators on soil solution speciation. A comprehensive literature search was conducted into the contributing factors of soil and soil solution composition and this resulted in a chosen set of components for the proposed model. The next step was to aquire equilibrium constants, solubility products, redox equilibria and Henry's law constants for all the possible dissolved species and potential solids that could possibly occur as a result of the components selected. Most of the constants were obtained from recent critical stability constant compilations [Mar74], [Mar75], [Mar76], [Mar77], [Mar82] and [Mar89]. As part of this study, the aqueous equilibria of some plant growth regulators and metal ion systems were examined potentiometrically. The unavailability of certain constants could result in one having to omit certain components from the model. For complexes deemed to be important, equilibrium constants could be estimated from similar systems. Although this is not the most satisfactory of methods, it is better to somehow account for these complexes as a total omission from the model could result in misleading conclusions. Equilibrium constants could also be determined from the standard molar Gibbs free energy of a reaction if calculation from more conventional methods such as potentiometry is difficult. The Gibbs free energy of a reaction can be determined from the standard molar enthalpy and standard molar entropy of a reaction. Once the equilibrium constants have been obtained, they are compiled in the form of a database as required by the input of MINEQL. Before this can be done, all the constants have to be corrected to an ionic strength of zero applicable at

a temperature of 25 ^{0}C. The basis for the selection of these conditions will be discussed later. Following is a brief description of the theory required.

The chemical potential of a species A, in solution, can be defined by the equation

$$\mu_A = \mu_A^o + RT\ln a_A \qquad \text{...eq. 5.1}$$

where μ_A^o is the chemical potential of A in the standard state,
a_A is the activity of species A in solution,
R is the gas constant equal to 8.314 JK^{-1} mol^{-1} and
T is the temperature in Kelvin.

The standard molar Gibbs free energy, G_m^o, for any reaction is defined as the difference between the sums of the chemical potentials of the products and the reactants. Using equation 5.1, the following relationship is established

$$G_m^o = -RT\ln K \qquad \text{...eq. 5.2}$$

By rearranging this equation, we can calculate lnK

$$\ln K = -\Delta G_m^o/RT \qquad \text{...eq. 5.3}$$

where ΔG_m^o is obtained from

$$\Delta G_m^o = \Delta H_m^o - T\Delta S_m^o \qquad \text{...eq. 5.4}$$

where ΔH_m^o is the standard molar enthalpy
and ΔS_m^o is the standard molar entropy.

As reported earlier, equilibrium constants often require adjustments of temperature and ionic strength as required by the conditions of the model. Corrections of temperature are made using the Gibbs-Helmholtz equation as applied to chemical reactions at constant pressure, P.

$$\{(\partial \Delta G/T) / \partial T\}_P = -\Delta H/T^2 \qquad \text{...eq. 5.5}$$

By substituting equation 5.2 into this, one obtains the Van't Hoff equation

$$\{(\partial \ \ln K) / \partial T\}_P = -\Delta H_m^o/RT^2 \qquad \text{...eq. 5.6}$$

where ΔH_m^o is as defined before and is temperature dependent.

Most equilibrium constants for metal - ligand reactions in aqueous solution are determined at 25 °C, and if not, they are usually quoted at 20 °C or 30°C. On the assumption that ΔH_m^o is constant over a small temperature range, the following relationship for adjusting equilibrium constants is obtained by integrating equation 5.6.

$$\ln(K_2/K_1) = (\Delta H_m^o/R)\,(1/T_1 - 1/T_2) \qquad \text{...eq. 5.7}$$

MINEQL contains a subroutine for adjusting equilibrium constants from 0.0 mol.dm^{-3} to any specified ionic strength using the Davies equation. All equilibrium constants compiled in the database thus had to be corrected to an ionic strength of 0.0 mol.dm^{-3}. This was done using the Davies equation [Dav62] which is applicable to solutions of ionic strength 0.1 mol.dm^{-3} and fits measured activities within 10%

[Pyt79]. In any computation using MINEQL, an ionic strength is specified and all equilibrium constants in the thermodynamic database are automatically corrected to the operative ionic strength. Computer calculations at other ionic strengths are thus easily handled by MINEQL making it a flexible program.

The ratio of the activity of an ion to its concentration in solution is called the activity coefficient. The Davies approximation for the activity coefficient γ of an ion in a medium of ionic strength μ is given by

$$\log \gamma = -Az^2[(\mu^{0.5}/1+\mu^{0.5}) - 0.3\mu] \qquad \text{...eq. 5.8}$$

where

z is the ionic charge,

A is 0.509 for water at 25 ^{0}C and

μ is the ionic strength, which is defined by

$$\mu = \tfrac{1}{2} \Sigma c_i z_i^2 \qquad \text{...eq. 5.9}$$

where

z_i is the ionic charge of species i and

c_i is the concentration of species i.

The thermodynamic equilibrium constant K for a reaction

$$a_1X_1 + ... + a_nX_n = C \qquad \text{...eq. 5.10}$$

where

X_j is reactant j,

a_j is the stoichiometric coefficient of X_j and

C is the resultant species formed,

is defined by

$$\{X_1\}^{a1} \text{ x } ... \text{ x } \{X_n\}^{an} . K = \{C\} \qquad ...eq. 5.11$$

where

{ } represents activity

This can also be written as

$$[X_1]^{a1} . \gamma_1^{a1} \text{ x } ... \text{ x } [X_n]^{an} . \gamma_n^{an} . K = [C] \gamma_C \qquad ...eq. 5.12$$

where

[ ] represents concentration in moles.dm^{-3} and

γ is the activity coefficient

This may be rearranged to

$$[X_1]^{a1} \text{ x } ... \text{ x } [X_n]^{an} . (\gamma_1^{a1} ... \gamma_n^{an})/\gamma_c . K = [C]$$

We can then define a constant corrected for ionic strength as

$$K' = (\gamma_1^{a1} ... \gamma_n^{an})/\gamma_c . K \qquad ...eq. 5.13$$

Using the fact that $Z_c = \Sigma a_j Z_j$ and the expression for log γ as given before, we can express the corrected ionic strength as

$$\log K' = [\Sigma a_i Z_j^2 - (\Sigma a_j Z_j)^2] \text{ x}$$
$$(-A (\mu^{0.5} / (1 + \mu^{0.5}) - 0.3\mu) + \log K \qquad ...eq. 5.14$$

The chemical speciation program MINEQL uses the equilibrium constant approach to find the concentration of components and specified complexes at equilibrium. The concentration of complexes in chemical equilibrium with its components can be expressed as a function of the specific component concentration by the mass action equation. This can be illustrated by the following simple example for the metal-ligand-proton complex, MLH_2.

$$[MLH_2] = \beta_{MLH^2} \times [M].[L].[H]^2$$

where β is the overall stability constant of the MLH_2 species.

Using the notation obtained from the MINEQL user's manual, [Wes76], equations such as the one described are generally expressed as

$$c_i = \beta_i \prod x X_j^{a(i,j)} \text{ for } i = 1,n \qquad \text{...eq. 5.15}$$

where

c_i is the concentration of complex i,

β_i is the stability constant of complex i,

X_j is the concentration of component j and

a(i,j) is the stoichiometric coefficient of component j in complex i.

The problem is reduced to finding the set of free concentrations of all components in the solution that will satisfy the mass balance condition. This condition states that the free concentration of component j plus the amount of j in all complexes should be equal to the total concentration of j, (T_j).

This can be determined as follows:

$$Y_j = T_j - \Sigma\, a(i,j).c_i \qquad \text{...eq. 5.16}$$

where Y_j is the difference between the total concentration of component j (T_j), and the amount of component j in all complexes c_i including the free ion j

The exact solution to the problem is thus the set

$$(X_j : j = 1,n)$$

such that all values of Y_j are equal to zero. To solve the problem, MINEQL calculates the concentration c_i of all complexes using initial estimates of the concentrations for each component X_j, as specified by the user. If all the differences Y_j are indeed zero, then the problem of aqueous speciation is effectively solved. However, since MINEQL uses an iterative method rather than an exact method for solving the system of non-linear equations, some criterion must be established such that when each Y_j becomes sufficiently close to zero, the system of equations is deemed to be "solved". Since each Y_j is the sum of terms which vary widely in order of magnitude, the convergence criterion used in MINEQL reflects the magnitude of Y_i relative to the maximum of the terms of which Y_i is the sum.

The criterion for convergence is given by

$$|Y_j| \,/\, \max(Y_j) < \epsilon \quad \text{for } j = 1 \text{ to } n \qquad \text{...eq. 5.17}$$

where max (Y_j) is the maximum of the absolute values of the set of terms ((a(i,j)).C_i, i = 1,m; T_j) of which Y_j is the sum, and ϵ is a small positive real number.

If the existing set of free concentrations has not resulted in convergence, the Newton-Raphson method for systems of non-linear equations is used to produce better estimates of the free concentrations [Wes76]. These new estimates are then used to recalculate the concentrations of all complexes, completing the first loop of the flow diagram as depicted in figure 5.1. MINEQL will continue to circulate in this loop until convergence is reached or the maximum number of iterations has been exceeded. Failure to converge within the specified maximum number of iterations could imply that the solution to the problem is diverging. This could arise if the initial guessed estimates of the component concentrations are poorly chosen, although it must be stressed that MINEQL is particularly robust in this regard and closes in on the final solution in most cases. By increasing the convergence criterion ϵ, a solution to the problem could be found. By using the calculated equilibrium concentrations of the various components as initial estimates in subsequent refinements, the convergence criterion can then be reduced again.

Once convergence has been obtained, MINEQL examines the solubility of all the potential solid phases. If the calculated free concentration of some components exceeds the solubility product, precipitation of those particular solids occur. MINEQL then recalculates the equilibrium concentrations of all the remaining dissolved species until convergence is obtained. Precipitated solids may dissolve in subsequent iterations, causing the dissolved concentrations of these components to increase once again. A solution to the chemical speciation problem is found when no further dissolution or precipitation of potential solids occurs and the convergence criterion is satisfied.

The output file of MINEQL includes the equilibrium concentrations of all components, specified complexes, redox species, precipitated solids (if any) and a summarised table giving all the complexes in which a component occurs in concentrations greater than and equal to 1% of its total concentration.

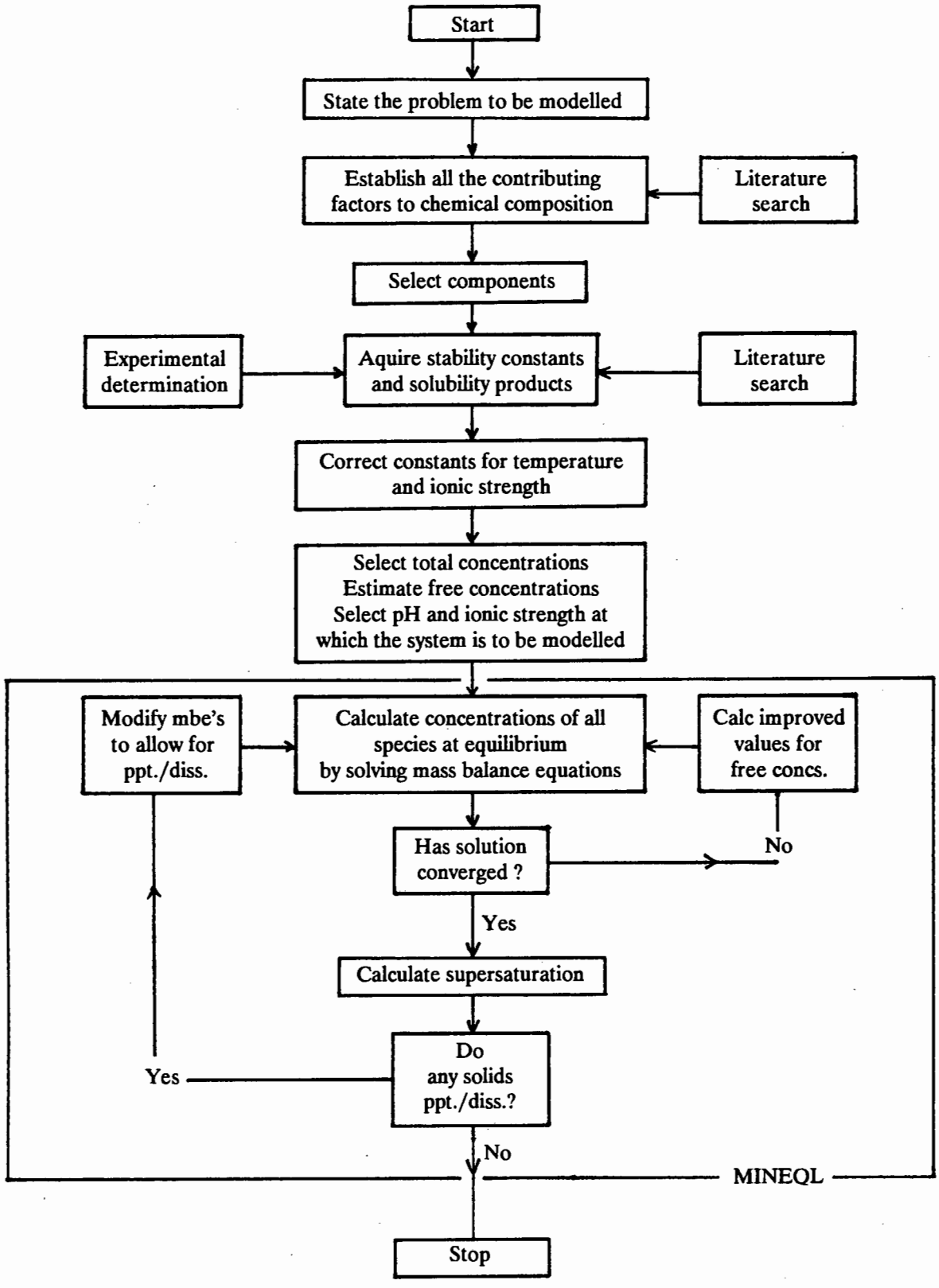


Figure 5.1 Flow diagram for the chemical modelling procedure as used in this study.

5.3 CONSTRUCTION OF A SOIL SOLUTION MODEL

5.3.1 SELECTION OF COMPONENTS

This study deals with the computer simulated effects of plant growth regulators on soil solution speciation. Soils, in general, have very diverse chemical compositions, therfore in this study the focus was on soils capable of supporting plant growth. A literature survey has been conducted into the various factors that could contribute to the chemical composition of a soil solution. This has been reported in chapter 1. Components were selected after due consideration of:

(i) The essential elements of plant nutrition.

(ii) Elements beneficial to plants.

(iii) Toxins

(iv) Soluble organic components

(v) Plant root exudates

(vi) Soil components

(vii) Other components

In the construction of the soil solution model, the effects of adsorbed ions and soil microorganisms on soil solution speciation were not considered.

5.3.1.1 The elements of plant nutrition.

As discussed in chapter 1.2, hydroponic plant nutrient solutions prepared from metal salts have played an important part in establishing metal ion essentiality to plants. The 13 elements that are essential to plants are calcium, magnesium, potassium, nitrogen, phosphorus, sulphur, (macronutrients) and manganese, iron, copper, zinc, molybdenum, boron and chlorine (micronutrients). The concentrations of components used in various plant nutrient solutions differ but are nevertheless of the same order of magnitude. The 13 elements essential to plant nutrition have been used a basis for constructing the soil solution model used in this study. Hoagland's

solution has been used as a guide for selecting approximate concentrations for the components chosen [Hew52]. These concentrations are fairly representative and have been used as a basis for numerous nutrient solution preparations [Smi83].

5.3.1.2 Elements beneficial to plants.

As discussed in chapter 1.2, the elements sodium, cobalt and nickel have been found to be beneficial to some plants. In fact, cobalt has been listed as an essential element by Fitzpatrick [Fit86]. Sodium ions are found in high concentrations in soils and have been included in a number of nutrient solution preparations [Smi83]. These three metal ions have therefore also been chosen as components of the soil solution model.

5.3.1.3 Toxins

The elements aluminium and cadmium are toxic to both man and plants and there is considerable concern regarding these elements as contaminants in the environment. Both elements have been chosen for inclusion in the soil solution model. Lead is another toxin to living organisms and its speciation in soil solutions is of great importance. However, lead has been excluded from the model owing to a lack of the necessary thermodynamic data particularly with reference to important organic components.

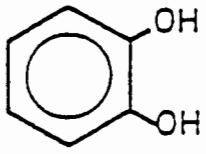
5.3.1.4 Soluble organic components.

Soil organic matter consists of humic acids and fulvic acids, the latter being soluble under slightly acidic conditions. Fulvic acids play an important role in retaining metal ions in solution, but due to their complex structures and high molecular weights, they cannot be fully characterised. Elemental and functional group analyses have also shown that fulvic acids vary somewhat from one soil to another.

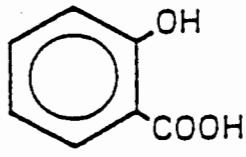
Using the program RANDOM, Murray has generated random organic molecules, which have been succesfully used to model the binding of metal ions to fulvic acids in soil solutions [Mur82]. This was accomplished by supplying relevant input data to RANDOM which included a knowledge of the molar mass, elemental and functional group concentrations of a typical fulvic acid. The inherent limitations of RANDOM have been reported by Murray [Mur82], but two of these will be highlighted here. Firstly, sulphur and nitrogen atoms were excluded from the input data supplied to RANDOM, and secondly, all aromatic carbon atoms were considered to be part of single aromatic ring structures only. It has been shown more recently that the exclusion of nitrogen containing organic compounds does not have much effect on the overall binding strength of the ligands used to model fulvic acid [Pre90].

Figure 5.2 depicts the 15 organic ligands generated by RANDOM. These compounds have been selected for inclusion in our soil solution model to account for metal ion interactions of soluble soil organic matter.

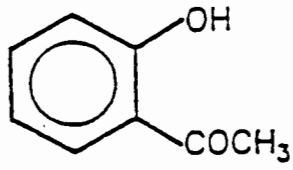
The output data of RANDOM includes the site concentrations of each organic compound which have been determined in milliequivalents per gram (meq/gram) of fulvic acid site. This has been summarised in table 5.1. For the purposes of this study, a fulvic acid concentration of 100 mg/dm^3 has been considered. By using the number of dissociable protons (NDP), of each organic compound, each of the site concentrations as generated by RANDOM can be converted from meq/gram to mmoles/gram. By using the chosen fulvic acid concentration, each of the site concentrations can be converted to a concentration in moles/dm^3 as required by the input of MINEQL. The concentrations calculated for each of these 15 organic compounds representing each of the fulvic acid sites are summarised in table 5.1.



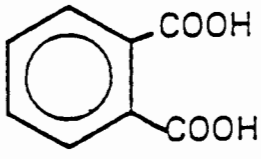
1 1,2-dihydroxybenzene



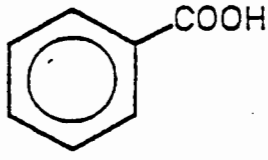
2 salicylic acid



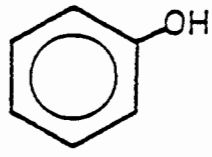
3 2-acetylphenol



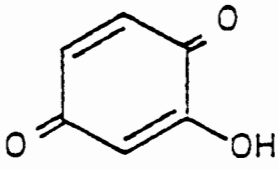
4 phthalic acid



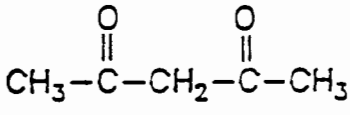
5 benzoic acid



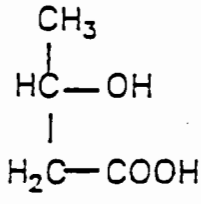
6 phenol



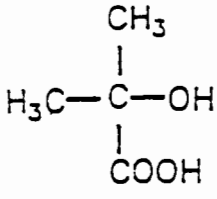
7 hydroxy-1,4 -benzoquinone



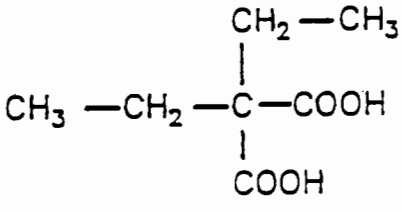
8 acetylacetone



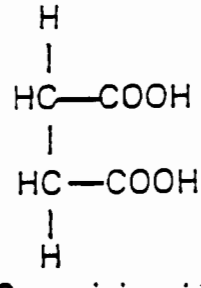
9 3-hydroxy-butanoic acid



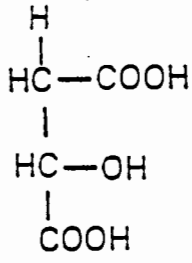
10 2-hydroxy-2-methyl propanoic acid



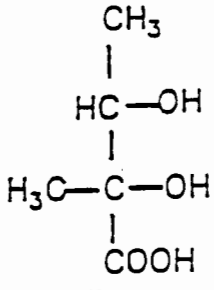
11 diethylmalonic acid



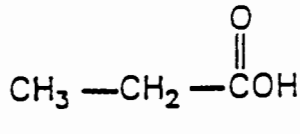
12 succinic acid



13 malic acid



14 2,3-dihydroxy-2-methylbutanoic acid



15 propanoic acid

Figure 5.2 Organic compounds used to model the metal binding sites of fulvic acids in a soil solution.

Table 5.1

Fulvic acid site concentrations as generated by RANDOM and soil solution input concentrations for each site determined by converting each site concentration from meq./gram to mmoles/gram and then to a concentration in moles.dm^{-3}.

Site No.	Site conc. meq./gram	NDP	Model input conc. mol.dm^{-3}
1	0.38	2	1.9 X 10^{-5}
2	0.61	2	3.1 X 10^{-5}
3	0.17	1	1.7 X 10^{-5}
4	0.15	2	0.8 X 10^{-5}
5	0.73	1	7.3 X 10^{-5}
6	1.20	1	1.2 X 10^{-4}
7	0.27	1	2.7 X 10^{-5}
8	0.13	1	1.3 X 10^{-5}
9	0.70	1	7.0 X 10^{-5}
10	0.49	1	4.9 X 10^{-5}
11	0.84	2	4.2 X 10^{-5}
12	0.63	2	3.2 X 10^{-5}
13	0.47	2	2.4 X 10^{-5}
14	0.26	1	2.6 X 10^{-5}
15	0.92	1	9.2 X 10^{-5}

5.3.1.5 Plant root exudates

Plant root exudates possess metal binding groups which affect metal ion speciation in soil solutions. Inskeep and Comfort have examined the effect of amino acid and carboxylic acid type plant root exudates on the speciation of selected metal ions in soil solutions [Ins86]. From thermodynamic predictions they concluded that if root exudates are present in sufficiently high concentrations, they may have a dramatic effect on soil solution speciation. They recommended that plant root exudates be accounted for in soil solution speciation studies in order to obtain a better description of the metal ion distribution. Linder et. al. have modelled the effect of caffeic acid, a plant root exudate, on the speciation of nutrient solution components [Lin90]. They found that caffeic acid had a great affinity for zinc(II) and copper(II) ions in the absence of a strong complexing agent such as EDTA. Lamy et. al. have chosen caffeic acid together with tyrosine, shikimic acid, chlorogenic acid and tiron in their studies of the mixed ligand complexes of copper(II) ions in natural systems [Lam85].

Plant root exudates, in general, have been discussed in chapter 1.3. Caffeic acid consists of a carboxylic acid group and an aromatic ring with two hydroxy groups ortho to each other. This could lead to the formation of metal ion complexes in the favourable 5 membered ring conformation. Caffeic acid is also easily oxidised to benzoquinone acrylic acid, releasing electrons and H^+ ions in the process. Caffeic acid exhibits most of the attributes of plant root exudates and is an ideal choice of compound to model the effects of plant root exudates in soil solution speciation studies.

Caffeic acid has been incorporated into the soil solution model used in this study at a concentration of 1×10^{-4} mol/dm^3 as used by Linder et. al. [Lin90].

5.3.1.6 Soil components.

Silicon is the second most abundant element of the earth's crust and constitutes the building block of silicate and aluminosilicate minerals [Lin79a]. These minerals almost always contain metal ions such as K^+, Na^+, Ca^{2+} and Fe^{3+} in their structures which with time are released into the soil solution. Silicic acid, (H_4SiO_4), is the soluble species of silicon as found in the soil solution and has been chosen as a component in the present study.

In the construction of this model, the soil solution has been considered to be in equilibrium with the soil atmosphere. The carbonate ion, CO_3^{2-}, has therefore been included in the model to account for interactions with atmospheric carbon dioxide and the subsequent formation of carbonate, bicarbonate and carbonic acid. Dissolved oxygen has also been incorporated into the model and these processes will be discussed further in a subsequent section.

5.3.1.7 Other components.

The H^+ ion has been defined as a component with an input concentration of zero and its presence in solution is accounted for by a facility in MINEQL whereby computations may be performed at a fixed pH value as chosen by the user (see section 5.3.2.1). Hydroxyl ions are taken into account implicitly by including the ionic product of water in the database of equilibrium constants and has therfore not been defined as a component.

The electron, e^-, has been defined as a component with a specific input concentration thus enabling one to determine the reduction potential of the soil solution at equilibrium. Redox potentials of solutions are reported by an E_h value which is related to the free electron concentration by the following expression:

$$E_h = 2.303RT/F \times pe \qquad \text{...eq. 5.18}$$

Selected redox states of manganese, cobalt, copper and iron ions have been defined in the component list (table 5.3) with an input concentration of zero. By including the relevant redox equilibria in the thermodynamic database, the equilibrium distributions of the various oxidation states will be determined by MINEQL.

5.3.1.8 Plant growth regulators.

Once the basic soil solution model had been constructed, the intention was to examine the effects of various concentrations of N - (Phosphonomethyl) glycine (Lig1) and N - (Phosphonomethyl) iminodiacetic acid (lig4) on the metal ion speciation in the model.

In studies examining the effects of Lig1 on indole acetic acid oxidation, Lee used concentrations of 0.2 to 2.0 mmoles/dm^3 [Lee82], [Lee83], [Lee85]. The maximum concentrations of Lig4 used by Elkins et. al. in their studies on grass growth regulation, have been reported as 4.5 kg/ha [Elk74a], [Elk74b]. This is equivalent to 19.81 moles/ha . The following considerations were used in an attempt to convert this to a soil solution concentration in moles/dm^3. A 1 dm^3 cube of soil with a height of 10 cm will have a cross-sectional area of 0.01 m^2. A Lig4 application rate of 19.81 moles/ha (1 hectare = 1 X 10^4 m^2) will result in 1.98 X 10^{-5} moles of Lig4 on a surface area of 0.01 m^2 or 1.98 X 10^{-5} moles/dm^3 (for a depth of 0.1 m). Soil moisture curves indicate that the water content of most soils rarely drops below 10% [Fot84]. This implies that Lig4 concentrations will have an approximate maximum of 1.98 X 10^{-4} moles/dm^3.

The Lig1 and Lig4 concentrations used in this study vary from 1.0 X 10^{-7} moles/dm^3 to 1.4 X 10^{-3} moles/dm^3.

5.3.2 IMPORTANT FACTORS CONSIDERED

5.3.2.1 pH

As this study deals with the examination of metal ion speciation at various concentrations of selected plant growth regulators, it was decided to fix the pH of the soil solution model at a carefully chosen value.

The natural pH of a soil solution is in a constant state of flux and is influenced by a network of soil interactions. The vast majority of field crops (wheat, rice etc.), vegetable crops (onions, tomatoes etc.), forest plants, fruit and weeds grow optimally in the pH range 5.5 to 7.0 [Fot84].

Siraj-Ali et. al. have examined the nutrient uptake of *Crysanthemum morifolium* from hydroponic solutions at pH levels of 4.5 to 7.5. They found that essential nutrient uptake was at a maximum at a pH of 6.5 indicating that nutrient bioavailability was at a maximum at a pH close to 6.5 [Sir87].

Figure 5.3 gives a diagramatic representation of plant nutrient availability at various pH values as presented by Foth [Fot84]. The availability of most nutrients appears to be optimal at a pH of 6.5.

A pH of 6.5 thus seems to be a reasonable choice of value at which to fix the soil solution model although it must be stressed that plants generally vary in their response to pH.

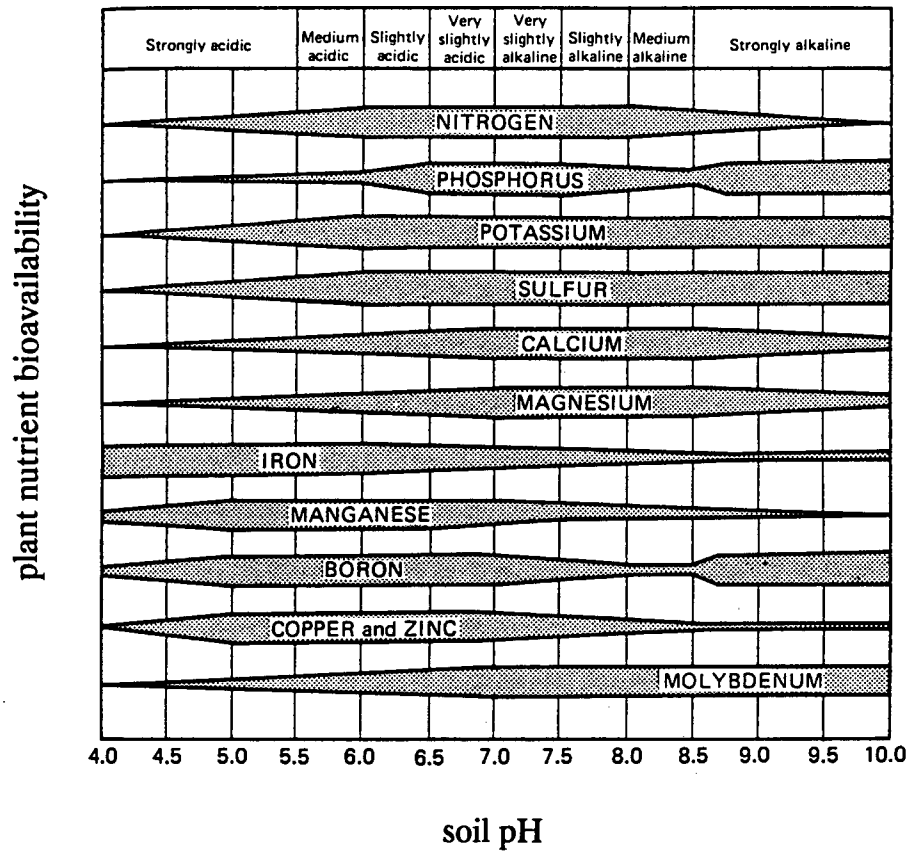


Figure 5.3 General relationship between soil pH and plant nutrient bioavailability:- The wider the bar, the greater the bioavailability [Fot84].

5.3.2.2 Temperature.

Soil temperature varies on a daily basis with the average daily temperature changing on a seasonal basis. In addition to this, soil temperature fluctuates with depth causing temperature gradients with the greatest changes occuring at the surface [Spa86]. Average soil surface temperatures vary greatly depending on geographical region and the range may be from below 10 ^{o}C to greater than 25 ^{o}C [Fot84].

A temperature of 25 ^{o}C was chosen for the soil solution model as this represents a satisfactory average value for plant growth. This was also convenient as most

equilibrium constants are reported at 25 °C resulting in very few adjustments having to be made. Where corrections for temperature had to be made, these were usually minor adjustments of up to 5 °C. The assumption of constant ΔH_m^0 as used in equation 5.7 is thus valid over a small temperature range.

5.3.2.3 Ionic strength

By considering the components with a relatively high concentration in the soil solution model, an ionic strength of 0.02 moles / dm^3, was determined for the soil solution. The only component concentrations varied in this study were those of Ligand 1 and Ligand 4. These were in the concentration ranges of 1.0 X 10^{-7} to 1.4 X 10^{-3} mol / dm^3. This was not expected to have any significant effect on the overall ionic strength even at the higher concentration ranges of Ligand 1 and Ligand 4. As a consequence of this, the stability constants of the species in the database could be regarded as valid throughout this study. An ionic strength of 0.02 moles / dm^3 was thus chosen as a fixed value in this study.

5.3.2.4 Potential solids.

Potential solids such as metal hydroxides, carbonates, phosphates, silicates, aluminosilicates etc that could possibly form as a result of the components selected have been considered in this study.

Most of the solubility products for these potential solids were obtained from Lindsay's "Chemical equilibria in Soils" [Lin79a]. Adjustments to solubility products were often neccessary in order that they be defined in terms of the components as specified in the input data of MINEQL. This is best illustrated by an example in which adjustments were made to the solubility product of $Ca(OH)_2(s)$, portlandite, which is given by equation 5.19 with log K_{sp} = -5.03 at an ionic strength of 0.0 mol.dm^{-3} and a temperature of 25 °C.

$$Ca(OH)_2\,(s) \rightleftharpoons Ca^{2+} + 2OH^- \qquad \text{...eq. 5.19}$$

Because the hydroxyl ion has not been specified as a component, all species containing this ion have to be specified in terms of protons (H^+ ions).

The formation reaction of portlandite is thus given by equation 5.20 with a log K = 5.03.

$$Ca^{2+} + 2OH^- \rightleftharpoons Ca(OH)_2\,(s) \qquad \text{...eq 5.20}$$

and by addition of twice the dissociation product of water one obtains equation 5.21

$$Ca^{2+} + 2H_2O \rightleftharpoons Ca(OH)_2\,(s) + 2H^+ \qquad \text{...eq. 5.21}$$

with a log K of -22.97 at an ionic strength of 0.0 moles.dm^{-3} and a temperature of 25 ^oC.

This was then incorporated into the thermodynamic database of MINEQL as a potential solid with a species number 80110 and component numbers for Ca^{2+} and H^+ of 1 and 50 respectively.

80110 -22.97 1 1 50 -2

5.3.2.5 Redox equilibria.

Oxidation and reduction reactions form an integral part of soil solution chemistry. The presence of protons, electrons, dissolved gases, ionic species and plant root

exudates are but some of the contributing factors in the complex network of electron acceptance and transfer. In this section a description is given of the procedure for estimating equilibrium constants for redox equilibria in terms of standard electrode potentials.

Redox equilibria are expressed in terms of E^o (mv) where E^o is the standard electrode potential when the half cell reactions are written as

$$\text{oxidised form} + ne^- \rightleftharpoons \text{reduced form} \qquad \text{...eq. 5.22}$$

and is related to the equilibrium constant K by the following expression

$$E^o = (2.303\ RT\log K)/nF \qquad \text{...eq. 5.23}$$

which reduces to

$$E^o = (59.16\ \log K)/n \qquad \text{...eq. 5.24}$$

Table 5.2 lists the standard electrode potentials of selected redox reactions at 25 °C as obtained from the CRC Handbook of Physics and Chemistry [Wea85] as well as the equilibrium constants obtained following substitution of these values into equation 5.24.

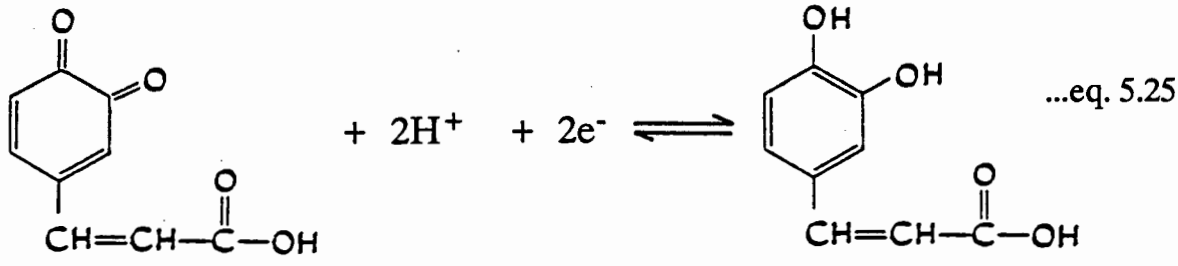
Table 5.2

Standard electrode potentials and equilibrium constants for selected redox reactions.

redox reaction	standard electrode potential (volts)	log equil. constant K
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	0.771	13.03
$Cu^{2+} + e^- \rightleftharpoons Cu^{+}$	0.153	2.59
$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$	1.542	26.06
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	1.83	30.93

Redox equilibria for the iron, copper, manganese and cobalt ions as represented in table 5.2 were incorporated into the soil solution model.

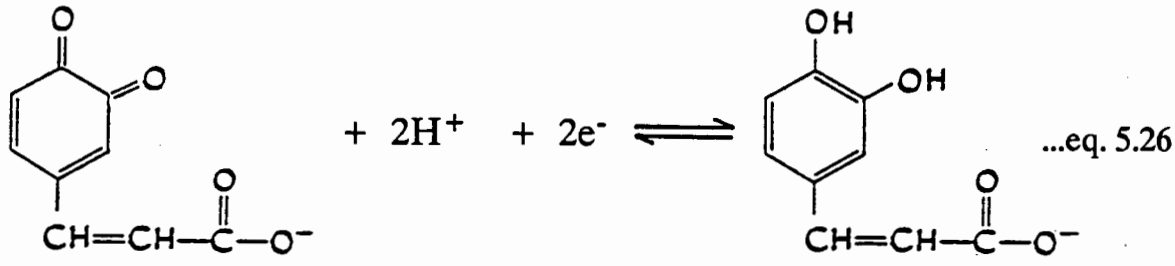
Caffeic acid (Caff) can be oxidised to benzoquinone acrylic acid (BQA) releasing protons and electrons into the soil solution. Horner and Geyer have reported a standard electrode potential of 793 mv [Hor65] for the reaction



...eq. 5.25

which gives a log K = 26.81 on substitution of the standard electrode potential in equation 5.24.

All ligands are defined in their fully deprotonated forms as components in MINEQL hence the equation required by us in fact



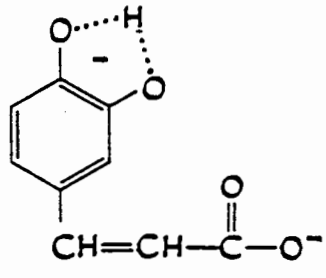
...eq. 5.26

So on the assumption that the reduction potential of the protonated species (equation 5.25) is the same as that of the deprotonated species, equation 5.26 has a log K = 26.81.

Equation 5.26 expressed in terms of its components and species as defined in MINEQL is as follows

$$BQA^- + 2H^+ + 2e^- \rightleftharpoons HCaff^- \qquad \text{...eq. 5.27}$$

As depicted below, caffeic acid has been defined as a dianion in MINEQL



$Caff^{2-}$

$HCaff^-$ as used in equation 5.27 is in fact a species which dissociates into the components H^+ and $Caff^{2-}$ as shown in equation 5.28 and has a dissociation constant of log K = -9.08 at at (I =0.0 mol/dm^3, T =25 ^oC) [Lin87].

$$HCaff^- \rightleftharpoons Caff^{2-} + H^+ \qquad \text{...eq. 5.28}$$

Addition of equation 5.28 to equation 5.27 results in equation 5.29

$$BQA^- + H^+ + 2e^- \rightleftharpoons Caff^{2-} \qquad \text{...eq. 5.29}$$

with a log K = 17.73 (I = 0.0 mol/dm^3, T = 25 ^oC). The component numbers of $Caff^{2-}$, BQA^-, H^+ and e^- have been defined as 161, 162, 50 and 99 respectively in MINEQL. The oxidation of caffeic acid to benzoquinone acrylic acid has thus been incorporated into the MINEQL database as complex number 80008 and is defined as follows,

80008 17.73 162 1 50 1 99 2 161 -1

5.3.2.6 Dissolved gases.

Since soils are open to the atmosphere, the soil solution contains dissolved oxygen and carbon dioxide. Following is a description of the methods used for including dissolved oxygen and carbonate equilibria in the model of soil solutions.

Truesdell and Jones used a value of logK = -21.50, determined from thermodynamic data, for the oxygen redox half reaction as in equation 5.25 [Tru74].

$$1/2\, H_2O \rightleftharpoons 1/4\, O_2(aq) + H^+ + e^- \qquad \text{...eq. 5.30}$$

The reaction,

$$O_2(g) \rightleftharpoons O_2(aq)$$

representing the solubility of oxygen in aqueous solution has a logK = -2.89. Adding this to equation 5.30 results in equation 5.31 with a logK = -20.78.

$$1/2\ H_2O \rightleftharpoons 1/4\ O_2(g) + H^+ + e^- \qquad \text{...eq. 5.31}$$

Oxygen has a partial pressure of 0.2095 atm. in air ($10^{-0.68}$) [Wea85]. By combining Henry's law with equation 5.31, the unbalanced equation

$$1/2\ H_2O \rightleftharpoons H^+ + e^- \qquad \text{...eq. 5.32}$$

with a conditional equilibrium constant of logK' = -20.61 is obtained.

Dissolved oxygen can thus be accounted for by combining equation 5.32 with any of the redox reactions previously defined in table 5.2. Using the the iron redox half reaction

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad \text{...eq. 5.33}$$

which has a logK of 13.03, the following unbalanced reaction,

$$Fe^{3+} \rightleftharpoons Fe^{2+} + H^+ \qquad \text{...eq. 5.34}$$

with a conditional equilibrium constant of logK' = -7.58 (I = 0.0 mol/dm^3 , T = 25 ^{O}C) was obtained. Using the appropriate component numbers as specified, equation 5.34 was incorporated into the thermodynamic database of MINEQL.

Carbon dioxide, $CO_2(g)$, has a partial pressure of 0.00033 atm. ($10^{-3.48}$) at atmospheric pressure [Lin79a], [Jan86]. In most soils the $CO_2(g)$ partial pressure is slightly higher than that in air because $CO_2(g)$ is continuously being released into the soil by the respiration of roots and soil microorganisms. In flooded soils the $CO_2(g)$ level increases rapidly since the diffusion of gases is slower in water than in air. Increased carbon dioxide levels in the soil solution lowers the pH and accordingly modifies soil solution speciation and solubility relationships. The carbonate ion, CO_3^{2-}, as mentioned in chapter 5.3.2.6 is thus an important component for the description of carbonate, bicarbonate and carbonic acid equilibria. Solubility products for carbonate species have also been included in the database.

The equilibrium between soil $CO_2(g)$ and the soil solution can be described by the following equation.

$$2H^+ + CO_3^{2-} \rightleftharpoons H_2O + CO_2(g) \qquad \text{...eq. 5.35}$$

The logarithm of the equilibrium constant for this reaction can be determined in the following way.

The reactions

$$H^+ + CO_3^{2-} \rightleftharpoons HCO_3^- \qquad \text{...eq. 5.36}$$

$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3^* \qquad \text{...eq. 5.37}$$

where $H_2CO_3^*$ is dissolved carbonic acid

have logK values of 10.33 and 6.36 respectively [Lin79a].

The addition of equations 5.36 and 5.37 results in

$$2H^+ + CO_3^{2-} \rightleftharpoons H_2CO_3^* \qquad \text{...eq. 5.38}$$

with a logK of 16.69 (I = 0.0 mol/dm^3, T =25 ^oC).

The solubility of carbon dioxide in water is described by the reaction

$$CO_2(g) + H_2O \rightleftharpoons H_2CO_3^* \qquad \text{...eq. 5.39}$$

which has a logK = -1.46 [Lin79a]. Addition of equations 5.38 and 5.39 effectively gives equation 5.35 with a logK = 18.15.

This gives at a fixed partial pressure for carbon dioxide of 0.00033 atm., ($10^{-3.48}$) at atmospheric conditions [Wea85], the unbalanced reaction

$$2H^+ + CO_3^{2+} \rightleftharpoons H_2O \qquad \text{...eq. 5.40}$$

with a conditional equilibrium constant of logK' = 21.63. Using the components as specified, equation 5.40 was included in the MINEQL database to account for carbonate equilibria.

5.3.3 CONSTRUCTION OF THE THERMODYNAMIC DATABASE

MINEQL requires the various components and equilibria to be defined in specific blocks [Wes76]. Components together with their total analytical concentrations are defined as type I species. The ionic charges of the cations and anions specified as type I species are compiled in a separate file which MINEQL refers to during any computation. All the soluble complexes that are possible as a result of the components selected are specified in terms of the components and together with their equilibrium constants are included as type II species. Type III species include redox equilibria and soluble species of fixed concentrations eg. pH and gases at fixed partial pressures. Type V species are dissolved solids which are subject to precipitation if the solubility products are exceeded.

Type IV species are precipitated solids subject to dissolution if the activity is less than zero and type VI species are dissolved solids which are not subject to precipitation. Neither of the latter two species were included in the model of soil solutions.

The thermodynamic database constructed in this study consists of 577 complexation equilibria, solubility products for 65 potential solids and selected redox and atmospheric equilibria. A complete listing of the database is presented in **appendix A** (page 374).

Most of the equilibrium constants were obtained from the critical stability constant compilations of Martell and Smith [Mar74], [Mar75], [Mar76], [Mar77], [Mar82] and [Mar89]. Lindsay's "Complex Equilibria in Soils" also proved to be a valuable and convenient source of information particularly with the aquisition of solubility products [Lin79a]. Constants for the hydrolysis of metal ions were taken from Baes and Mesmer [Bae76].

In cases where different equilibrium constant values for the same equilibria were found, the value chosen was based on the following criteria:

Conditions of ionic strength and temperature,
(I = 0.0 mol/dm^3 and T = 25 ^oC preferred),
Method of determination,
(Potentiometric determinations preferred),
Date of publication,
Journal of publication and
Authors of publication.

Equilibrium constants for N - (Phosphonomethyl) glycine (Ligand 1) with selected metal ions have been reported by Motekaitis and Martell [Mot85]. Most of the constants for N - (Phosphonomethyl) iminodiacetic acid (Ligand 4) have been determined in this study (See chapter 3). Additional constants for Ligand 4 metal ion systems were obtained from the collections of Martell and Smith. The aqueous equilibria of caffeic acid with selected metal ions have been studied by Linder and Voye [Lin87] as well as by Cocks-Wilson et. al. [Coc91].

5.3.4 The soil solution model.

This section describes the main features of the soil solution model used to examine the effects of selected plant growth regulators.

(i) The chemical symbols or abbreviations of all the components used in this study are presented in table 5.3.
(ii) All computer simulations are performed at :
a fixed pH of 6.5,
an ionic strength of 0.02 mol/dm^3 and

a temperature of 25 °C.

(iii) Thermodynamic data for:

soluble species,

redox equilibria,

atmospheric equilibria and

potential solids have been considered.

(iv) Computer simulations of the following have been examined:

inclusion of the $O_2(aq)/O_2(g)$ couple,

exclusion of the $O_2(aq)/O_2(g)$ couple,

inclusion of the $Caff^{2-}/BQA^-$ couple,

use of specified $Caff^{2-}$ and e^- concentrations to simulate the behaviour of the $Caff^{2-}/BQA^-$ couple and the examination of the effects of various concentrations of Lig1 and Lig4 (in independant computations) on soil solution speciation.

TABLE 5.3

Chemical symbols/abbreviations of the components used in the model of soil solutions.

CATIONS		LIGANDS	
Ca^{2+}	Calcium	CO_3^{2-}	Carbonate
Mg^{2+}	Magnesium	SO_4^{2-}	Sulphate
K^+	Potassium	Cl^-	Chloride
Na^+	Sodium	NH_3	Ammonia
Fe^{2+}	Iron(II)	PO_4^{3-}	Phosphate
Fe^{3+}	Iron(III)	NO_3^-	Nitrate
Zn^{2+}	Zinc	$B(OH)_4^-$	Borate
Cu^{2+}	Copper(II)	MoO_4^{2-}	Molybdate
Cu^+	Copper(I)	SiO_4^{4-}	Silicate
Mn^{3+}	Manganese(III)	*FA	Fulvate
Mn^{2+}	Manganese(II)	$Caff^{2-}$	Caffeate
Ni^{2+}	Nickel	BQA^-	Benzoquinone
Co^{2+}	Cobalt(II)		acrylate
Co^{3+}	Cobalt(III)	e^-	Electrons
Cd^{2+}	Cadmium	Lig1	N - (Phosphonomethyl)
Al^{3+}	Aluminium		glycinate
H^+	Protons	Lig4	N -(Phosphonomethyl)
			iminodiacetate

*FA represents the ligands used to model fulvic acids (page269)

TABLE 5.3 continued

* The fulvate component consisted of the following fifteen organic ligands as generated by RANDOM.

Site No.	Abbrev.	Organic ligand
1	DHBZ	1,2-Dihydroxybenzene
2	SAL	Salicylic acid
3	ACPH	2-Acetylphenol
4	PHTH	Phthalic acid
5	BZA	Benzoic acid
6	PHEN	Phenol
7	HBQN	Hydroxy-1,4 benzoquinone
8	ACAC	Acetylacetone
9	HBA	3-Hydroxy butanoic acid
10	HMPA	2-Hydroxy-2-methyl propanoic acid
11	DEMA	Diethyl malonic acid
12	SUCA	Succinic acid
13	MALI	Malic acid
14	DMBA	2,3-Dihydroxy-2-methyl butanoic acid
15	PROP	Propanoic acid

5.4 RESULTS AND DISCUSSION

5.4.1 SOIL SOLUTION MODEL IN THE PRESENCE OF DISSOLVED OXYGEN

Prior to examining the effects of N - (Phosphonomethyl) glycine (**I**) and N - (Phosphonomethyl) iminodiacetic acid (**IV**) on soil solution speciation, the results as simulated by the soil solution model were examined with particular interest in soil redox and in species affected by redox behaviour.

Table 5.4 shows the input concentrations of the components as used in the soil solution model in the presence of dissolved oxygen and in the absence of the $Caff^{2-}$ /BQA^{-} couple (equation 5.29). Dissolved oxygen was accounted for in the model by incorporating equation 5.34 into the thermodynamic database. This equation is in fact the sum of the expression for dissolved oxygen, eq. 5.32 and the iron redox half reaction as expressed in table 5.2 and equation 5.33.

Table 5.5 shows the equilibrium concentrations of selected species in the presence of dissolved oxygen with the entire output presented in **appendix B** (page 389). Of particular interest to us is the low total concentration of Fe^{2+} ions which at concentrations of 10^{-18} $mol.dm^{-3}$ is several orders of magnitude lower than the normal requirements for plant nutrition which has been suggested as $10^{-7.7}$ $mol.dm^{-3}$ by Lindsay [Lin82a]. The (pe+pH) value, which is a measure of the oxidation status of the soil is 18.35 which is just outside the already wide (pe+pH) range of 2 to 18 for soil solutions [Bar84] and [Lin79a]. By decreasing the oxygen partial pressure, a change to the conditional equilibrium constant of equation 5.32 is introduced. This in turn affects equation 5.34 in the thermodynamic database. However, this does not affect the (pe+pH) value of 18.35 and even unrealistically low oxygen partial pressures have little effect on the Fe^{2+} ion concentration when compared with the requirements for plant nutrition. The Fe^{2+} ions in solution occur predominantly as

free ions (84.9%) and as the $FeSO_4$ species (11.8%). A small percentage of Fe^{2+} ions is bound to fulvic acid (FeFA = 1.3%) where FeFA is the total concentration of Fe^{2+} ions bound to the various fulvic acid sites.

TABLE 5.4

List of components with chemical symbols / abbreviations and input concentrations as used in the model of soil solutions

Component	Concentration ($mol.dm^{-3}$)	Component	Concentration ($mol.dm^{-3}$)
Ca^{2+}	2.50×10^{-3}	SiO_4^{4-}	3.50×10^{-3}
Mg^{2+}	1.00×10^{-3}	$B(OH)_4^-$	5.00×10^{-5}
K^+	5.00×10^{-3}	MoO_4^{2-}	0.30×10^{-7}
Na^+	2.00×10^{-3}	NO_3^-	6.00×10^{-3}
Fe^{3+}	2.00×10^{-5}	DHBZ	1.90×10^{-5}
Fe^{2+}	0.00	SAL	3.10×10^{-5}
Zn^{2+}	5.00×10^{-6}	HMPA	4.90×10^{-5}
Cu^{2+}	1.00×10^{-6}	ACPH	1.70×10^{-5}
Cu^+	0.00	HBA	7.00×10^{-5}
Mn^{2+}	1.00×10^{-5}	DEMA	4.20×10^{-5}
Mn^{3+}	0.00	ACAC	1.30×10^{-5}
Cd^{2+}	1.00×10^{-6}	PHTH	8.00×10^{-6}
Co^{2+}	1.00×10^{-6}	MALI	2.40×10^{-5}
Co^{3+}	0.00	SUCA	3.20×10^{-5}
Ni^{2+}	1.00×10^{-6}	DMBA	2.60×10^{-5}
Al^{3+}	1.50×10^{-6}	BZA	7.30×10^{-5}
H^+	0.00	PHEN	1.20×10^{-4}
e^-	0.00	PROP	9.20×10^{-5}
CO_3^{2-}	0.00	HBQN	2.70×10^{-5}
SO_4^{2-}	3.00×10^{-3}	$Caff^{2-}$	omitted
Cl^-	2.00×10^{-3}	BQA^-	omitted
NH_3	1.00×10^{-3}	Lig1	omitted
PO_4^{3-}	1.00×10^{-3}	Lig4	omitted

Lindberg and Runnels [Lin84b], examined the oxidation-reduction reactions of normal ground waters from diverse geographical areas. In this study, which represented the first comprehensive investigation of natural water E_h values, the authors concluded that due to the large discrepancy between observed and computed E_h values, internal redox equilibrium does not exist. Redox potentials measured in natural waters are mixed potentials and cannot be related to a single dominant redox couple in solution. The approach to computer modelling as recommended by Linberg and Runnels is thus to consider all the redox elements and to include each redox couple in the model which then allows them to distribute among their own redox species.

The results of the soil solution model indicate the precipitation of amorphous $Fe(OH)_3(s)$ as indicated in table 5.5. The solubility product of $Fe(OH)_3(s)$ has been reported as -3.20 at an ionic strength of 0.0 mol.dm^{-3} (T = 25 ^{o}C) [Mar86]. When corrected to an ionic stength of 0.02 mol.dm^{-3} log K_{sp} = -3.56 and from the expression

$$K_{sp} = 10^{-3.56} = [Fe^{3+}][H^{+}]^{-3}$$

one obtains the Fe^{3+} equilibrium concentration of 1.15 X 10^{-16} mol.dm^{-3} as determined by MINEQL. Iron solubility thus increases in acidic soils.

The speciation results of the soil solution model in the presence of dissolved oxygen also indicate the precipitation of calcium hydroxy apatite, $Ca_5(PO_4)_3OH(s)$ and gibbsite, $Al(OH)_3(s)$ incorporating 64.5% and 75% of the total Ca^{2+} and Al^{3+} ion concentrations respectively. $Fe(OH)_3$ is the major soluble complex of Fe^{3+} ions with a concentration of 4.90 X 10^{-7} mol.dm^{-3} (2.4%).

Table 5.5

Equilibrium concentrations of selected species in the presence of the $O_2(aq)/O_2(g)$ couple.

Species	Concentration (mol.dm^{-3})	% [Component]^T
Fe^{3+}	1.15 X 10^{-16}	negl.
Fe^{2+}	5.25 X 10^{-18}	84.9
$FeSO_4$	7.32 X 10^{-19}	11.8
FeFA	8.09 X 10^{-20}	1.3(Fe^{2+})
$Fe(OH)_3$	4.90 X 10^{-7}	2.4
electrons	1.40 X 10^{-12}	100
$Fe(OH)_3(s)$	1.95 X 10^{-5}	97.5
$Ca_5(PO_4)_3OH(s)$	3.23 X 10^{-4}	64.5(Ca^{2+})
$Al(OH)_3(s)$	1.13 X 10^{-6}	75.0(Al^{3+})

5.4.2 SOIL SOLUTION MODEL IN THE ABSENCE OF DISSOLVED OXYGEN.

Table 5.4 lists the input concentrations of the components used in the soil solution model in the absence of dissolved oxygen.In this computation, equation 5.34 was omitted from the thermodynamic database. The Fe^{3+} ion input concentration has been chosen as 2.0 X 10^{-5} mol/dm^3 and the Fe^{2+} ion concentration as 0.0 mol/dm^3. By incorporating the iron redox couple (equation 5.33) in the thermodynamic database, the two redox species of iron would be allowed to distribute among themselves. In the study involving dissolved oxygen, equation 5.33 was combined with equation 5.32.

The results of selected species of the soil solution model in the absence of dissolved oxygen are presented in table 5.6 with the entire output presented in **appendix C** (page417).

The only significant change from the results presented in the presence of the oxygen couple, table 5.5, is that of the total soluble Fe^{2+} ion concentration which has increased approximately 100 fold. $FeSO_4$ and FeFA remain the two significant soluble complexes of Fe^{2+} ions. This is however still inadequate for the purposes of plant nutrition.

The concentrations of precipitated solids as well as those of most soluble species were unaffected by the omission of the oxygen couple. It should be noted that the solubility of iron is controlled by amorphous $Fe(OH)_3$ (s) under these conditions.

The $O_2(aq)/O_2(g)$ couple was omitted from all subsequent computations in this study since it made very little difference to the oxidation status of the model. This couple has also been omitted by Ball et. al. in their studies on natural water systems as it is reported to be kinetically inhibited and grossly out of equilibrium [Bal79].

Table 5.6

Equilibrium concentrations of selected species in the absence of the $O_2(aq)/O_2(g)$ couple.

Species	**Concentration** ($mol.dm^{-3}$)	**% [Component]^T**
Fe^{3+}	1.15×10^{-16}	negl.
Fe^{2+}	7.50×10^{-16}	85.4
$FeSO_4$	1.05×10^{-16}	11.9
FeFA	1.16×10^{-17}	1.3(Fe^{2+})
$Fe(OH)_3$	4.90×10^{-7}	2.4
electrons	1.40×10^{-12}	100
$Fe(OH)_3(s)$	1.95×10^{-5}	97.5
$Ca_5(PO_4)_3OH(s)$	3.23×10^{-4}	64.5(Ca^{2+})
$Al(OH)_3(s)$	1.13×10^{-6}	75.0(Al^{3+})

5.4.3 SOIL SOLUTION MODEL INCLUDING THE CAFFEIC ACID / BENZOQUINONE ACRYLATE, $Caff^{2-}$ / BQA^{-}, COUPLE.

Caffeic acid has been found to be released by certain plant species under conditions of iron stress (chapter 1.3). As previously reported in chapter 5.3.1.5, caffeic acid has been chosen as one of the components of the soil solution model. The oxidation of caffeic acid to benzoquinone acrylate has been incorporated into the model by inclusion of the $Caff^{2-}/BQA^{-}$ redox couple as described in equation 5.29. The input concentrations of the soil solution model as examined in the presence of the $Caff^{2-}/BQA^{-}$ couple are presented in table 5.4. An input concentration of 1.00×10^{-4} $mol.dm^{-3}$ has been chosen for caffeic acid and 0.0 $mol.dm^{-3}$ for benzoquinone acrylate. The presence of the $Caff^{2-}/BQA^{-}$ redox couple in the thermodynamic database thus allows each component to distribute among their redox species.

The equilibrium concentrations of selected species in the present model are presented in table 5.7 with the entire output presented in **appendix D** (page 445).

The most striking difference in concentration is that of soluble Fe^{2+} ions which at 3.47×10^{-10} $mol.dm^{-3}$ has increased by a factor of 4.6×10^{6} from the concentrations calculated in the absence of the $Caff^{2-}/BQA^{-}$ couple. This is still somewhat lower than the minimum Fe^{2+} ion requirement of 2×10^{-8} $mol.dm^{-3}$ suggested by Lindsay [Lin82a], but nevertheless, the model is now more realistic with respect to redox equilibria than in the absence of the caffeic acid couple.

The calculated (pe + pH) value for the model including the caffeic acid/BQA couple is 12.58 which is slightly higher than the value of 12 suggested by Lindsay, greater than which an adequate supply of Fe^{2+} ions will not be met for plant nutrition [Lin82a].

The results in table 5.7 indicate that the solubility of iron under the new redox conditions is controlled by ferrosic hydroxide, $Fe_3(OH)_8(s)$. This is in accordance with Lindsay [Lin82a], who has reported that iron solubility would be controlled by ferrosic hydroxide in moderately oxidised soils and by the amorphous $Fe(OH)_3(s)$ species in highly oxidised soils which is what we observed in the computations performed in the absence of the caffeic acid couple.

Caffeic acid is present primarily as the diprotonated species $HCaff^-$ at equilibrium, ($Caff^{2-}$ has been defined as the monoprotonated species; see chapter 5.3.2.5). Caffeic acid not only releases electrons into the soil solution upon oxidation, but also complexes with Fe^{2+} ions as well as all the other metal ions in the soil solution model. Its function is therefore two-fold, that of an electron releasing agent and a chelating agent.

Calcium hydroxy apatite is a commonly occuring mineral controlling calcium(II) ion and phosphate solubily in most soils and Lindsay has reported that gibbsite $Al(OH)_3(s)$ is the sparingly soluble aluminium species that usually controls Al^{3+} ion activity in solution. The precipitated amounts of either of the above species remained unchanged both in the absence and presence of the $Caff^{2-}/BQA^-$ couple thereby implying that the total soluble concentrations of Ca^{2+}, PO_4^{3-} and Al^{3+} ions remained unchanged despite the change in redox equilibrium and the introduction of a complexing compound such as caffeic acid. A contributing factor to this is the fact that equilibrium constants for caffeic acid and Ca^{2+} and Al^{3+} ions are not available.

Table 5.7

Equilibrium concentrations of selected species in the presence of the $Caff^{2-}$/BQA^- couple.

Species	Concentration ($mol.dm^{-3}$)	% [Component]^T
Fe^{3+}	8.90×10^{-17}	negl.
Fe^{2+}	3.47×10^{-10}	negl.
$Caff^{2-}$	4.33×10^{-7}	0.004
$HCaff^-$	9.49×10^{-5}	98.5
FeCaff	5.46×10^{-12}	negl.
BQA^-	3.69×10^{-6}	100
$Fe(OH)_3$	3.80×10^{-7}	2.4
electrons	8.32×10^{-7}	100
$Fe_3(OH)_8$ (s)	6.54×10^{-6}	100(Fe^{2+})
		97.1(Fe^{3+})
$Ca_5(PO_4)_3OH$ (s)	3.23×10^{-4}	64.5(Ca^{2+})
$Al(OH)_3$ (s)	1.13×10^{-6}	75.0(Al^{3+})

5.4.4 USE OF SPECIFIED CAFFEIC ACID AND ELECTRON CONCENTRATIONS TO MODEL THE EFFECTS OF THE $CAFF^{2-}/BQA^-$ COUPLE.

It had been hoped that the model of table 5.4 in the presence of the $Caff^{2-}/BQA^-$ couple, as described in section 5.4.3, could be used to investigate the effects of Lig1 and Lig4 on metal ion speciation in a soil solution. For unexplained reasons, however, convergence of the program MINEQL, was reached at certain concentrations of Lig1 and Lig4 and not at others. A poor estimation of initial equilibrium component concentrations could lead to non-convergence of the program [Wes76]. Numerous attempts were made at changing the estimated equilibrium concentrations of the various components, without success. This proved to be problematic as the effects of plant growth regulators on soil solution speciation was to be examined over a range of Lig1 and Lig4 concentrations.

A specified caffeic acid and electron concentration effectively models the behaviour of the $Caff^{2-}/BQA^-$ couple. By trial and error it was discovered that convergence of the program was achieved over a wide range of Lig1 and Lig4 concentrations when the $Caff^{2-}/BQA^-$ couple was substituted by specified caffeic acid and electron concentrations. It was then decided to use this indirect approach in the model of soil solutions. The $Caff^{2-}/BQA^-$ couple expressed in terms of equation 5.29 in the thermodynamic database was omitted in all subsequent computations.

This approach neccesitated the omission of BQA^- from the list of components in the model. This never introduced any major change to the model as equilibrium constants for BQA^- with various metal ions have not been established and were expected to be weak in any case.

The list of components constituting the soil solution model using specified caffeic acid and electron concentrations is presented in table 5.4. An input concentration of 9.5×10^{-5} mol.dm^{-3} for caffeic acid and 1.0×10^{-5} mol.dm^{-3} for e^- has been found to produce similar equilibrium concentrations for $Caff^{2-}$ and e^- as in the presence of the caffeic acid redox couple when the caffeate ion had an initial value of 1.0×10^{-4} mol.dm^{-3} and e^- had an initial concentration of 0.0 mol.dm^{-3}. Selected results of this model are presented in table 5.8 with the entire output presented in **appendix E** (page 477) and can be compared with the results determined in the presence of the caffeic acid redox couple previously presented in table 5.7, a subset of **appendix D** (page 445).

The component list together with the input concentrations presented in table 5.4 was taken as the soil solution model to which various concentrations of Lig1 and Lig4 would be added to examine their effects on soil solution speciation. In its output, MINEQL computes the equilibrium concentrations of every component specified in the input list as well as that of every complex specified in the thermodynamic database. It also highlights all components and species consisting of more than 1% of the total concentration of any component. An example of the latter obtained from the present model using specified caffeic acid and electron concentrations (**appendix E**) is presented in table 5.9. The concentrations of components representing fulvic acids have been combined and have been recorded as FA.

With the exception of Cu^{2+} ions, most of the divalent metals are present predominantly as aqua ions in solution, ie. Mg^{2+}(85.9%), Mn^{2+}(83.3%), Zn^{2+}(58.1%), Cd^{2+}(67.3%), Ni^{2+}(75.1%) and Co^{2+}(78.9%). The free Ca^{2+} ion concentration has been determined as 29.4% of the total concentration of which 35.5% is in solution. Thus 82.8% of dissolved calcium is therefore also present as

the free Ca^{2+} ion. The speciation results also indicate that the sulphate ion, SO_4^{2-}, is the most highly complexed inorganic component to metal ions of the soil solution model, ie. $CaSO_4$(5.3% of soluble Ca^{2+}), $MgSO_4$(12.8%), $MnSO_4$(13.3%), $ZnSO_4$(12.3%), $CdSO_4$(17.1%), $NiSO_4$(14.5%) and $CoSO_4$(15.2%).

In contrast to the other divalent metal ions in the model, the strongly complexing properties of the Cu^{2+} ion is clearly evident as 80.5% of the total copper ion concentration is bound to the fulvic acid components, CuFA, and a further 10.3% is bound to caffeic acid, CuCaff. Significant concentrations of Zn^{2+}(25.4%), Ni^{2+}(7.1%) and Co^{2+}(2.5%) ions are also bound to the components constituting fulvic acids in the model.

The components K^+(98.7%), Na^+(99.1%), SO_4^{2-}(88.5%), NO_3^-(99.5%) and Cl^-(97.5%) are essentially present as free ions at equilibrium. This is to be expected with regard to the major anions in soil [Boh85] but K^+ and Na^+ ions are usually found in smaller concentrations in the soil solution. This is because of strong adsorption to soil minerals, a feature omitted in the construction of the model. The results of the present soil solution model show that the predominant phosphate, PO_4^{3-}, and carbonate, CO_3^{2-}, species at equilibrium are $H_2PO_4^-$ and HCO_3^- which is supported by the literature [Boh85]. Boric acid, H_3BO_3, and silicic acid, H_4SiO_4 have been reported as the major soil solution species of borate, $B(OH)_4^-$ and silicate, SiO_4^{4-} ions in soil solution. These have been found as the major species at equilibrium in this study. The species Mn^{3+} and Cu^+ are present in very small concentrations when compared with their respective divalent species and consequently make a negligible contribution to soil redox.

The trends observed in the equilibrium speciation of the present soil solution model are reasonable and compare well with the major forms of soil components as reported in the literature [Lin79a], [Bar84] [Spo84] and [Boh85].

Table 5.8

Equilibrium concentrations of selected species in the presence of specified caffeic acid and electron concentrations.
($Caff^{2-}$/BQA^{-} couple omitted)

Species	**Concentration (mol/dm^3)**	**% [Component]^T**
Fe^{3+}	5.56×10^{-17}	negl.
Fe^{2+}	8.89×10^{-10}	negl.
$Caff^{2-}$	4.28×10^{-7}	0.004
$HCaff^{-}$	9.36×10^{-5}	98.5
FeCaff	1.38×10^{-11}	negl.
$Fe(OH)_3$	3.80×10^{-7}	1.8
electrons	3.41×10^{-6}	100
$Fe_3(OH)_8$ (s)	6.59×10^{-6}	100(Fe^{2+})
		97.1(Fe^{3+})
$Ca_5(PO_4)_3OH$ (s)	3.23×10^{-4}	64.5(Ca^{2+})
$Al(OH)_3$ (s)	1.13×10^{-6}	75.0(Al^{3+})

TABLE 5.9

Equilibrium concentrations of the major species of the soil solution model in the absence of ligand1 and ligand4

(pH = 6.5 ; I = 0.02)

Component	Species	% Component bound in species	Species concentration (moles.dm^{-3})	Total component conc. at equi.
Ca^{2+}	Ca^{2+}	29.4	7.35 X 10^{-4}	2.50 X 10^{-3}
	$CaSO_4$	5.3	1.32 X 10^{-4}	
	$Ca_5(PO_4)_3OH$ (s)	64.5	3.23 X 10^{-4}	
Mg^{2+}	Mg^{2+}	85.9	8.59 X 10^{-4}	1.00 X 10^{-3}
	$MgSO_4$	12.8	1.28 X 10^{-4}	
K^+	K^+	98.7	4.93 X 10^{-3}	5.00 X 10^{-3}
Na^+	Na^+	99.1	1.98 X 10^{-3}	2.00 X 10^{-3}
Fe^{3+}	$Fe(OH)_3$	1.8	2.37 X 10^{-7}	1.34 X 10^{-5}
	$Fe_3(OH)_8$(s)	98.2	6.59 X 10^{-6}	
Fe^{2+}	$Fe_3(OH)_8$(s)	100.0	6.59 X 10^{-6}	6.59 X 10^{-6}
Mn^{2+}	Mn^{2+}	83.3	8.33 X 10^{-6}	1.00 X 10^{-6}
	$MnSO_4$	13.3	1.33 X 10^{-6}	
Cu^{2+}	Cu^{2+}	2.3	2.28 X 10^{-8}	1.00 X 10^{-6}
	$CuB(OH)_4$	4.2	4.22 X 10^{-8}	
	CuFA	80.5	8.05 X 10^{-7}	
	CuCaff	10.3	1.03 x 10^{-7}	

TABLE 5.9 continued

Component	Species	% Component bound in species	Species concentration (moles.dm^{-3})	Total component conc. at equi.
Zn^{2+}	Zn^{2+}	58.1	2.91 X 10^{-6}	5.00 X 10^{-6}
	$ZnSO_4$	12.3	6.13 X 10^{-7}	
	ZnFA	25.4	1.27 X 10^{-6}	
Cd^{2+}	Cd^{2+}	67.3	6.73 X 10^{-7}	1.00 X 10^{-6}
	$CdSO_4$	17.1	1.71 X 10^{-7}	
	$CdCl^+$	7.2	7.22 X 10^{-8}	
	$CdHPO_4$	4.7	4.69 X 10^{-8}	
Ni^{2+}	Ni^{2+}	75.1	7.51 X 10^{-7}	1.00 X 10^{-6}
	$NiSO_4$	14.5	1.45 X 10^{-7}	
	NiFA	7.1	7.06 X 10^{-8}	
Co^{2+}	Co^{2+}	78.9	7.89 X 10^{-7}	1.00 X 10^{-6}
	$CoSO_4$	15.2	1.52 X 10^{-7}	
	$CoHPO_4$	1.0	1.05 X 10^{-8}	
	CoFA	2.5	2.49 X 10^{-8}	
Al^{3+}	$Al(OH)_2^+$	2.7	3.98 X 10^{-7}	1.50 X 10^{-6}
	$Al(OH)_3$	21.1	3.16 X 10^{-7}	
	$Al(OH)_3(s)$	75.0	1.13 X 10^{-6}	
$B(OH)_4^-$	$HB(OH)_4$	99.7	4.98 X 10^{-5}	5.00 X 10^{-5}
MoO_4^{2-}	MoO_4^{2-}	99.8	0.29 X 10^{-7}	0.30 X 10^{-7}
SiO_4^{4-}	H_4SiO_4	100.0	3.50 X 10^{-3}	3.50 X 10^{-3}
PO_4^{3-}	$H_2PO_4^-$	2.2	2.15 X 10^{-5}	1.00 X 10^{-3}
	$Ca_5(PO_4)_3OH(s)$	96.8	3.23 X 10^{-4}	

TABLE 5.10 continued

Component	Species	% Component bound in species	Species concentration (moles.dm^{-3})	Total component conc. at equi.
SO_4^{2-}	SO_4^{2-}	88.5	2.65 X 10^{-3}	3.00 X 10^{-3}
	$CaSO_4$	4.4	1.32 X 10^{-4}	
	$MgSO_4$	4.3	1.28 X 10^{-4}	
	KSO_4^-	1.6	4.76 X 10^{-5}	
CO_3^{2-}	HCO_3^-	64.0	1.99 X 10^{-5}	3.11 X 10^{-5}
	H_2CO_3	34.4	1.07 X 10^{-5}	
	$MgHCO_3^+$	1.1	3.50 X 10^{-7}	
NO_3^-	NO_3^-	99.5	5.97 X 10^{-3}	6.00 X 10^{-3}
NH_3	NH_4^+	93.6	9.36 X 10^{-4}	1.00 X 10^{-3}
	NH_4Cl	4.4	4.38 X 10^{-5}	
	$NH_4SO_4^-$	1.8	1.84 X 10^{-5}	
Cl^-	Cl^-	97.5	1.95 X 10^{-3}	2.00 X 10^{-3}
	NH_4Cl	2.2	4.38 x 10^{-5}	
$Caff^{2-}$	$HCaff^-$	98.5	9.36 X 10^{-5}	9.50 X 10^{-5}
	H_2Caff	1.0	8.74 X 10^{-7}	
FA	FA	97.5	5.84 X 10^{-5}	5.99 X 10^{-5}
	CaFA	0.7	4.28 X 10^{-6}	
	MgFA	0.6	3.85 X 10^{-6}	
	CuFA	0.13	8.05 X 10^{-7}	
	ZnFA	0.21	1.27 X 10^{-6}	
e^-	e^-	100.0	3.41 X 10^{-6}	3.41 X 10^{-6}

5.4.5. THE COMPUTER SIMULATED EFFECTS OF N - (PHOSPHONOMETHYL) GLYCINE (Ligand 1) AND N - (PHOSPHONOMETHYL) IMINODIACETIC ACID (Ligand 4) ON METAL ION SPECIATION IN A SOIL SOLUTION.

In the preceeding sections, 5.4.1., 5.4.2., 5.4.3. and 5.4.4., the species distributions of the soil solution model were presented. In this section, Ligand 1 or Ligand 4 is introduced to the model as a component in order to establish whether it has any effect on the speciation of important metal ions found in soil solutions. Initially, the intention was to examine the effects of Ligands 2 and 3 on soil solution speciation as well, however, time never allowed for the determination of the necessary thermodynamic data.

Table 5.10 represents the final soil solution model used in this study. In every MINEQL computation, either Ligand 1 or Ligand 4 was fixed at a concentration between 1×10^{-7} mol.dm^{-3} and 1.4×10^{-3} mol.dm^{-3}. Initially the computations were performed over a wide range of Ligand 1 and Ligand 4 concentrations to establish the minimum requirement, if within the chosen limits, to effect a change in metal ion speciation for the various metals under investigation. Once this minimum had been established for a given metal ion, the computations were performed using smaller increments of Ligand 1 and Ligand 4 in order to present their effects graphically.

The computer simulated effects of Ligand 1 and Ligand 4 on the soil solution speciation of magnesium(II), calcium(II), iron(II)/iron(III), zinc(II), copper(II), manganese(II), cadmium(II), cobalt(II), nickel(II) and aluminium(III) ions are presented graphically in figures 5.4 to 5.25.

TABLE 5.10

List of components with chemical symbols / abbreviations and input concentrations as used in the **FINAL SOIL SOLUTION MODEL.**

Components	Concentration (mol.dm^{-3})	Components	Concentration (mol.dm^{-3})
Ca^{2+}	2.50 X 10^{-3}	SiO_4^{4-}	3.50 X 10^{-3}
Mg^{2+}	1.00 X 10^{-3}	$B(OH)_4^-$	5.00 X 10^{-5}
K^+	5.00 X 10^{-3}	MoO_4^{2-}	0.30 X 10^{-7}
Na^+	2.00 X 10^{-3}	NO_3^-	6.00 X 10^{-3}
Fe^{3+}	2.00 X 10^{-5}	DHBZ	1.90 X 10^{-5}
Fe^{2+}	0.00	SAL	3.10 X 10^{-5}
Zn^{2+}	5.00 X 10^{-6}	HMPA	4.90 X 10^{-5}
Cu^{2+}	1.00 X 10^{-6}	ACPH	1.70 X 10^{-5}
Cu^+	0.00	HBA	7.00 X 10^{-5}
Mn^{2+}	1.00 X 10^{-5}	DEMA	4.20 X 10^{-5}
Mn^{3+}	0.00	ACAC	1.30 X 10^{-5}
Cd^{2+}	1.00 X 10^{-6}	PHTH	8.00 X 10^{-6}
Co^{2+}	1.00 X 10^{-6}	MALI	2.40 X 10^{-5}
Co^{3+}	0.00	SUCA	3.20 X 10^{-5}
Ni^{2+}	1.00 X 10^{-6}	DMBA	2.60 X 10^{-5}
Al^{3+}	1.50 X 10^{-6}	BZA	7.30 X 10^{-5}
H^+	0.00	PHEN	1.20 X 10^{-4}
e^-	1.00 X 10^{-5}	PROP	9.20 X 10^{-5}
CO_3^{2-}	0.00	HBQN	2.70 X 10^{-5}
SO_4^{2-}	3.00 X 10^{-3}	$Caff^{2-}$	9.50 X 10^{-5}
Cl^-	2.00 X 10^{-3}	BQA^-	omitted
NH_3	1.00 X 10^{-3}	Lig1	various
PO_4^{3-}	1.00 X 10^{-3}	Lig4	various

Each of the species graphically represented in the figures has been determined from 13 to 15 individual computations at various concentrations of Ligand 1 or Ligand 4 within the specified range. In total approximately 100 MINEQL computations were performed in order to produce figures 5.4 to 5.25. A sample of the MINEQL output showing the effect of a Ligand 4 concentration of 1 X 10^{-4} mol.dm^{-3} on soil solution speciation has been presented in **appendix F** (page 507). The species represented in the figures are expressed as a percentage, a concentration (mol.dm^{-3}) or a log concentration of the respective metal ion, whichever it was felt would best illustrate the effect of Ligand 1 and Ligand 4 on metal ion speciation. Inorganic complexes in the figures are indicated by their accepted chemical formulae together with the overall charge of the complex. Complexes between metal ions and fulvic acid, caffeic acid, Ligand 1 and Ligand 4 are indicated as the total percentage/concentration of metal ion bound to the organic species irrespective of its overall charge(s). eg. CuFA, CuCaff and CuLig4. Species represented in the figures are predominantly those in which more than 1% of the total metal ion concentration is bound. However, in the discussion of each of the figures, references are frequently made to complexes not represented in the figures. In such cases the relevant percentages or concentrations will be reported.

Prior to the discussion of the effects of Ligand 1 and Ligand 4 on the speciation of selected metal ions, the total concentrations of the metal ion and the Ligand 1 / Ligand 4 range is reported.

Solubility products for a number of potential solids have been included in the thermodynamic database of this study. In the discussion of the effects of Lig1 and Lig4 on metal ion speciation, selected solid species are refered to in order to compare the results of this study with others reported in the literature.

5.4.5.1. The effect of Ligand 1 and Ligand 4 on magnesium(II) speciation.

Total concentrations

$[Mg^{2+}] = 1.0 X 10^{-3}$ mol.dm^{-3}

[Lig1] and [Lig4] = 0 to $10 X 10^{-4}$ mol.dm^{-3}

Magnesium(II) speciation is only slightly affected in the Lig1 and Lig4 concentration range from 0 to 10 X 10^{-4} mol.dm^{-3} as depicted in figures 5.4 and 5.5.

In figure 5.4, where the species are represented as a log concentration, the major species at a Lig1 concentration of 1 X 10^{-4} mol.dm^{-3} are Mg^{2+}(85%) and $MgSO_4$(13%). Minor species at this concentration of Lig1 are MgFA(0.3%), $MgHPO_4$(0.17%) and $MgHCO_3^+$(0.03%). $MgCO_3$ and $Mg(OH)^+$ concentrations are of the order 10^{-8} mol.dm^{-3}.

An increase in Lig1 concentration to 1 X 10^{-3} mol.dm^{-3} reduces the Mg^{2+} ion concentration to 75% and that of $MgSO_4$ to 11.2%. At this concentration of Lig1, MgLig1 has a concentration of 1.26 X 10^{-4} mol.dm^{-3} (12.6% of Mg^{2+}). The concentrations of minor species are virtually unaffected by the presence of Lig1.

In figure 5.5, the major species at a Lig4 concentration of 1 X 10^{-4} mol.dm^{-3} are Mg^{2+}(85%) and $MgSO_4$(13%). A ten-fold increase in Lig4 concentration reduces Mg^{2+} to 68% and $MgSO_4$ to 10.6% and results in a MgLig4 concentration of 20%.

The simulated effects of Lig1 and Lig4 on magnesium(II) speciation in soil solutions suggests that high concentrations of the above-mentioned plant growth regulators moderately affect the free Mg^{2+} ion concentration at equilibrium. In most soils, Mg^{2+} ions have a high soil solution concentration and also forms part of the group

Figure 5.4 The effect of Ligand 1 on magnesium(II) speciation

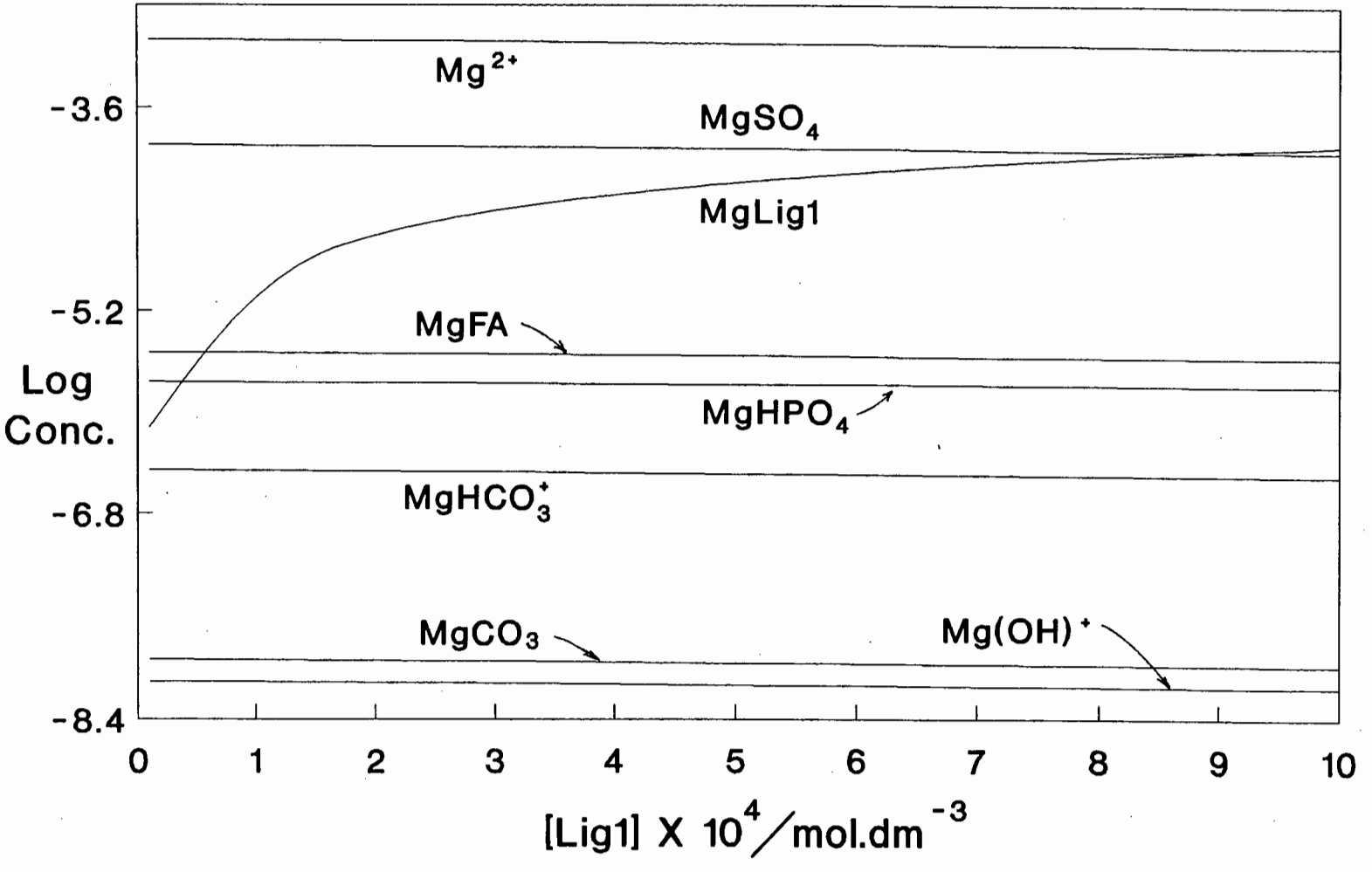
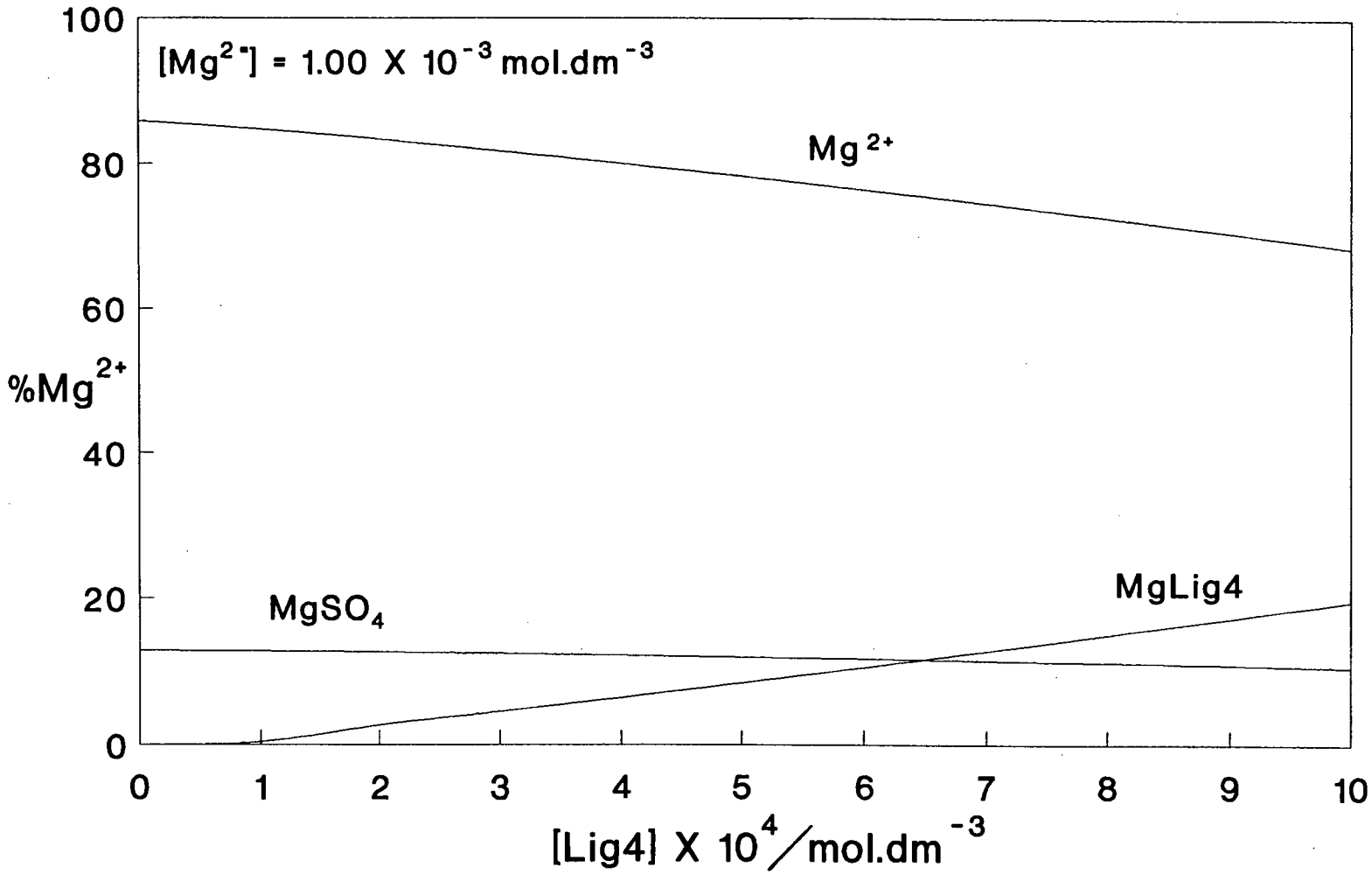


Figure 5.5 The effect of Ligand 4 on magnesium(II) speciation



of exchangable cations in soil [Boh85], and any reduction in Mg^{2+} ion concentration is likely to be easily restored by the process of desorption from solid surfaces.

Solubility products for potential solids such as $CaCO_3$-$MgCO_3$ (s), dolomite, $Mg(OH)_2$ (s), brucite and $MgCO_3$ (s) magnesite have been included in the thermodynamic database. From the magnesium(II) speciation results obtained in this study, all of the species are in solution. From thermodynamic predictions, Lindsay has reported that magnesium minerals are too soluble to persist in soils below a pH of 7.5 [Lin79a].

5.4.5.2. The effect of Ligand 1 and Ligand 4 on calcium(II) speciation.

Total concentrations

$[Ca^{2+}] = 2.5 X 10^{-3}$ mol.dm^{-3}

[Lig1] and [Lig4] = 0 to $10 X 10^{-4}$ mol.dm^{-3}.

The effect of Lig1 and Lig4, in the concentration range 0.0 to 1 X 10^{-3} mol.dm^{-3}, on calcium(II) speciation is presented in figures 5.6 and 5.7 respectively. In both figures, the calcium hydroxyapatite species, $Ca_5(PO_4)_3OH$(s) dominates the speciation of calcium(II) ions. In the present context, the concentration of a solid species is defined as the difference between the total Ca^{2+} concentration (2.5 X 10^{-3} mol.dm^{-3}) and the sum of the concentrations of all the dissolved Ca^{2+} species. In the absence of Lig1/Lig4, the species complexed to more than 1% of the total calcium(II) concentration are $Ca_5(PO_4)_3OH$(s) (64.5%), Ca^{2+} aqua ion (30% of the total calcium(II) concentration) and $CaSO_4$(5.3%).

At a Lig1 concentration of 1 X 10^{-4} mol.dm^{-3} the major species are $Ca_5(PO_4)_3OH$(s) (3.23 X 10^{-4} mol.dm^{-3}, 64.5%), Ca^{2+}(29%) and $CaSO_4$(5.3%).

CaLig1 has a concentration of 2.69 X 10^{-6} mol.dm^{-3} (0.1%) and the other minor species indicated in figure 5.6 are CaFA(0.3%), $CaCl^{+}$(0.1%), $CaHPO_4$(0.05%) and $CaCO_3$(2.0 X 10^{-9} mol.dm^{-3}). When the Lig1 concentration is increased to 1 X 10^{-3} mol.dm^{-3}, the speciation is as follows, $Ca_5(PO_4)_3OH$ (s) (64.5%), Ca^{2+}(28.3%), $CaSO_4$(5.1%) and CaLig1(1.2%).

At a Lig4 concentration of 1 X 10^{-4} mol.dm^{-3} the $Ca_5(PO_4)_3OH$(s) concentration is 3.23 X 10^{-4} mol.dm^{-3} (64.5%). The total dissolved calcium(II) ion concentration is thus 8.95 X 10^{-4} mol.dm^{-3}. From figure 5.7, the Ca^{2+} ion concentration is 27.5% which amounts to 77% of the total dissolved calcium(II) ion concentration. With reference to the dissolved calcium(II) ion concentration, the distribution of other species of is as follows; $CaSO_4$(14%) and CaLig4(7.1%). Increasing the Lig4 concentration to 1 X 10^{-3} mol.dm^{-3}, has a solubilising effect on $Ca_5(PO_4)_3OH$(s) which now has a concentration of 2.96 X 10^{-3} mol.dm^{-3} (59.2%) leaving a dissolved calcium(II) concentration of 1.02 X 10^{-3} mol.dm^{-3}. The speciation of the dissolved component is CaLig4(59.3%), Ca^{2+}(33.5%) and $CaSO_4$(6.2%).

The results depicted in figures 5.6 and 5.7 indicate that Lig4 has a greater effect on calcium(II) speciation than Lig1 in the specified concentration ranges. Lig4 complexes to Ca^{2+} ions to such an extent that the free ion is no longer the most concentrated soluble species. The nett result of the addition of Ligands 1 and 4 is the increased concentration of dissolved calcium(II) ions which could have a positive effect on plant growth in certain soils, since Ca^{2+} and HCO_3^{-} ions in the soil solution released by the wheathering of limestone, $CaCO_3$, are leached away [Boh85].

Under the conditions of the model, phosphate ion solubility is controlled by $Ca_5(PO_4)_3OH$(s), calcium hydroxyapetite, which at the same time controls Ca^{2+} ion

Figure 5.6 The effect of Ligand 1 on calcium(II) speciation

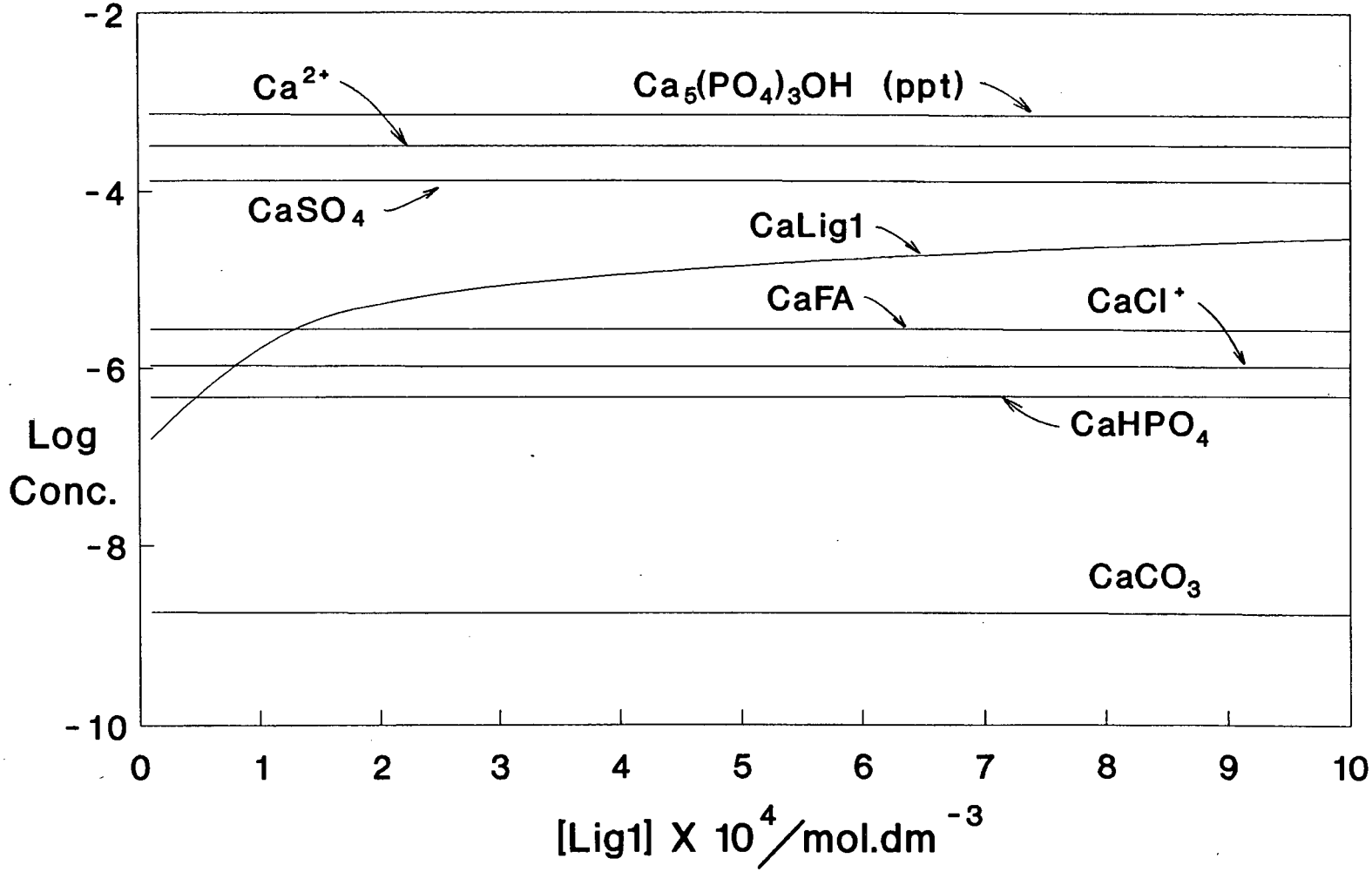
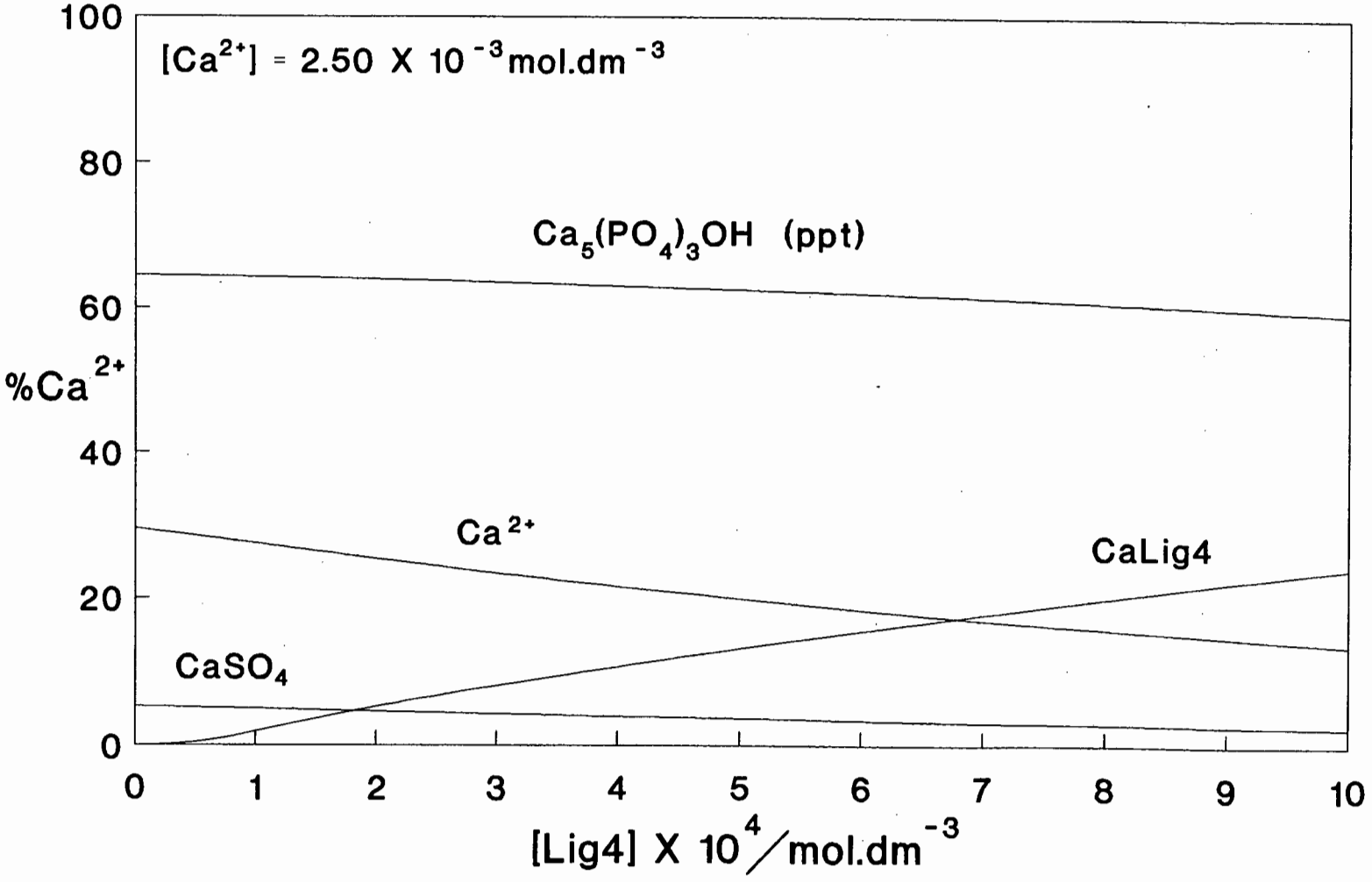


Figure 5.7 The effect of Ligand 4 on calcium(II) speciation



solubility. Solubility products for the calcium(II) minerals, $CaSO_4.2H_2O$ (gypsum), $CaCO_3$ (calcite / limestone), $CaCO_3$-$MgCO_3$ (dolomite), $Ca_4H(PO_4)_3.2.5H_2O$ (octacalcium phosphate), ß-Ca_2SiO_4 (larnite) and γ-Ca_2SiO_4 (Ca olivine) have been included in the thermodynamic database of this study but none of their solubility products are exeeded at equilibrium.

The adsorption of metal ions to insoluble organic and inorganic surfaces is a feature which has not been incorporated into the present soil solution model. Conclusions made on the availability of metal ions to plants, as a result of the simulated equilibrium concentrations, should thus be made bearing this feature in mind particularly with reference to the major exchangable ions Mg^{2+}, Ca^{2+} and Al^{3+}.

5.4.5.3. The effect of Ligand 1 and Ligand 4 on iron(II)/iron(III) speciation.

Total concentrations

$[Fe^{3+}] = 2.0 X 10^{-5} mol.dm^{-3}$

$[Fe^{2+}] = 0.0$

[Lig1] and [Lig4] = $1.0 X 10^{-7}$ to $1.0 X 10^{-3}$ $mol.dm^{-3}$.

The input concentrations of Fe^{2+} and Fe^{3+} are as indicated above and the respective equilibrium concentrations are determined by the inclusion of the iron redox couple, equation 5.28, which has been previously reported.

The effect of Lig1 on iron(II)/iron(III) speciation is presented in figure 5.8. The oxidation state of iron in all of the complexes has been specified in order to distinguish between iron(II) and iron(III) complexes, for example, $Fe^{3+}(OH)_3$ is the neutral iron(III) hydroxide complex. Fe^{2+}Caff is the total concentration of all iron(II) - caffeic acid complexes irrespective of the overall charge(s) and "$Fe^{2+}{}_T$ +

$Fe^{3+}{}_T$" is the total dissolved iron(II) + iron(III) concentration. The Y - axis label "log [Fe]" implies the logarithm to the base 10 of all iron complexes, whether iron(II) or iron(III).

Ligand 1 has a solubilising effect on the metastable species $Fe_3(OH)_8(s)$. The ferrosic hydroxide species concentration decreases from 6.59 X 10^{-6} to 5.25 X 10^{-6} mol.dm^{-3} as the Lig1 concentration is increased from 1 X 10^{-7} to 1 X 10^{-3} mol.dm^{-3}. Most of the iron solubilised in the process is bound to Lig1. The trends observed with Lig1 in figure 5.8 are very similar to those observed in figure 5.9 with Lig4. Concentrations (mol.dm^{-3}) for the various species indicated in figure 5.8 at Lig1 concentrations of 1 X 10^{-7} and 1 X 10^{-3} mol.dm^{-3} are Fe^{3+}(5.56 X 10^{-17}, 4.98 X 10^{-17}) (not in figure 5.8), Fe^{2+}(8.89 X 10^{-10}, 1.11 X 10^{-9}), $Fe_T{}^{2+}$(1.0 X 10^{-9}, 5.0 X 10^{-9}), $Fe_T{}^{2+}$ + $Fe_T{}^{3+}$(2.29 X 10^{-7}, 4.27 X 10^{-6}), Fe^{2+}Caff(1.38 X 10^{-11}, 1.73 X 10^{-11}), Fe^{3+}Lig1(4.4 X 10^{-11}, 4.1 X 10^{-6}) and Fe^{2+}Lig1(2.7 X 10^{-14}, 4.0 X 10^{-9}).

The effect of Lig4 on iron(II) and iron(III) speciation is graphically represented in figures 5.9 and 5.10 on a log concentration and concentration scale respectively for iron. The metastable species ferrosic hydroxide, $Fe_3(OH)_8(s)$, controls the solubility of iron in solution. At a Lig4 concentration of 1 X 10^{-7} mol.dm^{-3}, the concentration of $Fe_3(OH)_8(s)$ is 6.59 X 10^{-6} mol.dm^{-3} resulting in a total dissolved iron concentration ($Fe_T{}^{2+}$ + $Fe_T{}^{3+}$) of 2.3 X 10^{-7} mol.dm^{-3}. The total dissolved iron(II) concentration, $Fe_T{}^{2+}$, is 1 X 10^{-9} mol.dm^{-3} of which the free Fe^{2+} ion is the most concentrated component with a concentration of 8.9 X 10^{-10} mol.dm^{-3}.

An increase in the Lig4 concentration has a solubilising effect on $Fe_3(OH)_8$ (s). This results in an increase in the total dissolved iron concentration ($Fe_T{}^{2+}$ + $Fe_T{}^{3+}$) which can be seen clearly in figure 5.10. The Fe^{2+}Lig4 and Fe^{3+}Lig4 concentrations

Figure 5.8 The effect of Ligand 1 on iron(II) / iron(III) speciation

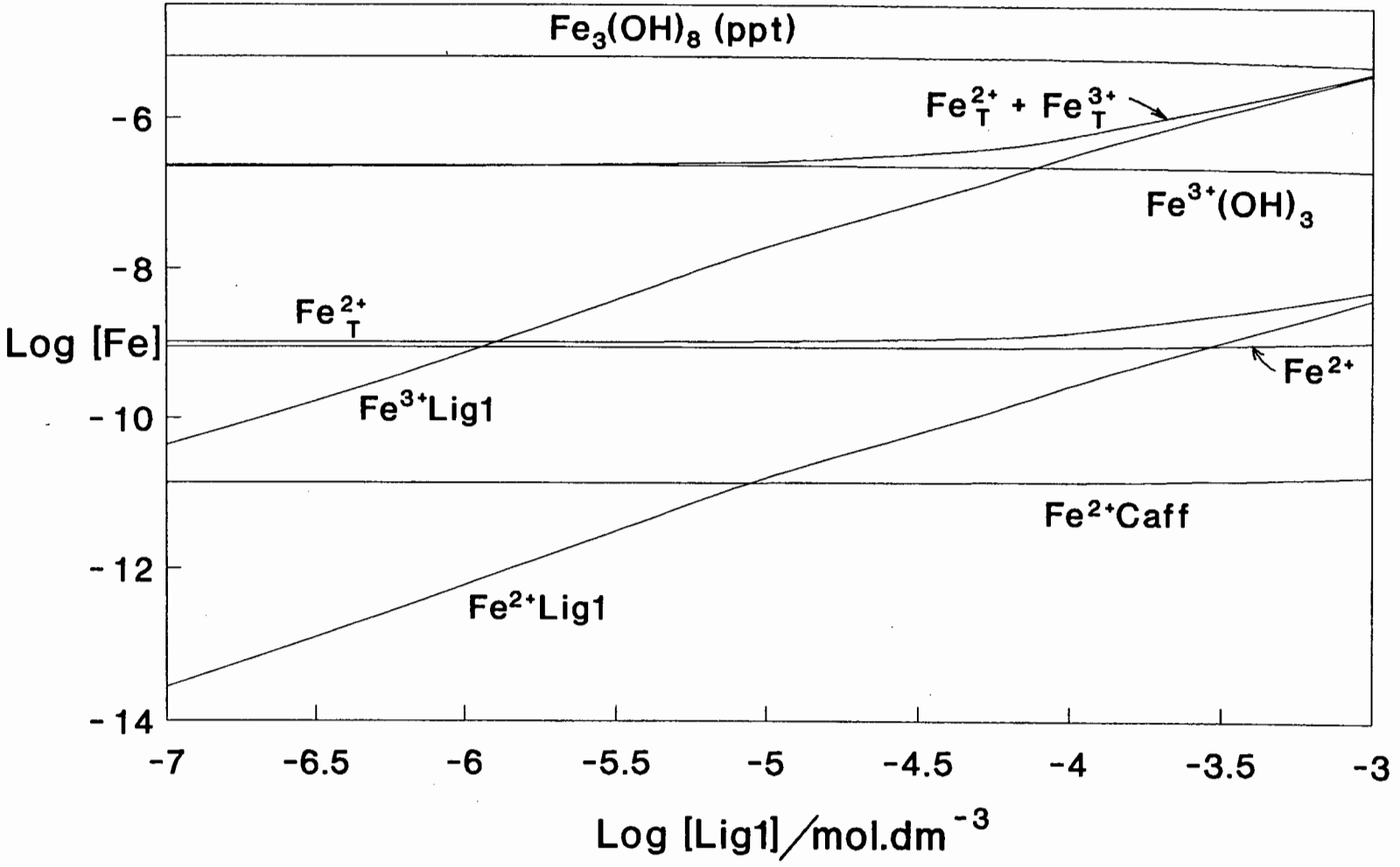


Figure 5.9 The effect of Ligand 4 on iron(II) / iron(III) speciation

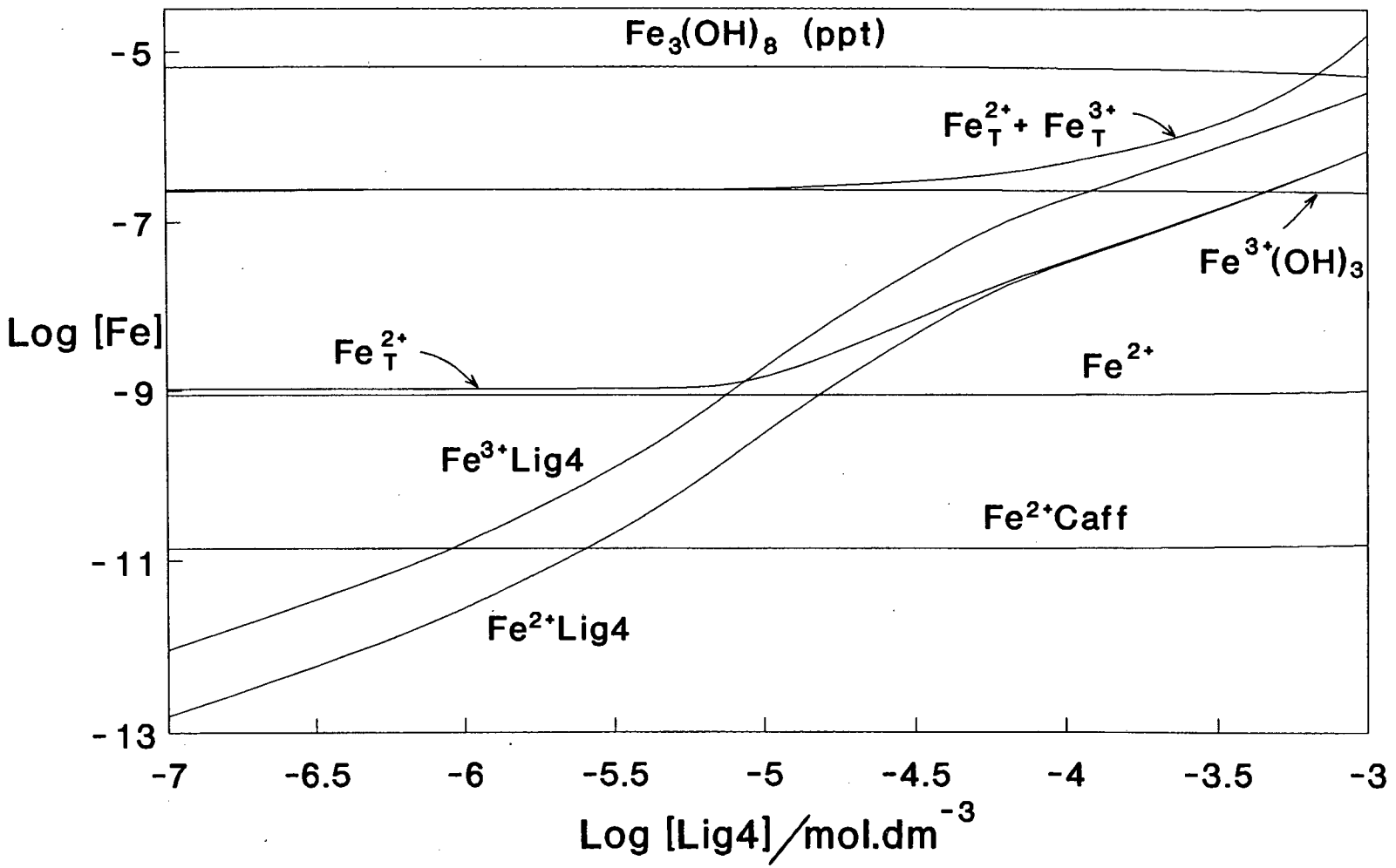
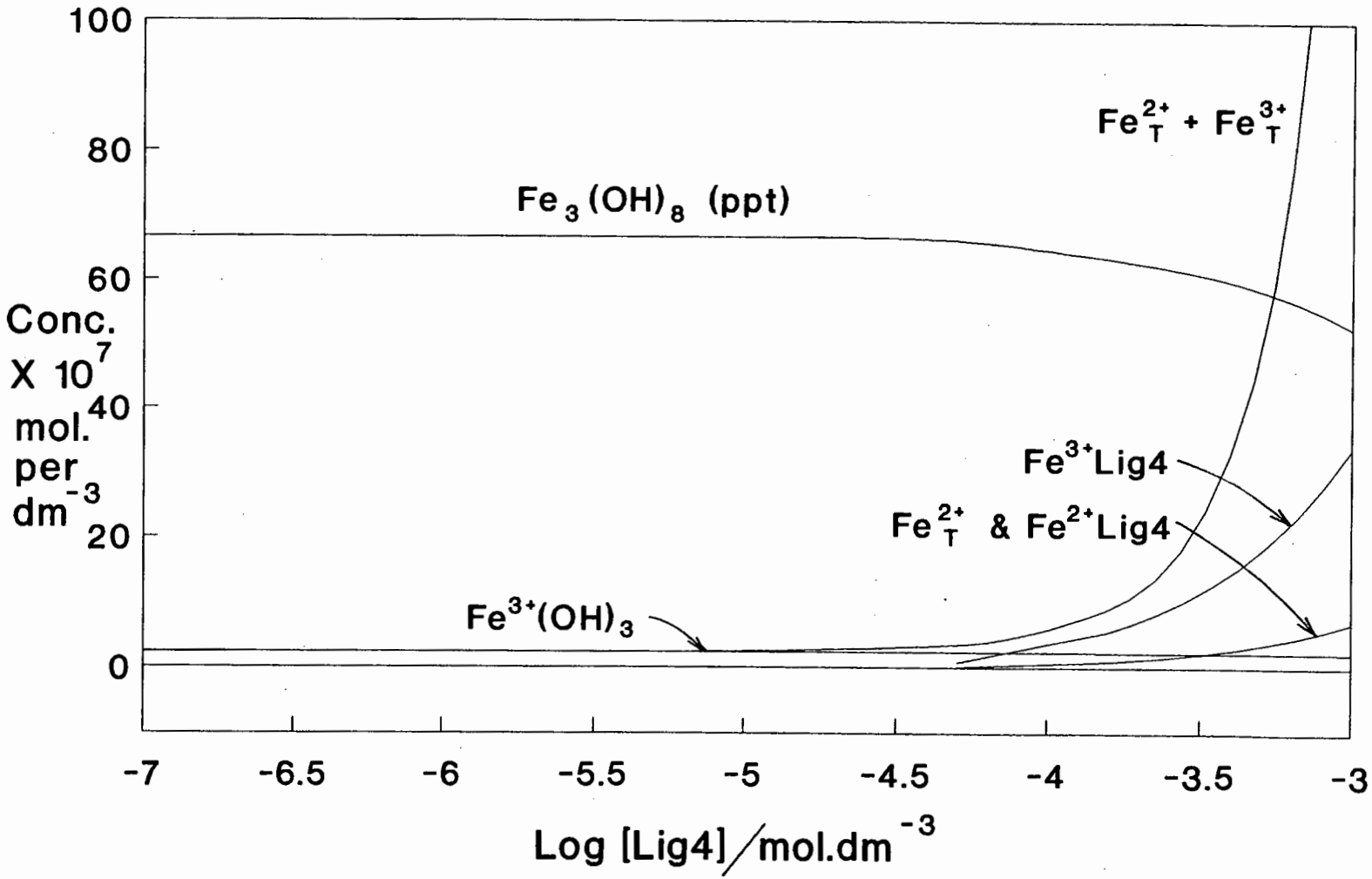


Figure 5.10 The effect of Ligand 4 on iron(II) / iron(III) speciation



increase with increasing Lig4 concentration and at a Lig4 concentration of 1 X 10^{-3} mol.dm^{-3} their respective concentrations are 6.92 X 10^{-7} and 3.39 X 10^{-6} mol.dm^{-3}.

The concentrations of the dissolved iron(III) hydroxide species, $Fe(OH)_3$, and the Fe^{2+}Caff species remain approximately constant at the various Lig4 concentrations. The Fe^{3+} ion concentration (not indicated in figures 5.9 and 5.10) also remains constant at 5.56 X 10^{-17} mol.dm^{-3}.

Iron is present in abundance in most soils yet the problem of iron deficiency in plants is a common occurance. This is a result of the low solubility of iron in soils and the low concentrations of the bioavailable Fe^{2+} species. The ability of root exudates to reduce Fe^{3+} ions to Fe^{2+} ions is regarded by many authors (as reported in chapter 1.3) as fundamental for the supply of adequate Fe^{2+} ions for plant nutrition. The simulated results of the present study also suggest that Lig1 and Lig4, like most chelating compounds, are capable of increasing the total soluble concentrations of both Fe^{2+} and Fe^{3+} ions in the soil solution.

5.4.5.4. The effect of Ligand 1 and Ligand 4 on zinc(II) speciation.

Total concentrations

$[Zn^{2+}]$ = 5.0 X 10^{-6} mol.dm^{-3}

[Lig1] = 1.0 X 10^{-5} to 1.4 X 10^{-4} mol.dm^{-3}

[Lig4] = 1.0 X 10^{-6} to 1.4 x 10^{-5} mol.dm^{-3}

The effect of Lig1 on zinc(II) speciation is illustrated in figures 5.11 and 5.12. In the absence of Lig1 and Lig4, the major zinc(II) species are Zn^{2+}(58%), ZnFA(25.4%) and $ZnSO_4$(12.3%).

Lig1 has a profound effect on zinc(II) speciation in the concentration range 1 X 10^{-5} to 1.4 X 10^{-4} mol.dm^{-3}. At a Lig1 concentration of 1.4 X 10^{-4} mol.dm^{-3}, the ZnLig1 concentration is 4.7 X 10^{-6} mol.dm^{-3} (93.9%) as indicated in figure 5.11. The trends followed by some of the minor species are indicated in figure 5.12 and their concentrations (mol.dm^{-3}) at a Lig1 concentration of 1 X 10^{-5} mol.dm^{-3} are $Zn(OH)_2$(1.11 X 10^{-8}), ZnCaff(4.94 x 10^{-9}), $ZnHPO_4$(7.05 X 10^{-9}) and $ZnCl_2$(3.20 X 10^{-11}).

The effect of Lig4 on zinc(II) speciation is shown in figure 5.12. Lig4 exhibits similar trends to Lig1 on zinc(II) speciation in the concentration range 1.0 X 10^{-6} to 1.4 X 10^{-5} mol.dm^{-3}, which is one tenth of the Lig1 concentration used for the same effect.

At a Lig4 concentration of 1.4 X 10^{-5} mol.dm^{-3}, the ZnLig4 concentration is 4.88 X 10^{-6} mol.dm^{-3} (97.5%). The percentage of free Zn^{2+} ions has dropped from 58% to 1.4% and this could have an effect on the avaiability of Zn^{2+} to plants.

The speciation results observed for zinc(II) ions is in accordance with the literature which reports that at pH values below 7.7, the predominant species is the Zn^{2+} ion with the $ZnSO_4$ species also significant [Lin79a]. Zinc complexes with organic matter to form dissolved and solid complexes which together with dissolved Zn^{2+} ions and exchangable zinc may eventually become available for absorption. [Bar84].

Thermodynamic data for $ZnCO_3$ (smithsonite), amorphous $Zn(OH)_2$, Zn_2SiO_4 (willemite) and $Zn_3(PO_4)_2.4H_2O$ (hopeite) has been incorporated into the database but none of their solubility products were exceeded at equilibrium.

Figure 5.11 The effect of Ligand 1 on zinc(II) speciation

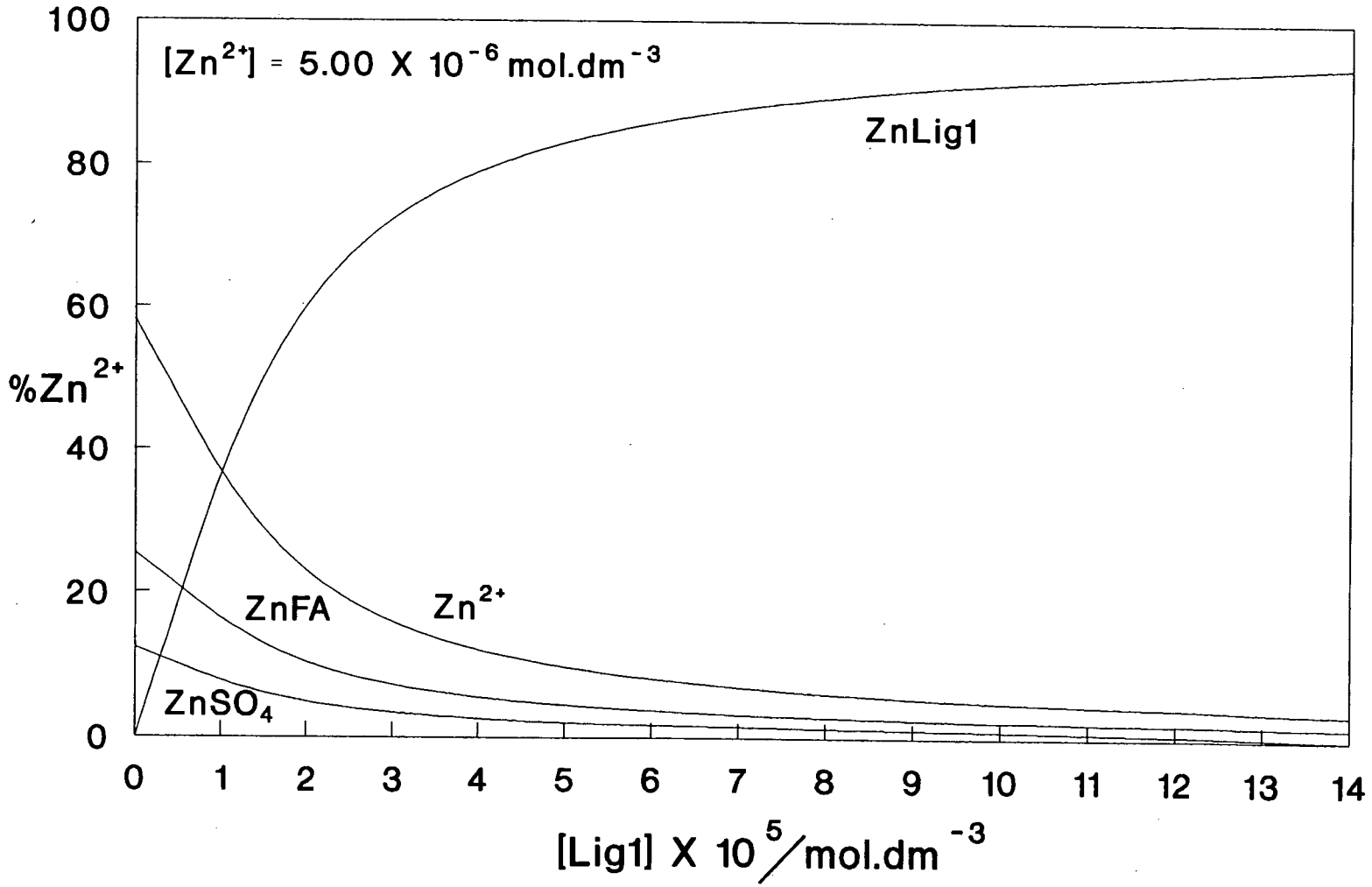


Figure 5.12 The effect of Ligand 1 on zinc(II) speciation

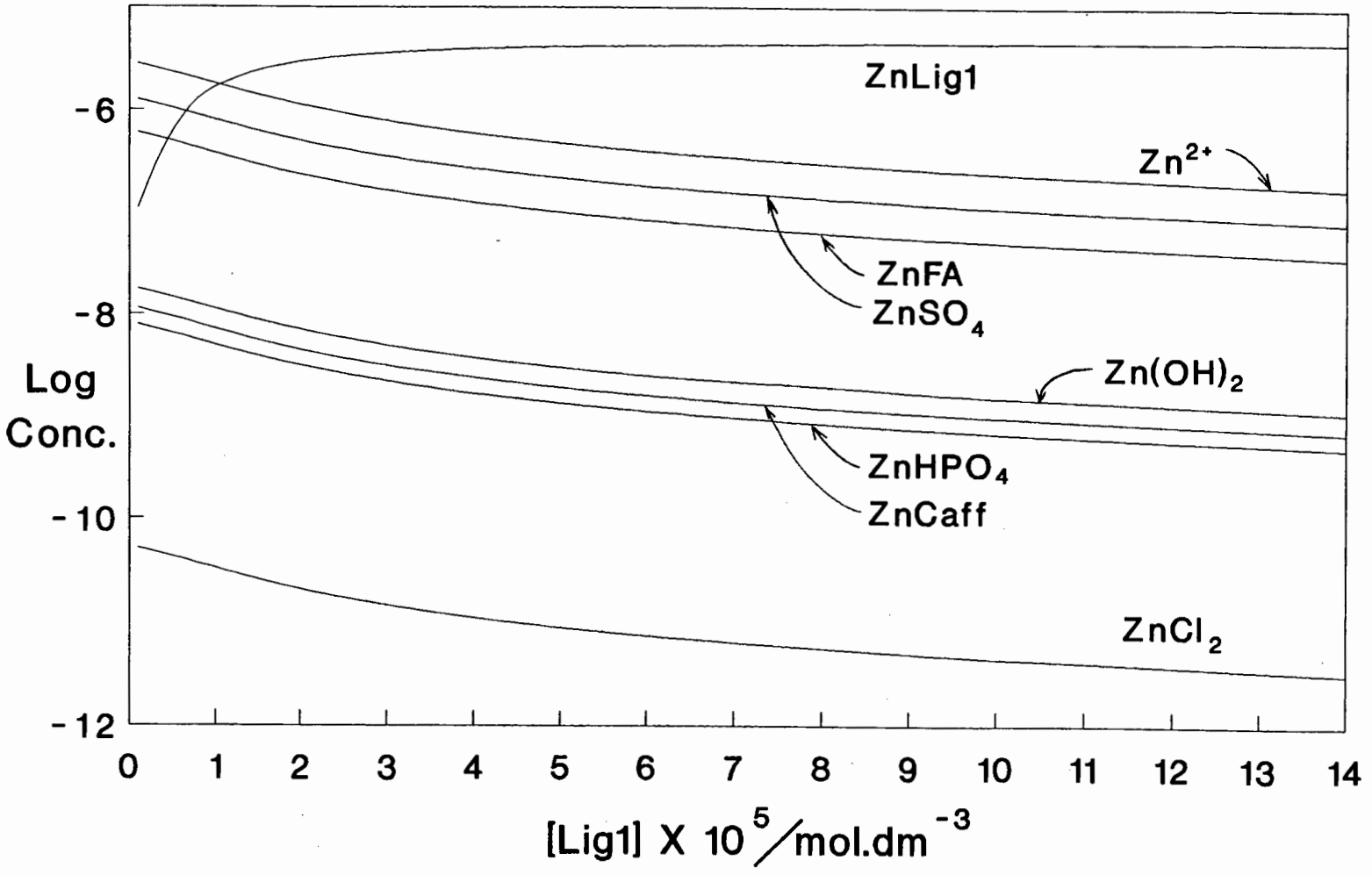
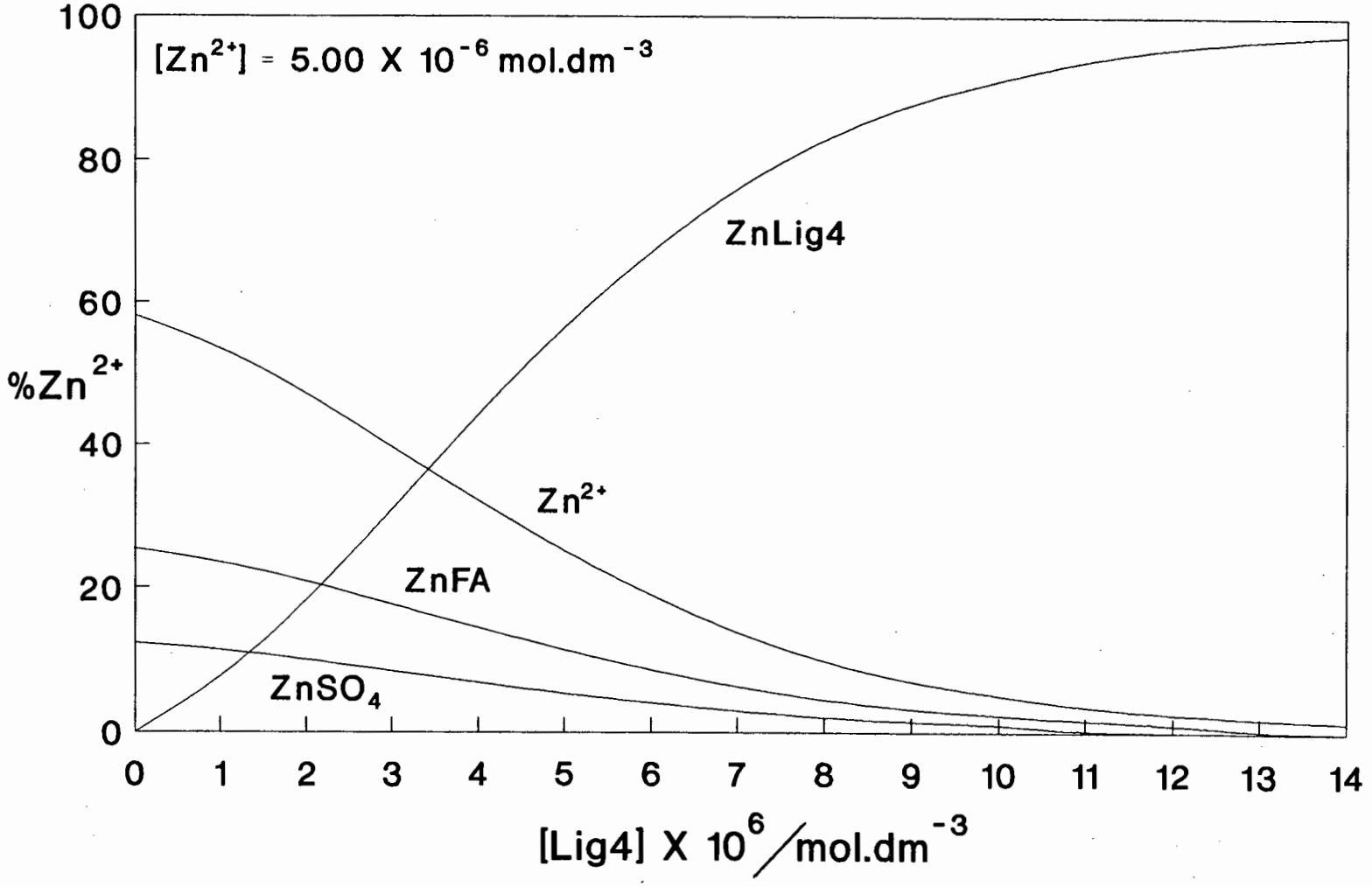


Figure 5.13 The effect of Ligand 4 on zinc(II) speciation



5.4.5.5. The effect of Ligand 1 and Ligand 4 on copper(II) speciation.

Total concentrations

$[Cu^{2+}] = 1.0 X 10^{-6}$ mol.dm^{-3}

[Lig1] and [Lig4] = $0.4 X 10^{-6}$ to $5.2 X 10^{-6}$ mol.dm^{-3}.

Lig1 and Lig4 both affect copper(II) speciation in the specified concentration ranges as indicated in figures 5.14 and 5.15 respectively.

At negligible Lig1 and Lig4 concentrations the major copper(II) species as simulated by the soil solution model are CuFA(80.6%), CuCaff(10.3%), $CuB(OH)_4$(4.2%) and Cu^{2+}(2.3%). The CuLig1 and CuLig4 complexes dominate the copper(II) species distribution as the Lig1 and Lig4 concentrations are increased. At Lig1 and Lig4 concentrations of 5.2 X 10^{-6} mol.dm^{-3}, CuLig1 and CuLig4 consist of 93.2% and 96.0% of the total Cu^{2+} ion concentration.

The concentrations (mol.dm^{-3}) of some of the minor species at a Lig1 concentration of 1 X 10^{-6} mol.dm^{-3} which are not reflected in figure 5.14 are $Cu(OH)_2$(1.2 X 10^{-10}), $CuSO_4$(1.9 X 10^{-9}) and $CuHPO_4$(2.43 X 10^{-10}).

The strong affinity of Cu^{2+} ions for organic species is evident from the simulated results in figures 5.14 and 5.15. This is supported by the literature [Lin79a] and [Bar84]. The accompanying decrease in concentration of all the major copper(II) species in the presence of Lig1 and Lig4 could lead to desorption of Cu^{2+} ions from insoluble organic matter to restore their equilibria. The equilibrium concentrations of the Cu^{2+} ion are low and often less than the minimum copper requirement by plants as reported by Nielson of 4.5 X 10^{-8} mol.dm^{-3} [Nie76]. This has led to the belief that complexed copper may be absorbed in addition to the free Cu^{2+}ion.

Figure 5.14 The effect of Ligand 1 on copper(II) speciation

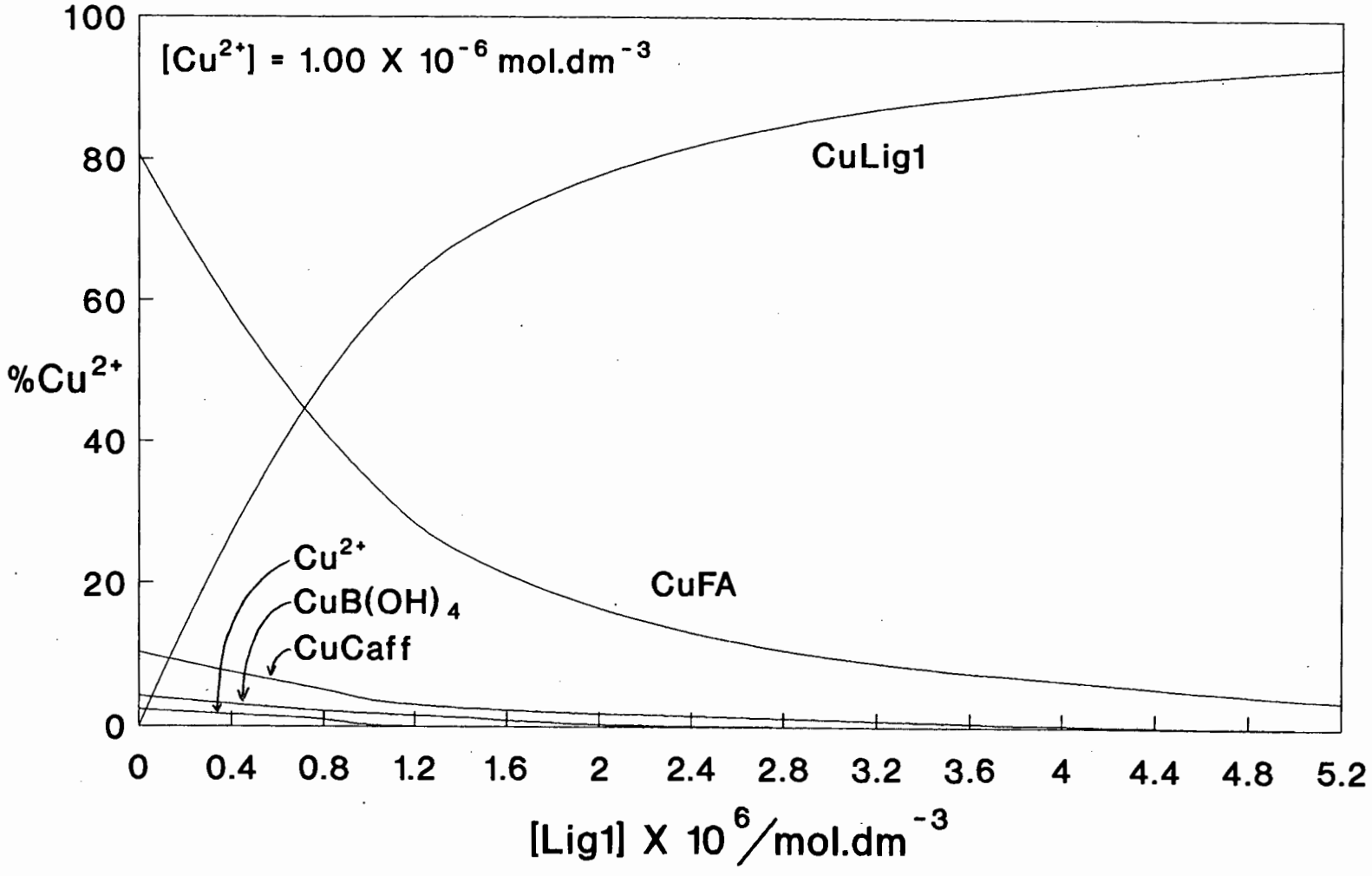
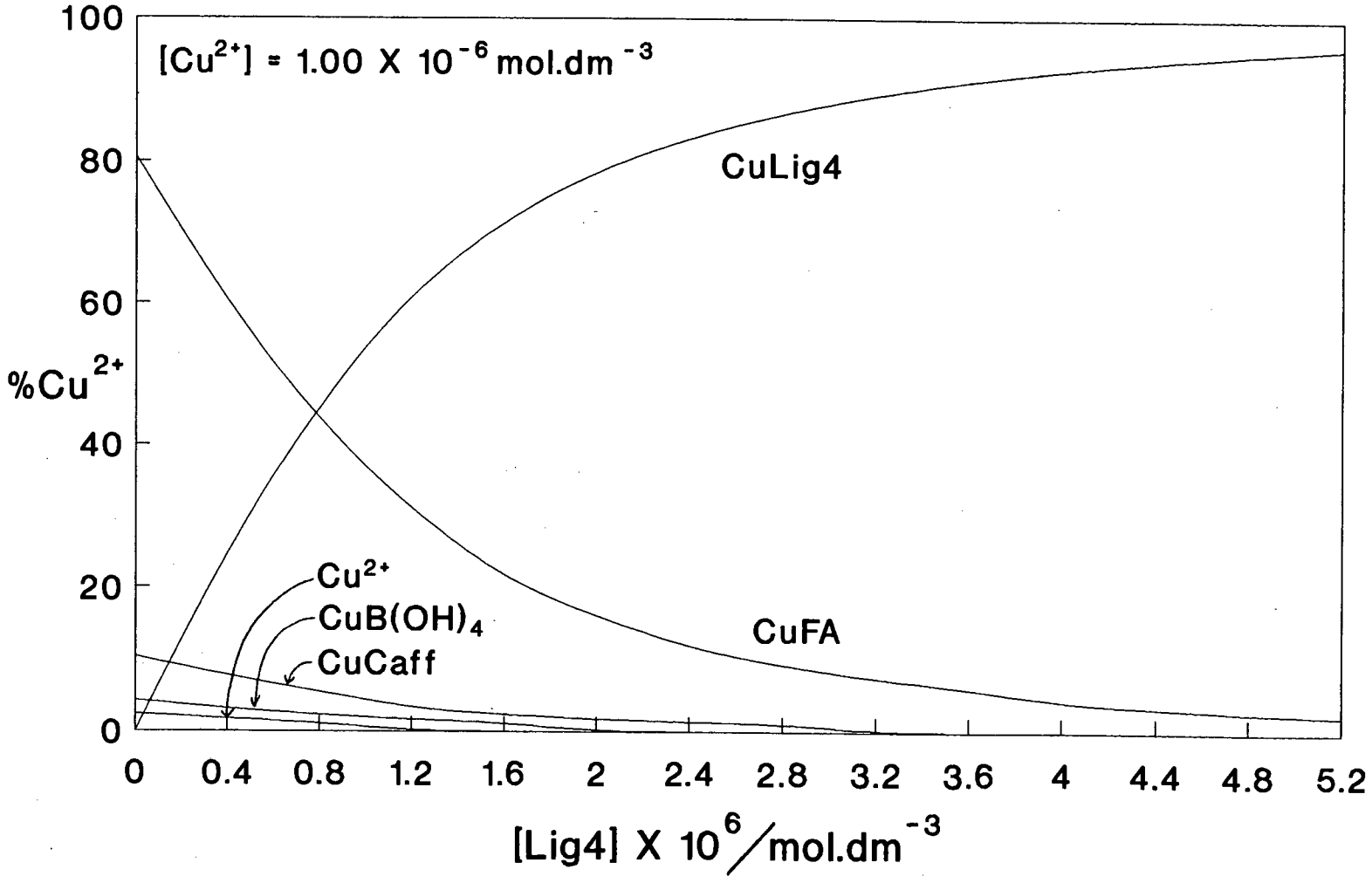


Figure 5.15 The effect of Ligand 4 on copper(II) speciation



The soil minerals governing the solubility of copper are not known [Lin79a]. However, the potential solids considered in this study are, $CuCO_3(s)$, $Cu_3(OH)_2(CO_3)_2$ (azurite), $Cu_2(OH)_2CO_3$ (malachite) and $Cu(OH)_2$ (s) none of which have been found to "precipitate" at the equilibrium solution of the model.

5.4.5.6. The effect of Ligand 1 and Ligand 4 on manganese(II) speciation.

Total concentrations

$[Mn^{2+}] = 1.0 X 10^{-5}$ mol.dm^{-3}

[Lig1] and [Lig4] = 0 to $1.0 X 10^{-3}$ mol.dm^{-3}.

The simulated effect of Lig1 and Lig4 on manganese(II) speciation is illustrated in figures 5.16 and 5.17 respectively. Manganese(II) speciation in the absence of Lig1 and Lig4 is as follows; Mn^{2+}(83.3%) and $MnSO_4$(13.3%). This distribution of Mn^{2+} ions in soil solutions is supported by Graham [Gra88].

At a Lig1 concentration of 1.0 X 10^{-3} mol.dm^{-3}, the speciation is Mn^{2+}(61.9%), MnLig1(25.5%) and $MnSO_4$(10%) and at the same Lig4 concentration the speciation is MnLig4(92.2%), Mn^{2+}(6.3%) and $MnSO_4$(1.0%).

Manganese occurs in three redox forms in soils namely Mn(II), Mn(III) and Mn(IV) of which Mn(II) is the most abundant [Kab84]. Lig4 has a more pronounced effect on manganese(II) speciation than Lig1 at a concentration of 1 X 10^{-3} mol.dm^{-3}. Since Lig1 and Lig4 concentrations are unlikely to exceed 1.0 X 10^{-3} mol.dm^{-3} in field applications, the results of this study suggest that it is unlikely that Lig1 will significantly affect Mn^{2+} ion availability to plants. In the presence of high Lig4 concentrations, adsorbed Mn^{2+} ions could possibly be released into the soil solution

Figure 5.16 The effect of Ligand 1 on manganese(II) speciation

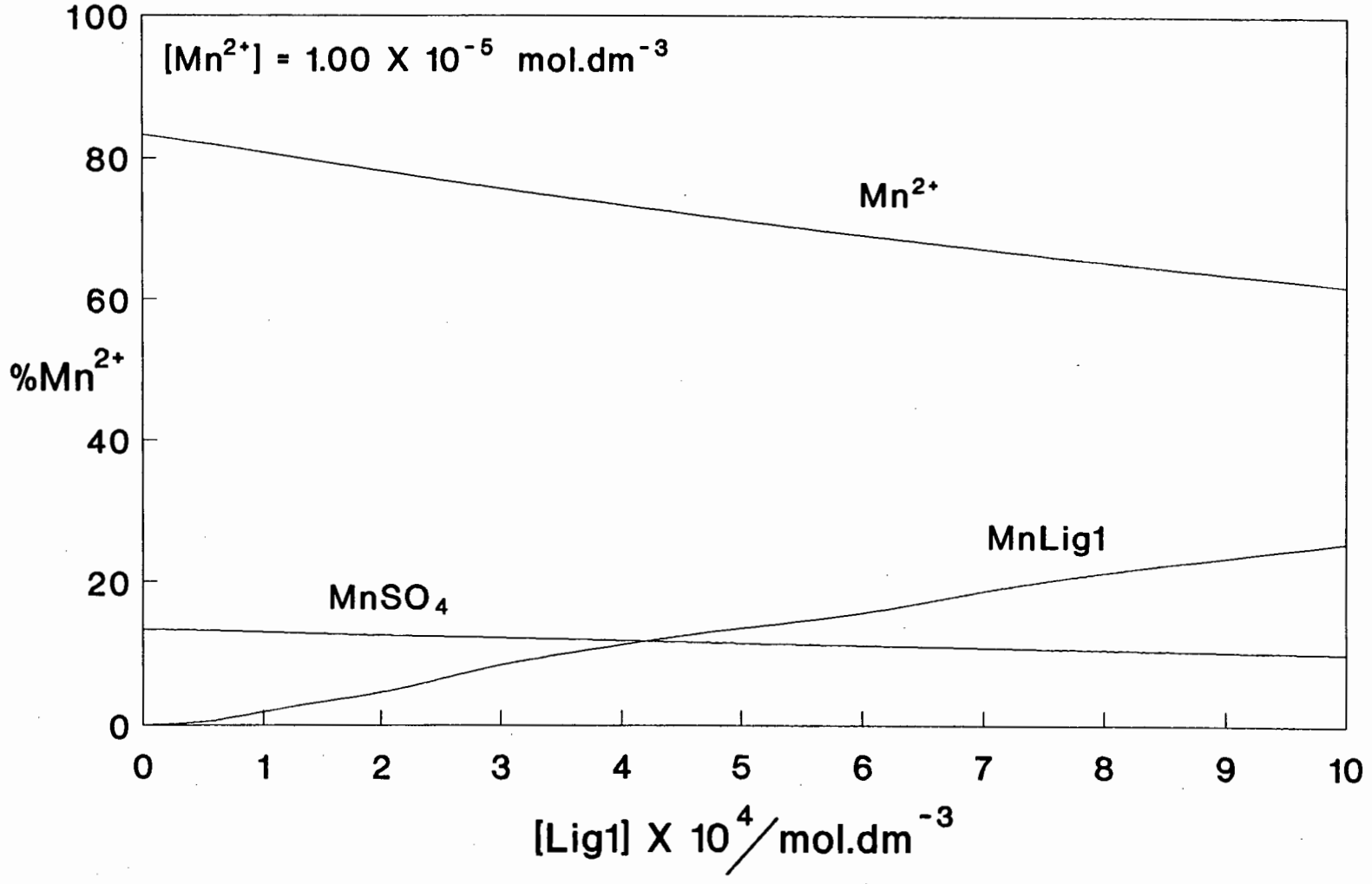
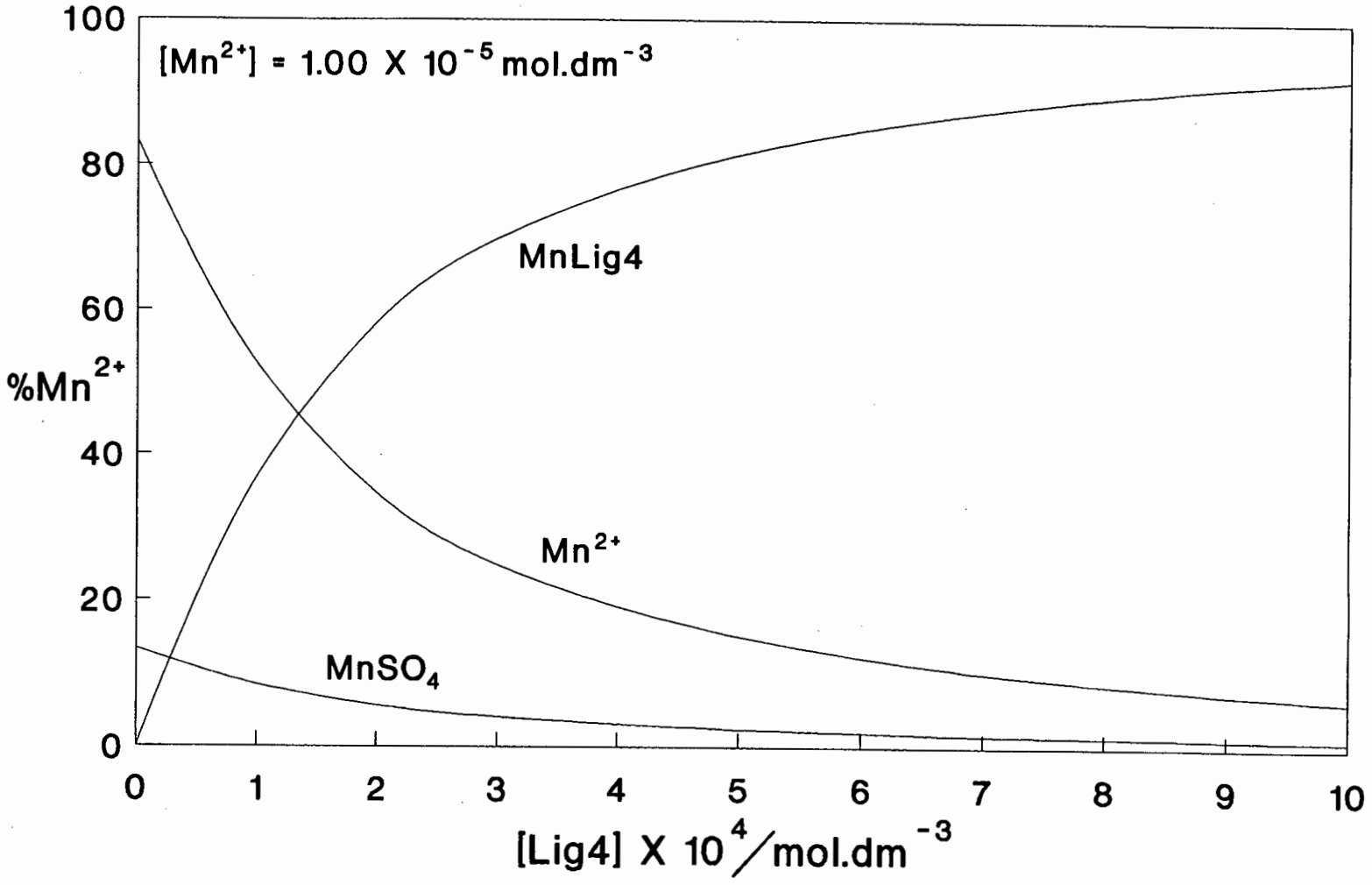


Figure 5.17 The effect of Ligand 4 on manganese(II) speciation



from insoluble organic and inorganic matter in order to reestablish the soil solution equilibrium.

Lindsay suggests that $MnCO_3$ (rhodochrosite), could control Mn^{2+} ion solubility when CO_2 (g) is $10^{-3.5}$ atmospheres and pe+pH is less than 15.67. Rhodochrosite together with $Mn(OH)_2$ (pyrochroite) and Mn_2SiO_4 (tephroite) have been considered as potential manganese solids in this study but the simulated results suggest that all the manganese is in solution at equilibrium.

5.4.5.7. The effect of Ligand 1 and Ligand 4 on cadmium(II) speciation.

Total concentrations

$[Cd^{2+}] = 1.0 X 10^{-6}$ mol.dm^{-3}

[Lig1] = 0 to $1.4 X 10^{-3}$ mol.dm^{-3}.

[Lig4] = 0 to $1.4 X 10^{-5}$ mol.dm^{-3}.

The effects of Lig1 and Lig4 on cadmium(II) speciation are presented in figures 5.18 and 5.19 respectively. In the absence of Lig1 and Lig4, the cadmium(II) speciation is as follows; Cd^{2+}(67.3%), $CdSO_4$(17.1%), $CdCl^+$(7.2%) and $CdHPO_4$(4.7%). Although not reflected in the figures, the concentrations of CdFA and CdCaff are $2.6 X 10^{-8}$ and $2.75 X 10^{-11}$ mol.dm^{-3} respectively.

The simulated results show that Lig1 affects cadmium(II) speciation at concentrations of $1 X 10^{-4}$ mol.dm^{-3} and greater whereas Lig4 alters speciation at concentrations of $1 X 10^{-6}$ mol.dm^{-3} and greater. At a Lig1 concentration of $1 X 10^{-3}$ mol.dm^{-3}, the CdLig1 concentration is $8.44 X 10^{-7}$ mol.dm^{-3} (84.4%) and at a Lig4 concentration of $1 X 10^{-5}$ mol.dm^{-3}, the CdLig4 concentration is

6.22 X 10^{-7} mol.dm^{-3} (62.8%). This is accompanied by a decrease in the concentrations of all the minor species.

At pH values greater than 7.5 and depending on CO_2 (g) pressure, the solubility of cadmium(II) is controlled by $CdCO_3$ (octavite). $Cd_3(PO_4)_2$ (s) could also play an important role in determining cadmium solubility depending on which mineral controls phosphate solubility [Lin79a]. Solubility products for the above-mentioned minerals together with $CdSO_4$ (s) have been considered in this study but all cadmium(II) species have been determined to be in solution at equilibrium.

Cadmium disturbs the enzyme activities of plants and is thus classified as a toxin. The chemistry of cadmium in soils is limited to cadmium(II) minerals and complexes. Cadmium minerals are generally soluble and form Cd^{2+} ions, inorganic and organic complexes. The Cd^{2+} ion shows a strong affinity for sulphydryl as well as the phosphate functional group [Kab84].

Both Lig1 and Lig4 strongly influence cadmium(II) solution speciation. The marked reduction in the concentration of the toxic Cd^{2+} ion could have a beneficial effect on plant growth.

Figure 5.18 The effect of Ligand 1 on cadmium(II) speciation

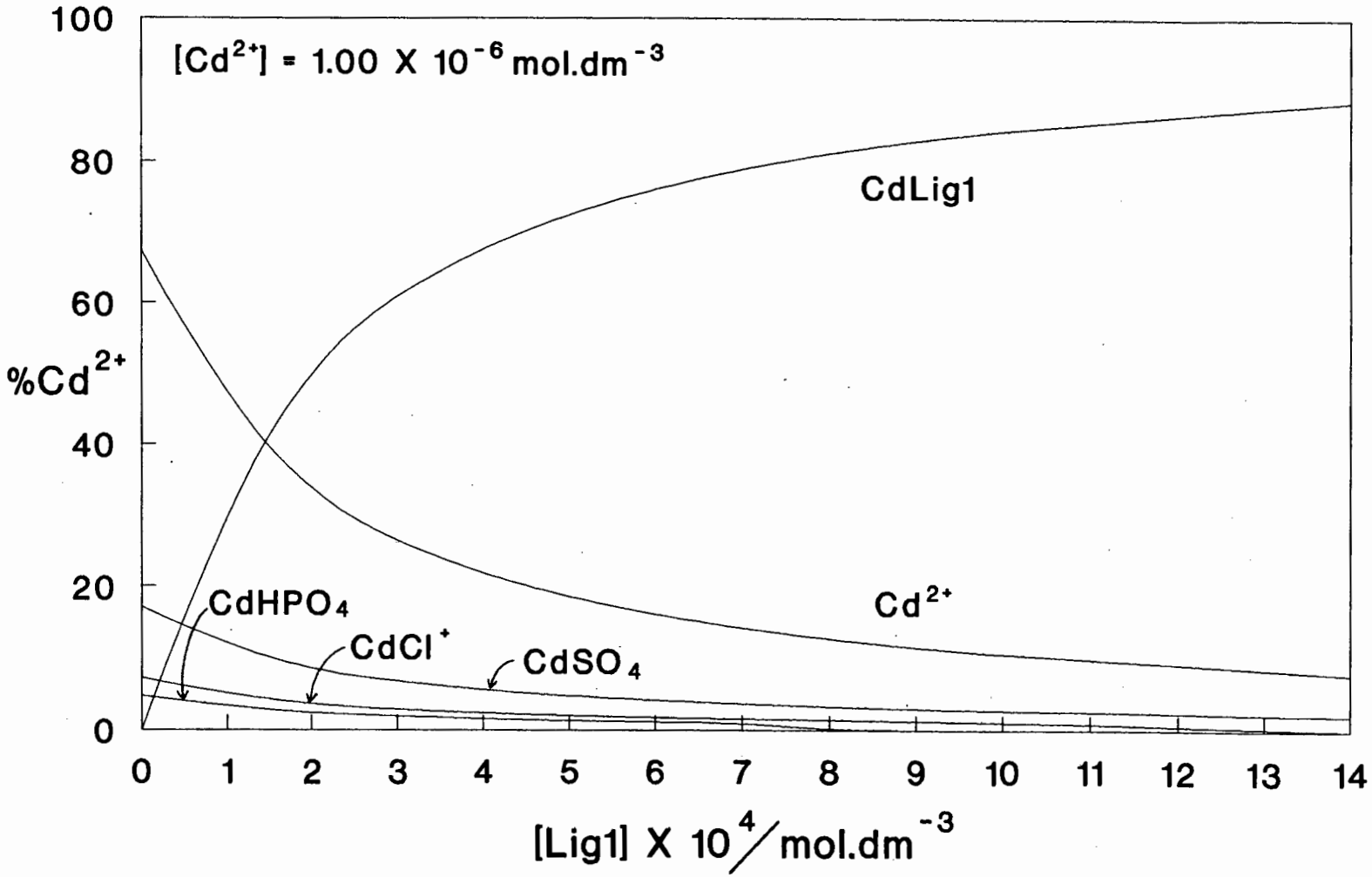
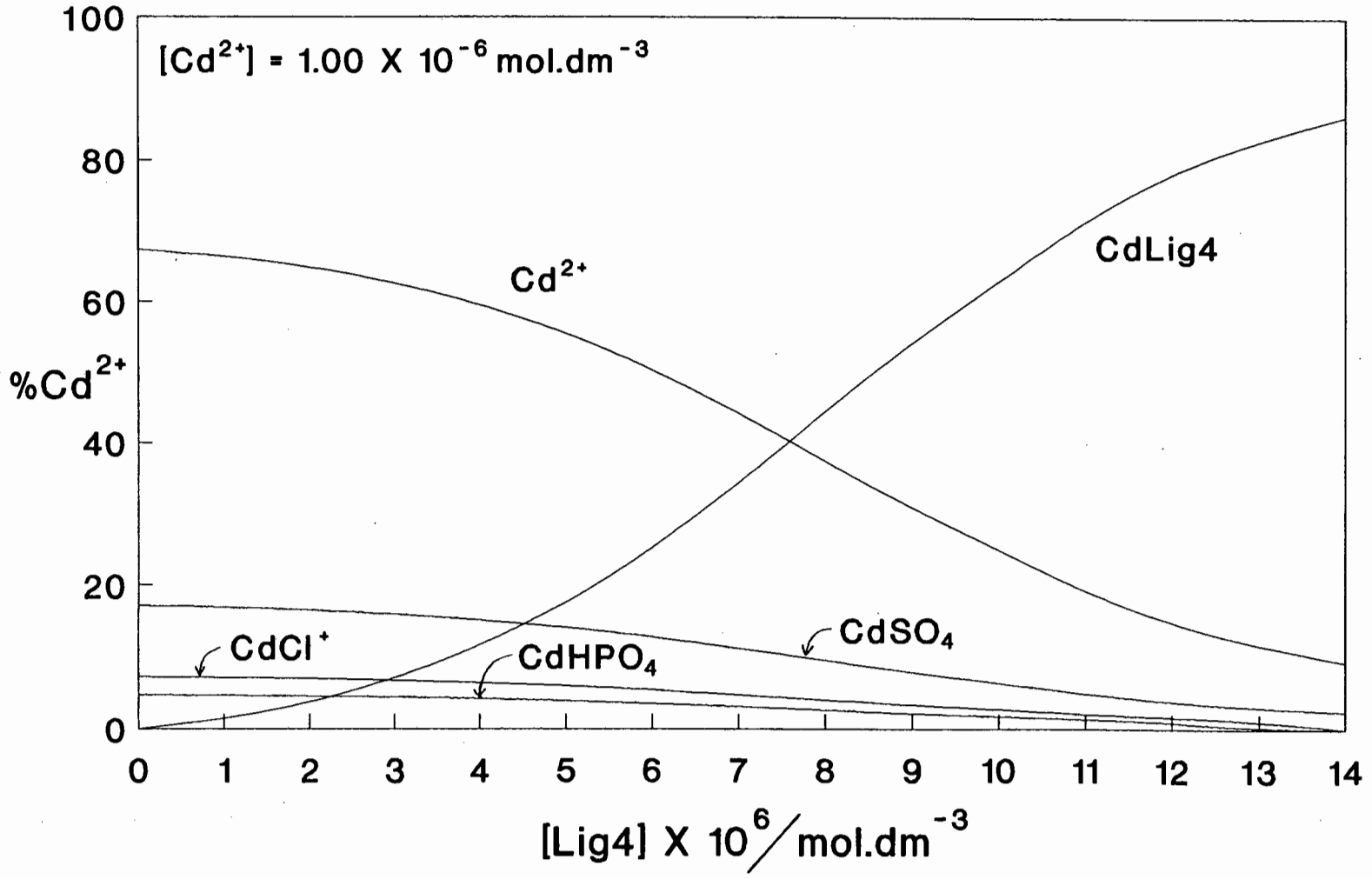


Figure 5.19 The effect of Ligand 4 on cadmium(II) speciation



5.4.5.8. The effect of Ligand 1 and Ligand 4 on cobalt(II) speciation.

Total concentrations

$[Co^{2+}] = 1.0 X 10^{-6}$ mol.dm^{-3}

[Lig1] = 0 to $1.4 X 10^{-3}$ mol.dm^{-3}.

[Lig4] = 0 to $1.4 X 10^{-5}$ mol.dm^{-3}.

The simulated speciation of cobalt(II) ions in the presence of Lig1 and Lig4 is presented in figures 5.20 and 5.21. At Lig1 and Lig4 concentrations of zero, the cobalt(II) speciation is Co^{2+}(78.9%), $CoSO_4$(15.2%), CoFA(2.5%) and CoCaff($1.90 X 10^{-10}$ mol.dm^{-3}).

Cobalt(II) speciation is significantly altered in the Lig1 concentration range of $1 X 10^{-4}$ mol.dm^{-3} and greater while smaller concentrations such as $1 X 10^{-6}$ mol.dm^{-3} and greater of Lig4 are sufficient to obtain similar effects.

At a Lig1 concentration of $1.4 X 10^{-3}$ mol.dm^{-3}, the most concentrated species is CoLig1(88.7%) and similarly, at a Lig4 concentration of $1.4 X 10^{-5}$ mol.dm^{-3}, the most concentrated species is CoLig4(91.1%). As indicated in the figures, this is accompanied by a corresponding decrease in the concentrations of all other cobalt(II) species.

Cobalt is an important element in both plant and animal nutrition. It does not fulfill all the criteria of essentiality in order to be considered an essential plant nutrient but has been shown to improve the yields of certain crop plants [Shu83]. Cobalt is present in vitamin B_{12} and plays an important role in the formation of haemoglobin and thus, animals fed on grasses grown in cobalt deficient soils may become anaemic [Kab84].

Figure 5.20 The effect of Ligand 1 on cobalt(II) speciation

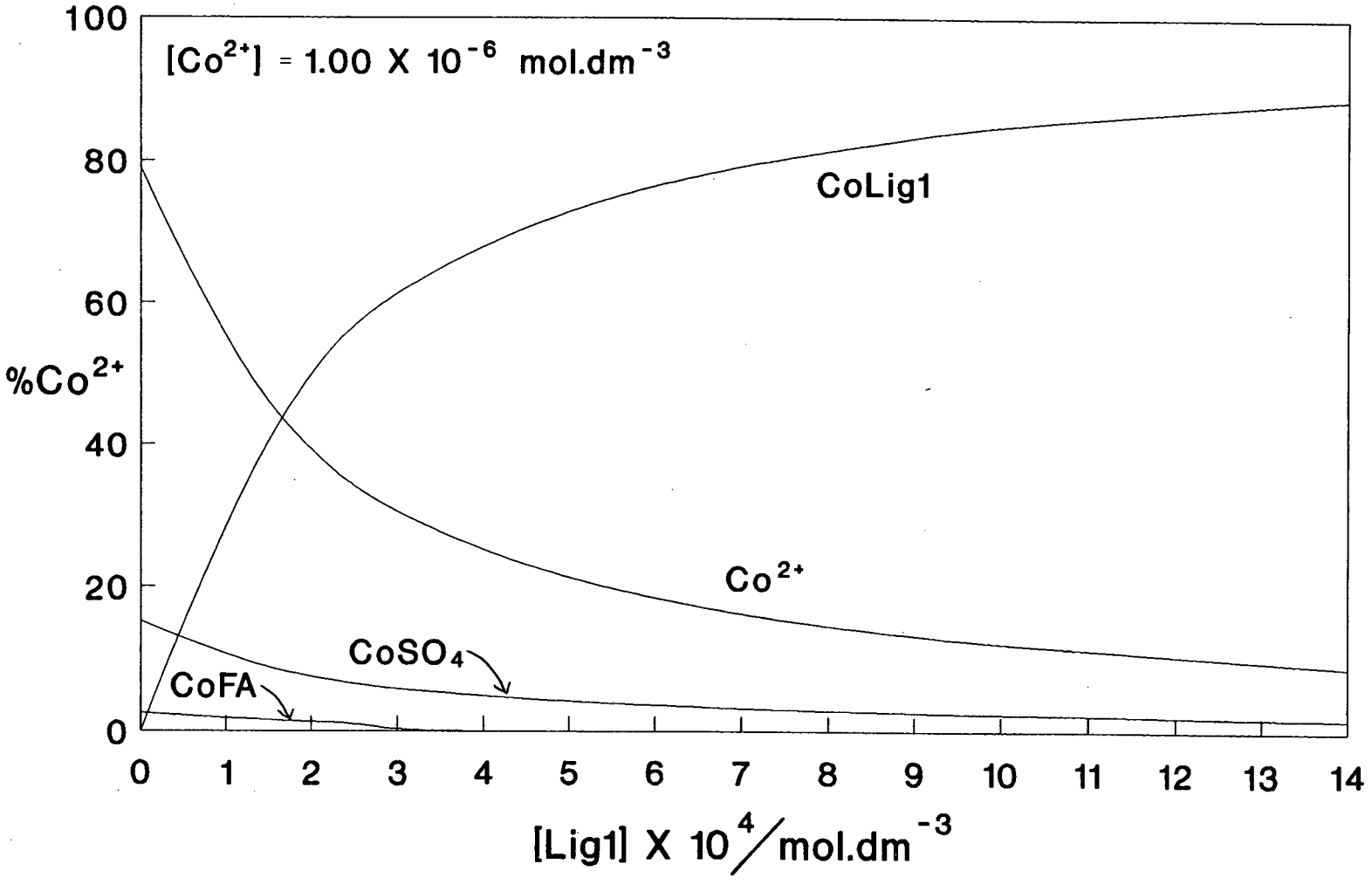
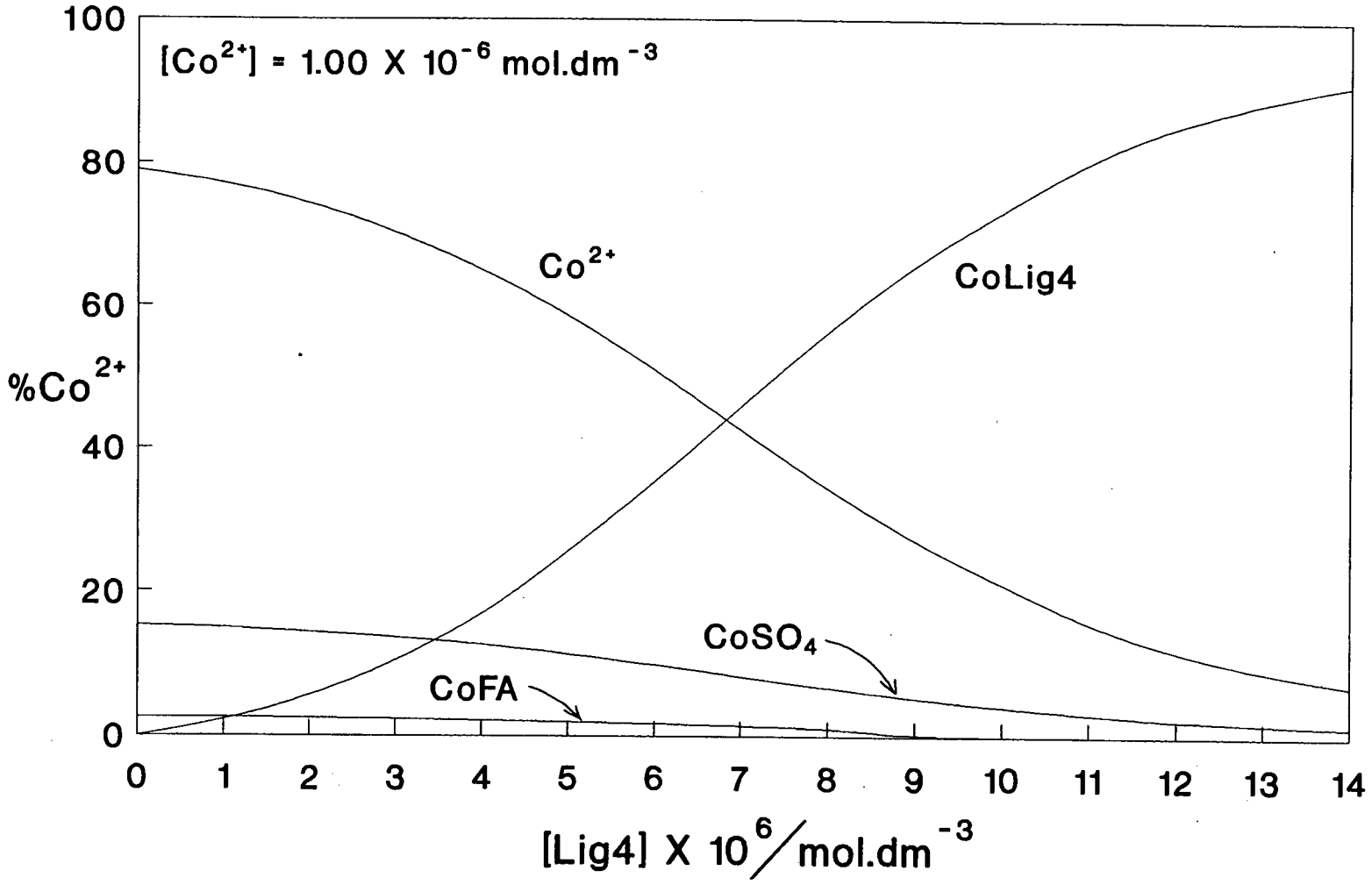


Figure 5.21 The effect of Ligand 4 on cobalt(II) speciation



Soil organic matter and clay content plays an important role in governing cobalt(II) distribution and behaviour in soils [Kab84]. According to the results of this study, concentrations of Ligand 1 and Ligand 4 comparible to that used in field studies [Elk74a] and [Elk74b], significantly affects the soil solution speciation of the cobalt(II) ion. This is largely the case with the free Co^{2+} ion and reestablishment of this equilibrium would depend on the organic matter and clay content of the soil.

5.4.5.9. The effect of Ligand 1 and Ligand 4 on nickel(II) speciation.

Total concentrations

$[Ni^{2+}] = 1.0 \times 10^{-6}$ *mol.dm*$^{-3}$

[Lig1] $= 0$ *to* 1.4×10^{-4} *mol.dm*$^{-3}$.

[Lig4] $= 0$ *to* 1.4×10^{-5} *mol.dm*$^{-3}$.

The simulated effects of Lig1 and Lig4 on nickel(II) speciation is presented in figures 5.22 and 5.23. At Lig1 and Lig4 concentrations of zero the major nickel(II) species are Ni^{2+}(75%), $NiSO_4$(14.5%)and NiFA(7.1%). The concentration of the sum of all caffeic acid species, NiCaff is 5.58×10^{-10} mol.dm^{-3}.

As the Lig1 and Lig4 concentrations are increased, the free Ni^{2+} concentration decreases rapidly with an increase in NiLig1 and NiLig4 concentrations. At a Lig1 concentration of 1.4×10^{-4} mol.dm^{-3} and a Lig4 concentration of 1.4×10^{-5} mol.dm^{-3} the speciation is as follows; NiLig1(83.3%) and NiLig4(96.9%).

Studies with nickel have been related mainly to its toxicity to man and animals [Kab84]. Increased availability of nickel to plants is not easily identifiable since it results in iron chlorosis in plants. Recently there has been a report of the beneficial effects of trace amounts of nickel on higher plant growth [Bro87]. Nickel content is

Figure 5.22 The effect of Ligand 1 on nickel(II) speciation

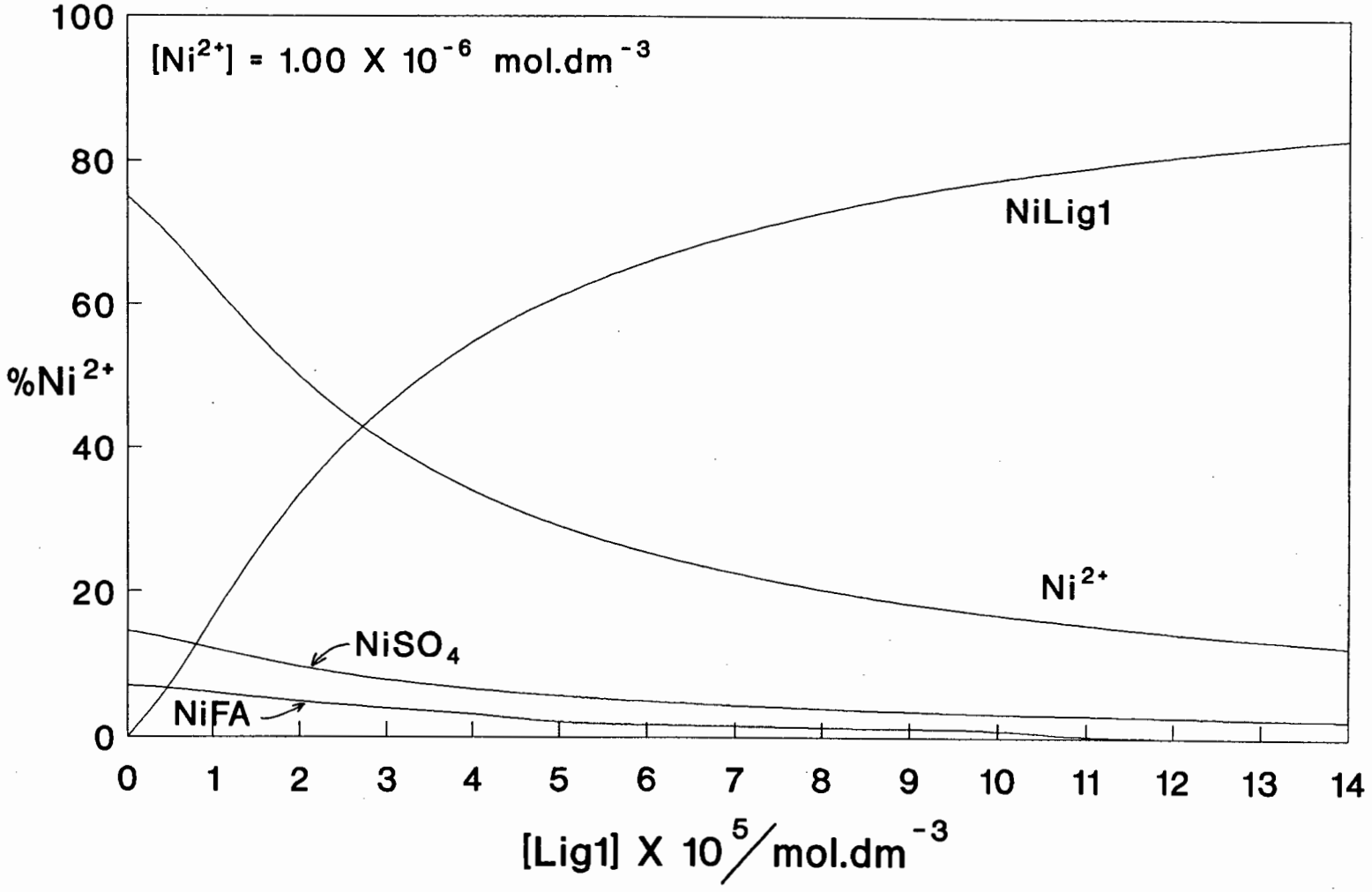
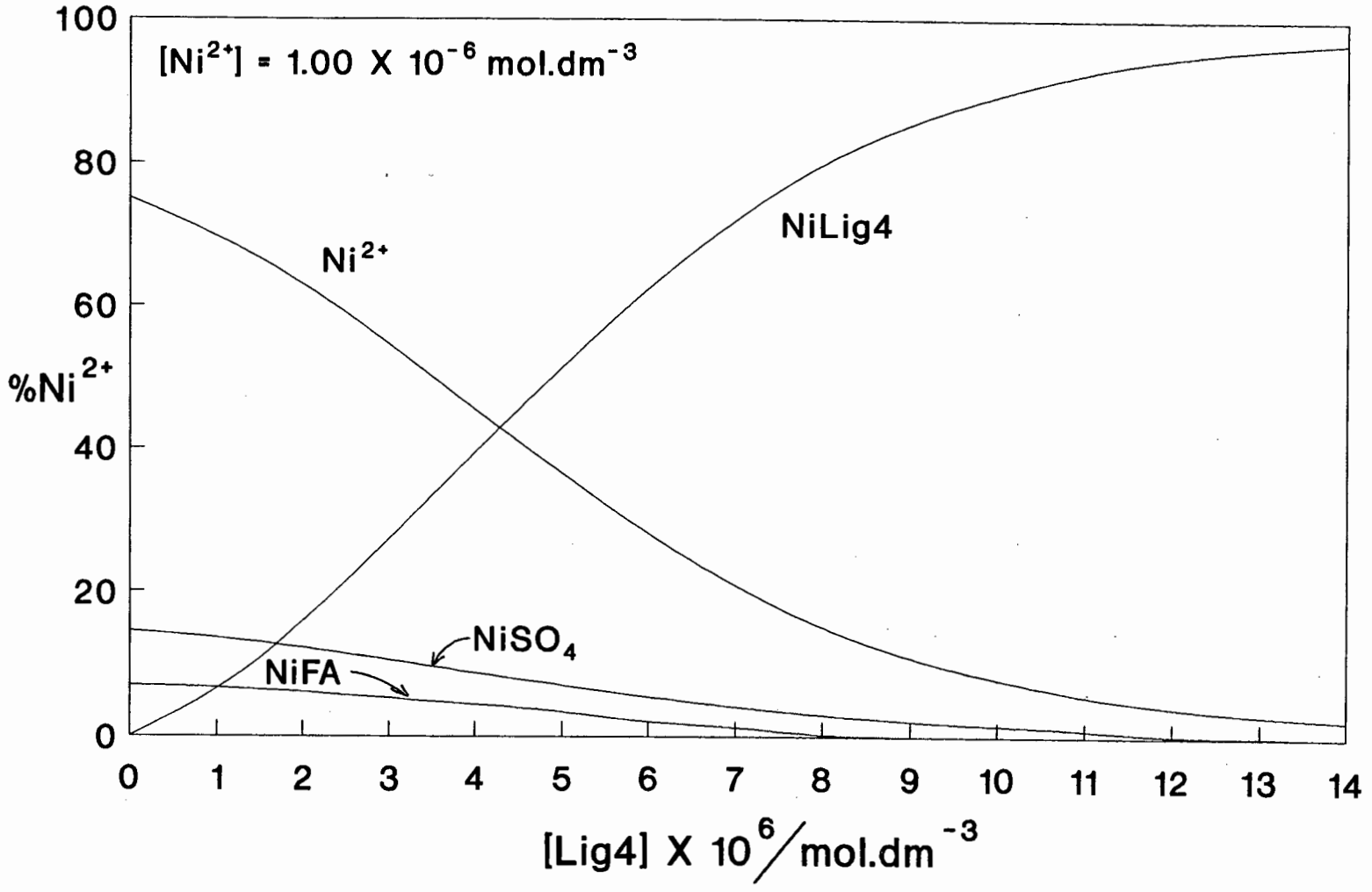


Figure 5.23 The effect of Ligand 4 on nickel(II) speciation



reported to be high in clay and loamy soils and occurs mainly as Ni^{2+} ions and in organically bound forms in solution.

Nickel has been reported to be absorbed by plants as the free Ni^{2+} ion as well as in chelated form [Kab84]. Although the speciation results of this sudy show that Lig1 and Lig4 strongly influences nickel(II) speciation, the overall effect of this change of Ni(II) speciation on plant growth depends on the total nickel content of soils.

5.4.5.10. The effect of Ligand 1 and Ligand 4 on aluminium(III) speciation.

Total concentration

$[Al^{3+}]$ = 1.5 X 10^{-6} mol.dm^{-3}

[Lig1] and [Lig4] = 0 to 1.4 X 10^{-5} mol.dm^{-3}.

The simulated effects of Lig1 and Lig4 on aluminium(III) speciation is presented in figures 5.24 and 5.25. Aluminium(III) ion speciation is dominated by the gibbsite $Al(OH)_3$ (s) species (75%) in the absence of Lig1 and Lig4. The most concentrated dissolved species is $Al(OH)_3$ (21.1%) and the minor species are $Al(OH)_2^+$, AlFA(1.2%) and Al^{3+}(1.82 X 10^{-11} mol.dm^{-3}).

At Lig1 and Lig4 concentrations of 1 X 10^{-6} mol.dm^{-3} and greater, both Lig1 and Lig4 have a solubilising effect on gibbsite, $Al(OH)_3$(s), yet interestingly have no effect on the concentrations of $Al(OH)_3$, $Al(OH)_2^+$, and other dissolved species until the dissolution of $Al(OH)_3$ (s) is complete. Once all the gibbsite has been calculated to be in solution, the concentrations of all dissolved species decline gradually with increasing Lig1 and Lig4. At Lig1 and Lig4 concentrations of 1.4 X 10^{-5} mol.dm^{-3}, the percentage concentrations of AlLig1 and AlLig4 are (94.2%) and (91.5%) respectively.

Figure 5.24 The effect of Ligand 1 on aluminium(III) speciation

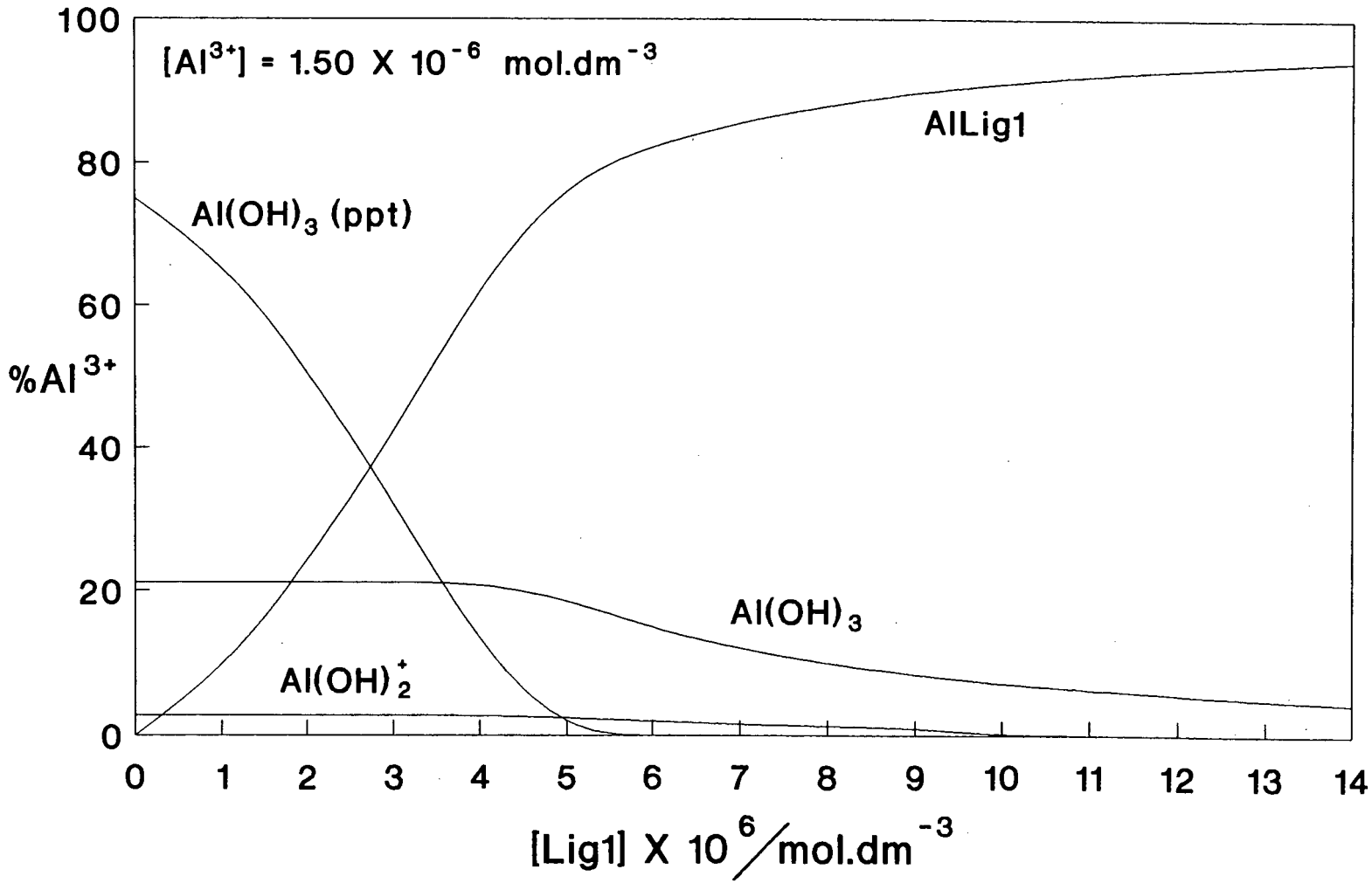
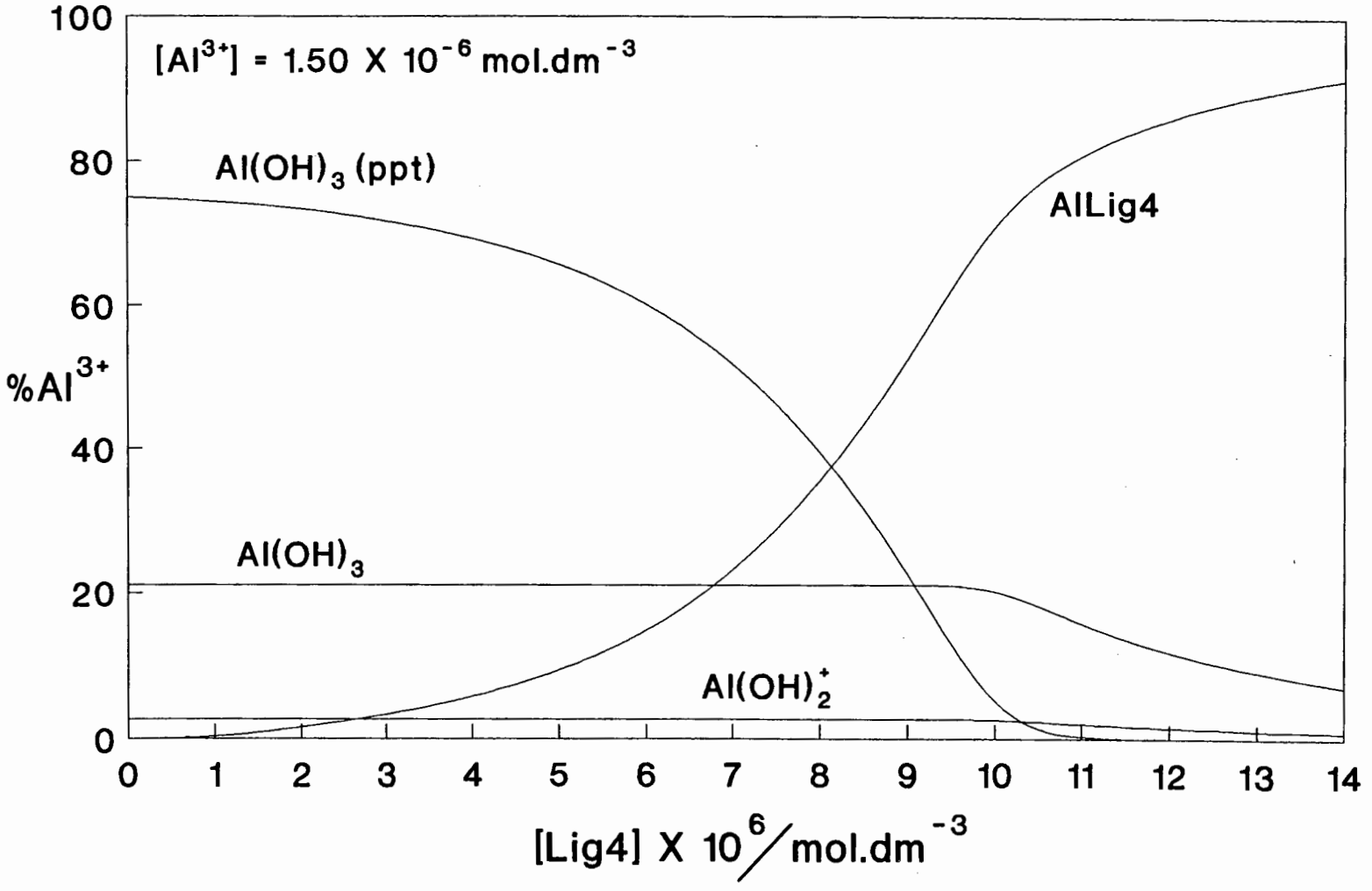


Figure 5.25 The effect of Ligand 4- on aluminium(III) speciation



Increased availability of aluminium(III) to plants results in a reduction of yields, injury and toxicity. Soil solution concentrations of Al^{3+} ions are strongly pH dependent and very often poor plant growth in acidic soils is more a result of increased Al^{3+} availability rather than high H^+ concentrations [Kab84]. The $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_4^-$ species have also been reported as being toxic [Ren89]. Al^{3+} ions are known to form organic complexes and show a strong affinity for oxygen bearing ligands. An excess of Al^{3+} ions reduces Ca^{2+}, Mg^{2+} and K^+ cation uptake and conversely, addition of Ca^{2+} and Mg^{2+} to soils reduces Al^{3+} toxicity.

The findings of this study is consistent with Lindsay's view that $Al(OH)_3$ (gibbsite) controls Al^{3+} solubility in soils under most conditions [Lin79a]. Solubility products for amorphous $Al(OH)_3$ (s), $Al(OH)_3$ (bayerite), $KAl_3(SO_4)_2(OH)_6$ (alunite), $NaAlSiO_4$ (nepheline) and $KAlSiO_4$ (kaliophilite) have been included in the thermodynamic database of this study in order to establish which species controls Al^{3+} ion solubility.

Both Ligand 1 and Ligand 4 complex strongly with Al^{3+} ions resulting in decreased concentrations of all other soluble Al(III) species. This effect ought to be beneficial to plant growth since it further reduces the biotoxic Al^{3+} ion concentration from 1.82×10^{-11} mol. dm^{-3} (Appendix E) to 2.79×10^{-13} mol. dm^{-3} at a Ligand 4 concentration of 1.0×10^{-4} mol. dm^{-3} (Appendix F).

CHAPTER 6

GENERAL DISCUSSION

CONSISTING OF

SYNTHESIS

POTENTIOMETRY

^{1}H, ^{13}C and ^{31}P NUCLEAR MAGNETIC RESONANCE

CHEMICAL MODELLING

CONCLUDING REMARKS

6.1 SYNTHESIS

Four organophosphorus plant growth regulators **I, II, III** and **IV** have been synthesised. A detailed description of the synthesis has been presented in chapter 2.

$$H_2O_3PCH_2NHCH_2CO_2H \quad (I)$$

N - (Phosphonomethyl) glycine (Ligand 1)

$$HO_2P(CH_2NHCH_2CO_2H)_2 \quad (II)$$

N,N'[Phosphinicobis(methylene)] bis glycine (Ligand 2)

$$(H_2O_3PCH_2)_2NCH_2CO_2H \quad (III)$$

N,N - bis(Phosphonomethyl) glycine (Ligand 3)

$$H_2O_3PCH_2NH(CH_2CO_2H)_2 \quad (IV)$$

N - (Phosphonomethyl) iminodiacetic acid (Ligand 4)

Ligand 1 was prepared using a synthetic scheme devised in our laboratory. This involved the condensation of methyleneaminoacetonitrile, formaldehyde and diethyl phosphite under strongly acidic conditions, followed by hydrolysis of the nitrile and ester functional groups. Ligands 2 and 3 were prepared according to methods described in the literature. Ligand 4 was prepared by using the reported experimental procedure for the synthesis of **III** and by substituting glycine for IDA as one of the precursors.

The final step in the synthesis of **II**, ie. the hydrogenation of N, N' - [Phosphinicobis(methylene)] bis benzylglycine using palladium on carbon, Pd/C, to give **II**, was found to be problematic despite following the literature method very closely [Mai80]. This step was repeatedly done on a small scale and often the oil

resulting from the hydrogenation reaction failed to crystallize. In cases where **II**, crystallized from solution, the yields were not as high as those reported in the literature. Other than the abovementioned problem, all other steps in the synthesis of ligands **I, II, III** and **IV**, proceeded without difficulty and resulted in good yields.

All four compounds were purified by recrystallization and characterised using nuclear magnetic resonance spectroscopy, microanalyses and melting point determination.

6.2 POTENTIOMETRY

The metal - ligand - proton systems investigated potentiometrically in this study have been presented in chapter 3. All the experiments have been conducted at a temperature of 25 ^{o}C and an ionic strength of 0.1 mol.dm^{-3} of chloride ions.

It was initially hoped that the aqueous equilibria of all four ligands **I, II, III** and **IV** with the metal ions Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} could be examined. However, shortly after the commencement of this study, Motekaitis and Martell reported the results of the aqueous equilibria of **I** with a series of divalent and trivalent metal ions [Mot85]. In addition to this, great difficulty was encountered with the analysis of potentiometric data owing to the high degree of binding at low pH between some metal ions and the ligands under investigation. It was then decided to examine the aqueous equilibria of **I, II, III** and **IV** with H^{+} and Ni^{2+} ions in order to gain some insight into the relative binding strengths of each of the ligands used in this study. It was further decided to restrict additional potentiometric studies to that of **IV** with selected metal ions. This was done after having decided that the computer modelling would consist of an examination of the effects of Ligands 1 and 4 on metal ion speciation in a soil solution. The necessary

thermodynamic data of Ligand 1 required for the computer modelling was taken from the literature [Mot85].

The protonation equilibria of **I, II, III** and **IV** in aqueous solution was examined in this study and have been compared and contrasted with some structural analogues. The protonation constants of **I** [Mot85], **III** [Wes65] and **IV** [Mot80] have been established previously and the results obtained in this study compare favourably with the values reported in the literature. The protonation constants of **II** have not been established prior to this study.

The aqueous equilibria of **I, II, III** and **IV** with Ni^{2+} ions was also examined. The results obtained in this study for nickel(II) - ligand 1 complexation compares favourably with previously reported data [Mot85]. Equilibrium constants for the nickel(II) ligand 3 system have been determined spectrophotometrically [Nik74] and the results obtained in this study are of the same order of magnitude. The complexation of **II** and **IV** with nickel(II) ions has not been established previously. The aqueous equilibria of ligands **I, II, III** and **IV** as well as some structurally related analogues with nickel(II) ions have been compared and discussed.

The complexation of ligand 4 with Mn^{2+}, Fe^{2+}, Co^{2+} and Zn^{2+} ions has also been established in this study. Majer et. al. have reported stability constants for the MLH complexes of ligand 4 with Mn^{2+}, Co^{2+} and Zn^{2+} ions which have been determined using paper electrophoresis [Maj80]. The MLH complex has been found in the speciation of the above - mentioned systems in this study and the formation constant values determined compare favourably with the reported constants. Investigation of the complexation between **IV** and Fe^{3+} and Cu^{2+} ions was also attempted but due to the high degree of binding at low pH, the potentiometric data could not be analysed. A similar problem was encountered with the Cu^{2+} - ligand 3 system.

The Cu^{2+} - ligand 4 system was successfully analysed in the presence of a competing ligand, 4 - Nitrocatechol. The choice of competing ligand was made after a series of theoretical speciation calculations for systems consisting of ligand 4, Cu^{2+} ions and a competing ligand (eg. EDDA, IDA and 4 - Nitrocatechol).

The concept of using a competing ligand is that at some pH, one of the ligands in solution will displace the other from the metal ion resulting in measurable concentrations of the free components which will then allow one to determine one or more of the stability constants for the metal - ligand system under investigation. For practical reasons it is important to select a competing ligand which competes with the ligand chosen in the initial study at very similar concentrations, say 1 : 1. This is also to avoid using one of the ligand components in high concentrations close to that of the background electrolyte.

The excellent fit between the experimental and theoretical metal formation and metal deprotonation curves for the Cu^{2+} - ligand 4 system shows that the use 4 - Nitrocatechol as a competing ligand worked well in establishing the aqueous equilibria of the Cu^{2+} - ligand 4 system.

Prior to solving the Cu^{2+} - ligand 4 system in the presence of 4 - Nitrocatechol, the aqueous equilibria of 4 - Nitrocatechol with H^+ and Cu^{2+} ions was determined and compared with the constants reported in the literature [Hak84].

Stability constants for the ML species of the Fe^{3+} and Cd^{2+} ions with ligand 4 have been estimated for use in the computer modelling studies. This was done by constructing a plot of log K_{ML} vs log K_{ML}, for ligand 4 and some structurally related ligand with various divalent and trivalent metal ions.

Plausible structures for the various species found during the potentiometric studies have been proposed. These structures are based largely on the possibilities found following construction of Dreiding models and using the knowledge of the protonation sequences of the various ligands as found in the nuclear magnetic resonance studies (chapter 4).

6.3 ^{1}H, ^{13}C AND ^{31}P NUCLEAR MAGNETIC RESONANCE

Nuclear magnetic resonance was used to establish the sequence of deprotonation of the ligands used in this study and has been discussed in chapter 4.

The results obtained in this study for ligand 1 compare favourably with the results reported by Appleton et. al. [App86]. The deprotation sequences of **II, III** and **IV** have been established unambiguously and the results of this study underline the suitability of nuclear magnetic resonance for elucidating deprotonation sequences of ligands with aminocarboxylate and aminophosphonate functionality.

6.4 CHEMICAL MODELLING

A computer model has been constructed to simulate the effects of selected plant growth regulators on metal ion speciation in a soil solution. A detailed description of the model has been presented in chapter 5.

In the construction of the model, chemical components were selected following an extensive literature survey of the essential and beneficial elements of plant nutrition, plant root exudates, toxic metal ions, soluble soil organic matter and soil components. Consideration was also given to soil pH, ionic strength, potential solids, temperature, redox equilibria and dissolved gases. A thermodynamic database consisting of stability constants, Henry's law constants, redox reactions and solubility

products has been constructed at an ionic strength of 0.0 $mol.dm^{-3}$ and a temperature of 25 ^oC. The computer programme MINEQL was used to calculate the equlibrium speciation of the model. A feature of this programme is that calculations may be determined at any specified ionic strength provided that the database has been contructed with all constants corrected to an ionic strength of 0.0 $mol.dm^{-3}$.

In the ensuing section, some general results of the soil solution model are discussed. Features which have not been considered in the construction of the model but which are nevertheless pertinent in studies of this type, are also discussed.

The equilibrium concentrations of the major ions and complexes of the soil solution model in the absence of the plant growth regulators have been presented in table 5.9 with the entire output data set presented in appendix E.

The equilibrium speciation of all the metal ions and inorganic ions is more or less consistent with that reported in the literature [Lin79a], [Bar84], [Spo84] and [Boh85]. For example all of the metal ions are predominantly present as aqua ions with the exception of Cu^{2+} ions where more than 90% is complexed to the organic components of the soil. The sulphate ion, SO_4^{2-}, dominates the speciation of most metal ions although this is of the order of 10% to 20% of the total metal ion concentration.

The solid compounds which "precipitated" at the equilibrium conditions of the model was indeed an encouraging aspect. The precipitation of gibbsite, ferrosic hydroxide and calcium hydroxyapatite which controls the dissolved concentrations of Al^{3+}, (Fe^{3+} and Fe^{2+}) and (Ca^{2+} and PO_4^{3-}) respectively is consistent with the literature [Lin79a], [Lin82a] and [Bar84]. Lindsay has reported that ferrosic

hydroxide controls iron solubility in moderately oxidised soils while amorphous iron(III) hydroxide, $Fe(OH)_3$, controls iron solubility in highly oxidised soils. The latter was observed in this study (table 5.6) prior to the incorporation of caffeic acid into the model. The abovementioned observations led to a high degree of confidence in the soil solution model constructed and consequently in the effects observed following the introduction of various concentrations of the two plant growth regulators **I** and **IV**.

Rohmheld et. al. have reported the enhanced uptake of Zn^{2+} and Mn^{2+} ions by iron - efficient plants during iron deficiency [Rom82]. This is presumably as a result of chelation by the organic compounds exuded by plants during iron stress. The results of this study (appendix E) show that the zinc(II) - caffeic acid concentration is 8.0×10^{-9} mol.dm^{-3} and the manganese(II) - caffeic acid concentration is 2.47×10^{-10}. This hardly affects the speciation of Zn^{2+} and Mn^{2+} ions where the free ion concentrations are 2.91×10^{-6} mol.dm^{-3} and 3.33×10^{-6} mol.dm^{-3} respectively both in the absence (appendix C) and presence of caffeic acid.

This can be explained by the fact that caffeic acid is a weak chelating agent when compared with other organic ligands exuded by plants such as glycine, oxalic acid, succinic acid etc [Ins86].

The results of this study clearly indicate that the inclusion of Ligand 1 and Ligand 4 to the soil solution model has a profound effect on the speciation of the various essential, beneficial and toxic metal ions under consideration. Although the effects of adsorption equilibria were not considered in this study, the solubility products of certain solid species for Ca^{2+}, Al^{3+}, Fe^{2+} and Fe^{3+} ions were exceeded in the absence of (**I**) and (**IV**) and the plant growth regulators under consideration were shown to increase the total dissolved concentrations of these metal ions. The plant

growth regulators considered in this study would thus be expected to play a dual role following application to crops ie. as a herbicide and a chelating agent which would solubilize metal ions.. From the literature it is evident that very little consideration has been given to the latter and since there is a positive correlation between the concentrations of metal aqua ions in soil solutions bathing plant roots and total uptake by plants [Kab84], the effects of **I** and **IV** on soil solution speciation is of concern. This is particularly so in view of the findings that NTA (1.3×10^{-2} mol.dm^{-3}) caused a slight toxicity of metal ions to bush beans growing in soil [Wal74]. The binding strength of NTA is intermediate between **I** and **IV** suggesting that lower concetrations of **IV** are expected to have similar effects on plants.

Metal chelates benefit nutrient uptake in plants by increasing the total concentration of metal ions in the soil solution which in turn provides greater diffusional gradients for the transport of metal ions to the plasma membrane of the absorbing cells of the root [Lin78c]. It has been proposed that chelating agents are separated from the metal ion at the plant root with only the aqua metal ion being absorbed [Wal80b]. This process of chelate dissociation is facilitated in the presence of ligands forming metal - chelate complexes of lower stability (the ligands used in this study are typical examples) than EDTA or DTPA complexes. However, there is also evidence of plant roots absorbing metal chelates [Wei54], [Hil57], [Wal57], [Tif61] and [Lin78a] and it is well known that soil microorganisms constantly attack plant roots allowing soluble ions and metal chelates to diffuse into the plant roots [Wal80b].

Herbicides are sprayed onto weeds and crops as a solution or applied directly to the soil. More specific to this study, Ligand 1 has been added to soils of varying composition and showed herbicidal activity in wheat plants grown in a quartz soil [Spr75a]. In the aforementioned case, the absorption of ligand 1, whether as a free

ligand or a metal chelate, by the plant roots is implicated. In the same study, Ligand 1 was rapidly inactivated in clay - loam soils as a result of adsorption onto the soil surface. Adsorption was shown to decrease on addition of high concentrations of phosphate to the soil. Sprankle et. al. concluded that Ligand 1 was adsorbed to soil surfaces through the phosphonic acid end of the molecule.

In soils where herbicides of the type considered in this study are allowed to accumulate, the possibility of metal ion toxicity exists. Plant tolerance levels for an excess of essential metal ions vary markedly. In general, plants are much more resistant to increased levels of essential elements than to insuficient amounts [Kab84]. Increased levels of one metal ion, whether below tolerance levels or not, often cause deficiency of other metal ions in plants.

Metal ion toxicities occur mainly in acid soils and not to any great extent in neutral or alkaline soils [Bin86]. Toxicities of metal ions such as Cd^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+} and Mn^{2+} occur under acidic conditions and in soils with a poor adsorptive capacity [Bin86]. These effects may be alleviated by liming the soil and increasing soil solution pH in the process or by increasing the adsorptive capacities of these soils.

The adsorption of inorganic and organic substances by solid surfaces in a soil solution is one of the factors not considered in this study. Adsorption is a chemical process involving specific interactions between solutes and reactive surface groups.

The most common inorganic adsorbants are hydrous metal oxides of iron, manganese, aluminium and silicon. Hydrous metal oxides all exhibit amphoteric behaviour in water and coordinate and dissociate protons and consequently aquire either a positive or negative surface charge, the sign of which is pH dependent. The binding of ions at the surface can be described by mass law equations and this

concept forms the basis of surface complexation models [Dzo87]. The concepts used to describe surface adsorption at the oxide - water interface are based on the classical double layer theory (Gouy - Chapman) and its extensions by Stern and Grahame [Dzo87].

Trace inorganic and organic adsorption differ significantly in their underlying principles with the latter being predicted with fewer parameters, for example, its organic carbon content [Kar84].

Another important aspect not considered in this study was the presence of mixed ligand complexes which statistically have a high probability of forming in a multi - metal multi - ligand system such as a soil solution [Mar73]. Lamy et. al. examined the mixed ligand complexes of copper(II) ions and five polyfunctional ligands, (caffeic acid, chlorogenic acid, tyrosine, shikimic acid and tiron), as models of natural substances [Lam85]. They concluded that the formation of only simple binary complexes in systems with many metals and ligands is more the exception than the rule and emphasized the importance of including mixed - ligand complex data in computer calculations of complex natural systems.

In selecting components for the soil solution model, emphasis was placed on the essential and beneficial elements of plant nutrition. In addition to this, some elements which are common in soil minerals as well as potential toxins were selected. The entire list of components has been presented in table 5.3. The toxins aluminium and cadmium were chosen but regretably, lead was omitted due to a lack of the necessary thermodynamic data of lead - organic complexes.

An interesting expansion of the present model would be to include additional elements which are essential for human and animal nutrition. These include selenium, chromium, vanadium, iodine and fluorine [Mer81].

Redox equilibria of selected metal ions were included in the soil solution model. An interesting addition to the model would be the inclusion of the various redox forms of the sulphur atom. At low pH and under strongly reducing conditions, the sulphide ion, S^{2-}, is abundant in soil solutions. This would be interesting since a number of metal ions which have high soil solution concentrations under acidic conditions, are known to precipitate as metal sulphides, for example, CuS (covellite) and ZnS (sphalerite), which effectively reduces the chances of excess metal uptake [Bin86] [Dav88].

Microorganisms play a major role in the cycling of nutients in soils. Despite the vast amount of research put into the study of natural systems by the most distinguished researchers in the field, no one has proposed any ideas on how the effects of soil microorganisms can be modelled.

As discussed in chapter 5.1, there are many computer programs available for simulating the chemical speciation of natural water systems. Most of the more recent programs have been developed using one or more of the earlier programs as a basis for its development. REDEQL2 [McD73] AND GEOCHEM [Mat79] include subroutines for dealing with ion exchange and adsorption/desorption processes and are among the more complex programs available. Until recently, all programs regarded all reactions as being fast reversible processes. Furrer et. al. have developed a program STEADYQL [Fur89] which is unique in the sense that it considers chemical processes in three different time frames ie. fast reversible reactions, slow kinetically controlled reactions and very slow reactions considered to

be invariant in time for solution of the system. These concepts have not as yet evoked any response in the literature from other authors but it is likely to be used as the basis for constructing the next generation of chemical speciation programs.

6.5 CONCLUDING REMARKS

The objectives of this study as reported in chapter 1.7 have largely been met. The computer simulated results show that the plant growth regulators, N - (Phosphonomethyl) glycine (**I**) and N - (Phosphonomethyl) iminodiacetic acid (**IV**) both have a significant effect on the speciation of metal ions in a soil solution. Similar results can be expected for (**II**) and (**III**).

The general trends of Ligand 1 and Ligand 4 on the soil solution speciation of metal ions at a practical level of 2.0 X 10^{-4} mol. dm^{-3} can be summarised as follows. Both Ligand 1 and Ligand 4 have little effect on Mg^{2+}, Ca^{2+}, Fe^{2+} and Fe^{3+} ion concentrations. Ligand 1 induces a small reduction in the concentration of Mn^{2+} and Zn^{2+} ions but causes a marked reduction in Cu^{2+} ion concentration. Ligand 4 causes a profound reduction in the concentration of Mn^{2+} Zn^{2+} and Cu^{2+} ions. Since these metal ions are essential for plant growth, any significant depletion of their bioavailability could affect plant growth adversly. Both Ligand 1 and Ligand 4 cause a decrease in Co^{2+}, Cd^{2+} and Ni^{2+} ion concentration as well as in dissolved Al(III) hydroxy and Al^{3+} ion species most of which have been reported as being toxic [Ren89]. This effect on the concentrations of biotoxic metal ions ought to be beneficial to plant growth. As a precaution, Cu^{2+} ions should be added concurrently with Ligand 1 applications to crops, and Cu^{2+}, Mn^{2+} and Zn^{2+} ions should be added when Ligand 4 is applied to crops.

Expansion of the present soil solution model to include the adsorption equilibria of soil organic and inorganic components would indeed be very interesting since

adsorption of N - (Phosphonomethyl) glycine, Glyphosate, in soils is reported as a means of inactivation in soils with high adsorptive properties. This phenomenon could be examined at various level of phosphate concentration since glyphosate inactivation in soils is reported to be lower in soils with a high phosphate concentration.

Herbicides and pesticides are added to crops and soils in large quantities for specific purposes. If these compounds possess stongly binding functional groups, and are allowed to accumulate in soils, they could have adverse effects on the environment and on plant growth in the long term.

REFERENCES

[Ada32] R. Adams and W. D. Langley,
Methyleneaminoacetonitrile.,
Organic Syntheses, 1932, **Coll. Vol. 1**, p347.

[Alb62] A. Albert and D. Serjeant,
Ionisation constants of acids and bases.,
Methuen and company limited, London, 1962.

[Alc88] E. N. Alcantara and D. L. Wyse,
Glyphosate as harvest aid for corn (*Zea mays*).,
Weed Technology, 1988, **2**, p410.

[Amr80] N. Amrhein, B. Deus, P. Gehrke and H. C. Steinrucken,
The site of the inhibition of the shikimate pathway by glyphosate.
II. Interference of glyphosate with chorismate formation
in *vivo* and in *vitro*.,
Plant Physiology, 1980, **66**, p830.

[App84] T. G. Appleton, J. R. Hall, A. D. Harris, H. A. Kimlin
and I. J. McMahon,
NMR study of acid - base equilibria of aminoalkylphosphonic acids.
$^{+}NH_3(CH_2)_nPO_3H^-$ (n = 1, 2, 3) : Evidence for cyclization in
solution.,
Australian Journal of Chemistry, 1984, **37**, p1833.

[App86] T. G. Appleton, J. R. Hall and I. J. McMahon,
NMR spectra of iminobis(methylenephosphonic acid),
$HN(CH_2PO_3H_2)_2$,and related ligands and their complexes with
platinum(II).,
Inorganic Chemistry, 1986, **25**, p726.

[Arn39] D. I. Arnon and P. R. Stout,
The essentiality of certain elements in minute quantity for
plants with special reference to copper.,
Journal of Plant Physiology, 1939, **14**, p371.

[Ass90] F. van Assche and H. Clijsters,
Effects of metals on enzyme activity in plants.,
Plant, Cell and Environment, 1990, **13**, p195.

[Bae76] C. F. Baes Jnr and R. E. Mesmer,
The hydrolysis of cations.,
John Wiley and sons, inc., New York, 1976.

[Bak49] W. Baker, W. D. Ollis and V. D. Poole,
Cyclic meso-ionic compounds. Part 1. The structure of the sydnones and related compounds.,
Journal of the Chemical Society, 1949, p307.

[Bal79] J. W. Ball, E. A. Jenne and D. K. Nordstrom,
WATEQ2 - A computerised chemical model for trace and major element speciation and mineral equilibria of natural waters.,
Chapter 36 *In* Chemical modeling in aqueous systems.,
edited by E. A. Jenne,
American Chemical Society Symposium Series 93, 1979.

[Ban86] F. Bangerth,
Natural and synthetic plant growth substances in fruit growing.,
In Plant Growth Substances 1986. Proceedings of the 12th International Conference on plant growth substances., edited by Martin Bopp,
Springer-Verlag, Berlin, Heidelberg, 1986, p387.

[Bar84] S. A. Barber,
Soil nutrient bioavailability - A mechanistic approach.,
John Wiley and Sons, Toronto, 1984.

[Bas83] J. Basset, R. C. Denney, G. H. Jeffrey and J. Mendham,
Vogel's textbook of quantitative inorganic analysis, 4th edition,
Longman, London, 1983.

[Bec69] E. D. Becker,
High resolution NMR.,
Academic Press, New York, 1969.

[Bec90] M. T. Beck and I. Nagypal,
Chemistry of complex equilibria.,
Ellis Horwood ltd., Budapest, 1990.

[Ben57] N. R. Benson, L. P. Batjer and I. C. Chmelir,
Response of some deciduous fruit trees to zinc chelates.,
Soil Science, 1957, **84**, p63.

[Ben82] J. Benton-Jones Jnr,
Hydroponics: Its history and use in plant nutrition studies.,
Journal of Plant Nutrition, 1982, **5**(8), p1003.

[Bie82] H.F.Bienfait, J.F.Duivenvoorde and W.Verkerke,
Ferric reduction by roots of chlorotic bean plants:
Indication for an enzymatic process.,
Journal of Plant Nutrition, 1982, **5**(4-7), p451.

[Bin86] F. T. Bingham, F. J. Peryea and W. M. Jarrell.
Metal toxicity to agricultural crops.,
In Metal ions in biological systems. Volume 20,
Concepts on metal ion toxicity., edited by Helmut Sigel,
Marcel Decker, Inc., New York and Basel, 1986, p119.

[Bje41] J. Bjerrum,
Metal amine formation in aqueous solution.,
P. Haase and son, Copenhagen, 1941.

[Boh85] H. L. Bohn, B. L. McNeal and G. A. O'Connor,
Soil Chemistry, 2nd edition.,
John Wiley and sons, Toronto, 1985.

[Bon82] M. Bonneau and B. Souchier,
Constituents and properties of soils.,
Academic Press, London, 1982.

[Bre80] B. J. Brecke and W. B. Duke,
Effect of glyphosate on Intact Bean Plants (*Phaseolus vulgaris L.*) and isolated cells.,
Plant Physiology, 1980, **66**, p656.

[Bre87] E. Breitmaier and W. Voelter,
Carbon - 13 NMR spectroscopy.,
VCH, Weinheim, 1987.

[Bri46] S. R. Brinkley,
Note on the conditions of equilibrium for systems of many constituents.,
Journal of Chemical Physics, 1946, **14**(9), p563.

[Bri47] S. R. Brinkly,
Calculation of the equilibrium composition of systems of many constituents.,
Journal of Chemical Physics, 1947, **15**(2), p107.

[Bro56] J. C. Brown,
Iron Chlorosis.,
Annual Review of Plant Physiology, 1956, **7**, p171.

[Bro73] J. C. Brown and J. E. Ambler,
"Reductants" released by roots of Fe-deficient soybeans.,
Agronomy Journal, 1973, **65**, p311.

[Bro78] J. C. Brown,
Mechanism of iron uptake by plants.,
Plant, Cell and Environment, 1978, **1**, p249.

[Bro86] J. C. Brown and V. D. Jolley,
An evaluation of concepts related to iron-deficiency chlorosis.,
Journal of Plant Nutrition, 1986, **9**(3-7), p175.

[Bro87] P. H. Brown, R. M. Welch, E. E. Cary and R. T. Checkai,
Beneficial effects of nickel on plant growth.,
Journal of Plant Nutrition, 1987, **10**(9-16), p2125.

[Bur88] J. Burgess,
Ions in solution - Basic principles of chemical interactions.,
Ellis Horwood ltd., Chichester, 1988.

[Cha81] M. Chand, N. S. Randhawa and D. R. Bhumbla,
Effectiveness of zinc chelates in zinc nutrition of greenhouse rice crop in a saline-sodic soil.,
Plant and Soil, 1981, **59**, p217.

[Che53] K. L. Cheng, R. H. Bray and T. Kurtz,
Determination of total iron in soils by disodium dihydrogen ethylenediamine tetraacetate titration.,
Analytical Chemistry, 1953, **25**, p347.

[Chr74] R. A. Christ,
A method to compare the effect of ionic iron and iron chelates in nutrient solution cultures.,
Plant Physiology, **54**, 1974, p579.

[Chu86] H. C. Chun,
N - Phosphonomethylglycine.,
British Patent, 2 154 588,
Chemical Abstracts, 1986, **104**, 130270q, p739.

[Cla80] D. T. Clarkson and J. B. Hanson,
The mineral nutrition of higher plants.,
Annual Review of Plant Physiology, **31**, 1980, p239.

[Coc91] S. Cocks-Wilson, P. W. Linder and A. Voye,
Potentiometric investigations of equilibria between caffeic acid and manganese(II), cobalt(II), nickel(II) and cadmium(II) ions in aqueous solution.,
In press, 1991.

[Dav62] C. W. Davies,
Ion Association.,
Butterworths, Washington, 1962.

[Dav80] B. E. Davies,
Applied soil trace elements.,
John Wiley and Sons, Chichester, 1980.

[Dav88] B. E. Davies,
Trace metals in soil.,
Chemistry in Britain, 1988, **24**(2), p149.

[Dek57] P. C. DeKock and R. L. Mitchell,
Uptake of chelated metals by plants.,
Soil Science, 1957, **84**, p55.

[Der87] A. E. Derome,
Modern NMR techniques for chemistry research.,
Pergamon Press, Oxford, 1987.

[Dha90] M. A. Dhansay, P. W. Linder, R. G. Torrington and T. A. Modro,
Organophosphorus herbicides and plant growth regulators.
Part 1. Synthesis and protonation behaviour of glyphosate and related compounds.,
Journal of Physical Organic Chemistry, 1990, **3**, p248.

[Dow70] D.N.Dower, W.B.Davis and B.R.Byers,
Repression of phenolic acid-synthesising enzymes and its relation to iron uptake in *Bacillus Subtilis*.,
Journal of Bacteriology, 1970, **101**, p181.

[Duk78] S. O. Duke and R. E. Hoagland,
Effects of glyphosate on metabolism of phenolic compounds.
I. Induction of phenylalanine ammonia lyase activity in dark-grown maize roots.
Plant Science Letters,1978, **11**, p185.

[Dzo87] D. A. Dzombak, A. M. ASCE and F. M. M. Morel,
Adsorption of inorganic pollutants in aquatic systems.,
Journal of Hydraulic Engineering, ASCE, 1987, **113**, p430.

[Ebs87] E. A. V. Ebsworth, D. W. H. Rankin and S. Cradock,
Stuctural methods in inorganic chemistry.,
Blackwell Scientific Publications, Oxford, 1987.

[Elk74a] D. M. Elkins and D. L. Suttner,
Chemical regulation of grass growth. I. Field and greenhouse studies with Tall Fescue.,
Agronomy Journal, 1974, **66**, p487.

[Elk74b] D. M. Elkins, J. A. Tweedy and D. L. Suttner,
Chemical regulation of grass growth. II. Greenhouse and field studies with intensively managed turfgrasses.,
Agronomy Journal, 1974, **66**, p492.

[Eps65] E. Epstein,
Mineral metabolism in plant biochemistry.,
Academic Press, New York, 1965.

[Eps72] E. Epstein,
Mineral nutrition of plants: Principles and perspectives.,
John Wiley and Sons, Toronto, 1972.

[Fal89] J. M. Falco, L. Vilanova, J. Segura,
Effects of glyphosate on phenolic compounds and free amino acids in oat seedlings.,
Agrochimica, 1989, **33**(3), p166.

[Fei72] F. Feigl and V. Anger,
Spot tests in inorganic analysis, 6th edition,
Elsevier publishing company, 1972.

[Fie52] E. K. Fields,
The synthesis of esters of substituted amino phosphonic acids.,
Journal of the American Chemical Society, 1952, **74**, p1528.

[Fit83] E. A. Fitzpatrick,
SOILS; Their formation, classification and distribution.,
Longman, New York, 1983.

[Fit86] E. A. Fitzpatrick,
An introduction to soil science, 2nd Ed.,
Longman, New York, 1986.

[Fle80] G. Flegmann and R. A. T. George,
Soils and other growth media.,
Avi Publishing Company, Connecticut, 1980.

[Flo82] T. M. Florence,
The speciation of trace elements in waters.,
Talanta, 1982, **29**, p345.

[Fot84] H. D. Foth,
Fundamentals of soil science, 7th edition.,
John Wiley and Sons, Toronto, 1984.

[Foy78] C. D. Foy, R. L. Chaney and M. C. White,
The physiology of metal toxicity in plants.,
Annual Review of Plant Physiology, **29**, 1978,p511

[Fra72] J. E. Franz,
Phytotoxic N - (Phosphonomethyl) glycine derivatives.,
German Patent 2 152 826,
Chemical Abstracts, 1972, **77**, 165079k, p451.

[Fur89] G. Furrer, J. Westall and P. Sollins,
The study of soil chemistry through quasi-steady-state models:
I. Mathematical definition of model.
Geochimica et Cosmochimica Acta, 1989, **53**, p595.

[Fur90] G. Furrer, P. Sollins and J. Westall,
The study of soil chemistry through quasi-steady-state models:
II. Acidity of soil solution.
Geochimica et Cosmochimica Acta, 1990, **54**, p2363.

[Gan85] P. Gans, A. Sabatini and A. Vacca,
SUPERQUAD: - An improved general program for computation of formation constants from potentiometric data.
Journal of the Chemical Society, Dalton Transactions, 1985, p1195.

[Gla60] P. K. Glasoe and F. A. Long
Use of glass electrodes to measure acidities in deuterium oxide.,
Journal of Physical Chemistry, 1960, **64**, p188.

[Gor84] D. G. Gorenstein,
Phosphorus - 31 NMR.,
Academic Press, New York, 1984.

[Gra88] R. D. Graham, R. J. Hannam and N. C. Uren,
Manganese in soils and plants.,
Kluwer Academic Publishers, Dordrecht, 1988.

[Gre79] P. M. Gresshoff,
Growth inhibition by glyphosate and reversal of its action by phenylalanine and tyrosine.,
Australian Journal of Plant Physiology, 1979, **6**, p177.

[Gun80] H. Gunther,
NMR Spectroscopy :- An introduction.,
John Wiley and Sons, New York, 1980.

[Had77] L. C. Haderlie, J. M. Widholm and F. W. Slife,
Effect of glyphosate on carrot and tobacco cells.,
Plant Physiology, 1977, **60**, p40.

[Hag69] R. Hagen and J. D. Roberts,
Nuclear magnetic resonance spectroscopy. ^{13}C spectra of aliphatic carboxylic acids and carboxylate anions.,
Journal of the American Chemical Society, 1969, **91**, p4504.

[Hak84] P. Hakinnen,
Formation of copper(II) and zinc(II) complexes of 1, 2 - dihydroxy - 4 - nitrobenzene in aqueous solution.,
Finnish Chemistry Letters, 1984, **1**, p9.

[Hal72a] M. Halman,
Analytical chemistry of phosphorus compounds.,
Wiley - Interscience, New York, 1972.

[Hal72b] A. D. Halvorson and W. L. Lindsay,
Equilibrium relationships of metal chelates in hydroponic solutions.,
Soil Science Society of America Proceedings, 1972, **36**, p755.

[Hal90] M. Halmann,
Synthetic plant growth regulators.,
Advances in Agronomy, 1990, **43**, p47.

[Har80] F. R. Hartley, C. Burgess and R. Alcock,
Solution equilibria.,
Ellis Horwood ltd., Chichester, 1980.

[Har83] W. R. Harris,
Structure - reactivity relation for the complexation of Ni, Cd, Zn, and Fe.,
Journal of Coordination Chemistry, 1983, **13**, p17.

[Her89] J. G. Hering and F. M. M. Morel,
Slow coordination reactions in seawater.
Geochimica et Cosmochimica Acta, 1989, **53**, p611.

[Hes80] J. Heslop-Harrison,
Darwin and the movement of plants: A retrospect.,
In Plant Growth Substances 1979. Proceedings of the 10th International Conference on Plant Growth Substances., Ed. by F. Skoog,
Springer-Verlag, Berlin Heidelberg, 1980, p3.

[Het84] N.H.Hether, R.A.Olsen, L.L.Jackson,
Chemical identification of iron reductants exuded by plant roots.,
Journal of Plant Nutrition, 1984, **7**(1-5), p667.

[Hew52] E. J. Hewitt,
Sand and water culture methods used in the study of plant nutrition.,
Bradley and Son Ltd, Reading, 1952.

[Hil57] D. G. Hill-Cottingham,
A spectrophotometric method of analysis of chelate solutions and its application to the study of iron chelates in soils and plants.,
Soil Science, 1957, **84**, p43.

[Hod69] J. F. Hodgson,
Contribution of metal-organic complexing agents to the transport of metals to roots.,
Soil Science Society of America Proceedings, 1969, **33**, p68.

[Hol80] H. Hollander and N. Amrhein,
The site of the inhibition of the shikimate pathway by glyphosate.
I. Inhibition by glyphosate of phenylpropanoid synthesis in buckwheat.,
Plant Physiology, 1980, **66**, p823.

[Hor65] L. Horner and E. Geyer,
Redoxpotentiale von brenzcatechin derivaten.,
Chemische Berichte, **98**, 1965, p2016.

[Ing64] N. Ingri and L. G. Sillen,
High speed computers as a supplement to graphical methods.
IV. An ALGOL version of LETAGROP VRID.,
Arkiv Kemi, 1964, **23**, p97.

[Ing67] N. Ingri, W. Kakolowicz, L. G. Sillen and B. Warnqvist,
High speed computers as a supplement to graphical methods:
V. HALTAFALL, a general program for calculating the composition of equilibrium mixtures.
Talanta, 1967, **14**, p1261.

[Ins86] W. P. Inskeep and S. D. Comfort,
Thermodynamic predictions for the effects of root exudates on metal speciation in the rhizosphere.,
Journal of Plant Nutrition, 1986, **9**(3-7), p567.

[Irv53] H. Irving and R. J. P. Williams,
The stability of transition metal complexes.,
Journal of the Chemical Society, 1953, p3192.

[Jan86] J. Jannick,
Horticultural science, 4th Ed.,
W. H. Freeman and company, New York, 1986.

[Jaw72] E. G. Jaworski,
Mode of action of N-Phosphonomethyl glycine: Inhibition of aromatic amino acid biosynthesis.,
Journal of Agriculture and Food Chemistry, 1972, **20**(6), p1195.

[Jen79] E. A. Jenne,
Chemical modelling - goals, approaches and priorities.,
Chapter 1 *In* Chemical modeling in aqueous systems.,
edited by E. A. Jenne,
American Chemical Society Symposium Series 93, 1979.

[Joh24] T. B. Johnson and W. W. Rinehart,
The isomeric modification of methyleneaminoacetonitrile and their biochemical significance.,
Journal of the American Chemical Society, 1924, **46**, p768.

[Jul83] G.Julian, H.J.Cameron and R.A.Olsen,
Role of chelation by ortho dihydroxy phenols in iron absorbtion by plant roots.,
Journal of Plant Nutrition, 1983, **6**(2), p163.

[Jun86] J. Jung,
Aims and possibilities of applied plant bioregulation.,
In Plant Growth Substances 1986. Proceedings of the 12th International Conference on plant growth substances., edited by Martin Bopp, Springer-Verlag, Berlin, Heidelberg, 1986, p363.

[Kab84] A. Kabata-Pendias and H. Pendias,
Trace elements in soils and plants.,
CRC Press, Florida, 1984.

[Kan87] S. Kannan and S. Ramani,
Mechanisms of Fe-deficiency tolerance in crop cultivars:
Effects of dibutyl phthalate and caffeic acid on Fe-chlorosis recovery.,
Journal of Plant Nutrition, 1987, **10**(9-16), p1051.

[Kar84] S. W. Karickoff,
Organic pollutant sorption in aquatic systems.,
Journal of Hydraulic Engineering, ASCE, 1984, **110**, p707.

[Kir73] A. Yu. Kireeva, B. V. Zhadanov, V. V. Sidorenko and N. M. Dyatlova,
Synthesis and acid dissociation of
[Bis(Phosphonomethyl)amino] acetic acid.,
Journal of General Chemistry, USSR (Eng. transl.), 1973, **43(11)**, p2494
or *Zhurnal Obshchei Khimii*, 1973, **43(11)**, p2508.

[Kos73] N. A. Kostromina,
The use of proton magnetic resonance in the study of complexones.,
Russian Chemical Reviews, 1973, **42**(4), p261.

[Kro57] H. Kroll,
The ferric chelate of ethylenediamine
di(O-hydroxyphenylacetic acid) for treatment of lime-induced chlorosis.,
Soil Science, 1957, **84**, p51.

[Lam85] I. Lamy, M. Seywert, M. Cromer and J-P. Scharff,
Simple and mixed ligand complexes of copper(II) with polyfunctional
phenolic compounds as models of natural substances.,
Analytica Chimica Acta, 1985, **176**, p201.

[Lan81] E.C.Landsberg,
Organic acid synthesis and release of hydrogen ions in response
to Fe deficiency stress of mono- and dicotyledonous plant species.,
Journal of Plant Nutrition, 1981, **3**(1-4), p579.

[Lee82] T. T. Lee,
Promotion of indole-3-acetic acid oxidation by glyphosate in
tobacco callus tissue.,
Journal of Plant Growth Regulation, 1982, **1**, p37.

[Lee83] T. T. Lee, T. Dumas and J.J. Jevnikar,
Comparison of the effects of glyphosate and related compounds on
indole-3-acetic acid metabolism and ethylene production in
Tobacco Callus.,
Pesticide Biochemistry and Physiology, 1983, **20**, p354.

[Lee84] T. T. Lee,
Release of lateral buds from apical dominance by glyphosate in
soybean and pea seedlings.,
Journal of Plant Growth Regulation, 1984, **3**, p227.

[Lee85] T. T. Lee,
Effect of glyphosate on indole-3-acetic acid metabolism in
tolerant and susceptible plants.,
Journal of Plant Growth Regulation, 1985, **4**, p29.

[Leg77] D. J. Leggitt,
Machine computation of equilibrium concentrations - some practical considerations.,
Talanta, 1977, **24**, p535.

[Leg85] D. J. Leggett,
Computational methods for the determination of formation constants.,
Plenum Press, New York, 1985.

[Ler88] Lerida Union Quimica S. A.,
Process for the preparation of N - (Phosphonomethyl) glycine.,
Spanish Patent, 553 523,
Chemical Abstracts, 1988, **109**, 73659a, p714

[Lev80] G. C. Levy, R. L. Lichter and G. L. Nelson,
Carbon - 13 nuclear magnetic resonance spectroscopy, 2nd edition.,
Wiley - Interscience, New York, 1980.

[Lil71] M. Liler,
Reaction mechanisms in sulfuric acid.,
Academic Press, New York, 1971.

[Lin67] W. L. Lindsay, J. F. Hodgson and W. A. Norvell,
The physico-chemical equilibrium of metal chelates in soils and their influence on the availability of micronutrient cations.,
International Society of Soil Science (Aberdeen, Scotland), Trans. Comm. II, IV, 1967, p305

[Lin69] W. L. Lindsay and W. A. Norvell,
Equilibrium relationships of Zn^{2+}, Fe^{3+}, Ca^{2+} and H^{+} with EDTA and DTPA in soils.,
Soil Science Society of America Proceedings, 1969, **33**, p62.

[Lin78a] D. J. Linehan,
The uptake by plants of polymaleic acid: A polycarboxylic acid structurally related to those of soils.,
Plant and Soil, 1978, **50**, p625.

[Lin78b] D. J. Linehan,
Humic acid and iron uptake by plants.,
Plant and Soil, 1978, **50**, p671.

[Lin78c] W. L. Lindsay,
Chemical reactions affecting the availability of micronutrients in soils.,
In A. Kamprath (ed.) Mineral nutrition of legumes in tropical and subtropical soils ., 1978, p153.

[Lin79a] W. L. Lindsay,
Chemical equilibria in soils.,
Wiley Interscience, New York, 1979.

[Lin79b] D. J. Linehan and H. Shepherd,
A comparative study of the effects of natural and synthetic ligands on iron uptake by plants.,
Plant and Soil, 1979, **52**, p281.

[Lin82a] W. L. Lindsay and A. P. Schwab,
The chemistry of iron in soils and its availability to plants.,
Journal of Plant Nutrition, 1982, **5**(4-7), p821.

[Lin82b] P. W. Linder and K. Murray,
Correction of formation constants for ionic strength from only one or two data points: An examination of the use of the extended Debye- Hückel equation.,
Talanta, 1982, **29**, p377.

[Lin84a] P. W. Linder, R. G. Torrington and D. R. Williams,
Analysis using glass electrodes.,
Open University Press, London, 1984.

[Lin84b] R. D. Lindberg and D. D. Runnels,
Ground water redox reactions: An analysis of equilibrium state applied to Eh measurements and geochemical modeling.,
Science, 1984, **225**, p925.

[Lin87] P. W. Linder and A. Voye,
Potentiometric investigations of the equilibria between caffeic acid and copper(II), zinc(II), iron(II) and hydrogen ions in aqueous solution.,
Polyhedron, 1987, **6**(1), p53.

[Lin88] P. W. Linder and A. Voye,
Influence of synthetic chelating agents on the speciation of copper, zinc and manganese in plant nutrient solutions.,
Journal of Co-ordination Chemistry, 1988, **17**, p381.

[Lin90] P. W. Linder, A. Voye and S. Cocks,
The effect of caffeic acid on the speciation of metal ions in plant nutrient solutions.,
In Metal speciation in the environment, NATO ASI Series, Springer Verlag, 1990.

[Lit84] J. Little,
Chemical modelling of urine.,
M.Sc Thesis, University of Cape Town, 1984.

[Mai80] L. Maier and M. J. Smith,
Organic phosphorus compounds. Part 72. Preparation and properties of bis(N-hydroxycarbonylmethylaminoethyl) phosphinic acid $(HO_2CCH_2NHCH_2)_2P(O)OH$ and its derivatives.,
Phosphorus and Sulfur, 1980, **8**(1), p67.

[Mai82] L. Maier,
N - Phosphonomethylglycine.,
European Patent, 55 695,
Chemical Abstracts, 1982, **97**, 182864t, p875

[Maj80] J. Majer, Trinh van Quy and I. Valaskova,
Elektrophoretisches studium der komplexbildenden eigenchaften der N - (Methylphosphon) iminodiessigsaure und der Glycine - N, N - bis (methylphosphonsaure).,
Chem. Zvesti, 1980, **34**(5), p637.

[Mar57] A. E. Martell,
The chemistry of metal chelates in plant nutrition.
Soil Science, 1957, **84**, p13.

[Mar73] R. P. Martin, M. M. Petit - Ramel and J. P. Scharff,
Mixed - ligand metal ion complexes of amino acids and peptides.,
In Metal ions in biological systems. Volume 2,
Mixed - ligand complexes., edited by Helmut Sigel,
Marcel Decker, Inc., New York, 1973, p1.

[Mar74] A. E. Martell and R. M. Smith,
Critical Stability Constants, Volume 1, Amino Acids.,
Plenum Press, New York, 1974.

[Mar75] A. E. Martell and R. M. Smith,
Critical Stability Constants, Volume 2, Amines.,
Plenum Press, New York, 1975.

[Mar76] A. E. Martell and R. M. Smith,
Critical Stability Constants, Volume 4, Inorganic Complexes.,
Plenum Press, New York, 1976.

[Mar77] A. E. Martell and R. M. Smith,
Critical Stability Constants, Volume 3, Other Organic Ligands.,
Plenum Press, New York, 1977.

[Mar82] A. E. Martell and R. M. Smith,
Critical Stability Constants, Volume 5, First Supplement.,
Plenum Press, New York, 1982.

[Mar86] H. Marshner,
Mineral nutrition of higher plants.,
Academic Press, London, 1986.

[Mar88] A. E. Martell and R. J. Motekaitis,
The determination and use of stability constants.,
VCH Publishers, New York, 1988.

[Mar89] A. E. Martell and R. M. Smith,
Critical Stability Constants, Volume 6, Second Supplement.,
Plenum Press, New York, 1989.

[Mat79] S. V. Mattigod and G. Sposito,
Chemical modeling of trace metal equilibria in contaminated soil solutions using the computer program GEOCHEM.
Chapter 37 *In* Chemical modeling in aqueous systems.,
edited by E. A. Jenne,
American Chemical Society Symposium Series 93, 1979.

[May76] P. M. May, P. W. Linder and D. R. Williams,
Ambivalent effect of protein binding on computed distributions of metal ions complexed by ligands in blood plasma.,
Experietia, 1976, **32**, p1492.

[May77] P. M. May, P. W. Linder and D. R. Williams,
Computer simulation of metal ion equilibria in biofluids:-
Models for the low molecular weight complex distribution of calcium(II), magnesium(II), manganese(II), iron(III), copper(II), zinc(II) and lead(II) ions in human blood plasma.,
Journal of the Chemical Society, Dalton Trans., 1977, p588.

[May82] P. M. May, D. R. Williams, P. W. Linder and R. G. Torrington,
The use of glass electrodes for the determination of formation constants - I. A definitive method for calibration.,
Talanta, 1982, **29**, p249.

[May85] P. M. May, K. Murray and D. R. Williams,
The use of glass electrodes for the determination
of formation constants - II. Simulation of
titration data.,
Talanta, 1985, **32**(6), p483.

[May87] P. M. May and K. Murray,
JESS (Joint Expert Speciation System).,
Talanta, 1987, **34**, p821.

[May88a] P. M. May, K. Murray and D. R. Williams,
The use of glass electrodes for the determination of formation
constants - III. Optimization of titration data:
The ESTA library of computer programs.,
Talanta, 1988, **35**(11), p825.

[May88b] P. M. May, K. Murray and D. R. Williams,
The use of glass electrodes for the determination
of formation constants - IV. Matters of weight.,
Talanta, 1988, **35**(12), p972

[McD73] R. E. McDuff and F. M. Morel,
Description and use of the chemical equilibrium program REDEQL2.,
Keck Laboratory Technical Report, EQ-73-02, California
Institute of Technology, Pasadena, 1973.

[Mel88] M. Meloun, J. Havel and E. Hogfeldt,
Computation of solution equilibria: A guide to methods in
potentiometry, extraction and spectrophotometry.,
Ellis Horwood Limited, Chichester, 1988.

[Mer81] W. Mertz,
The essential trace elements.,
Science, 1981, **213**, p1332.

[Mer89] Merck spectrum,
Merck publication 1/89, 1989.

[Merck] E. Merck,
Complexometric assay methods with titriplex, 3rd edition.,
Merck publication.

[Meu90] K. van der Meulen,
Computer modelling of the chemical speciation in sea water.,
M.Sc Thesis, University of Cape Town, 1990

[Moe66] K. Moedritzer and R. R. Irani,
The direct synthesis of a - aminomethylphosphonic acids.
Mannich - type reactions with orthophosphorous acid.
Journal of Organic Chemistry, 1966, **31**, p1603.

[Mor72] F. Morel and J. Morgan,
A numerical method for computing equilibria in aqueous
chemical systems.
Environmental Science and Technology, 1972, **6**(1), p58.

[Mot80] R. J. Motekaitis and A. E. Martell,
Galium complexes of multidentate ligands in aqueous solution.,
Inorganic chemistry, 1980, **19**, p1646.

[Mot82] R. J. Motekaitis and A. E. Martell,
BEST: - A new program for rigorous calculation of
equilibrium parameters of complex multicomponent
systems.,
Canadian Journal of Chemistry, 1982, **60**, p2403.

[Mot85] R. J. Motekaitis and A. E. Martell,
Metal chelate formation by N - Phosphonomethylglycine and
related ligands.,
Journal of Coordination Chemistry, 1985, **14**, p139.

[Muc88] R. M. C. Muchovej, V. G. Allen, D. C. Martens and J. J. Muchovej,
Effects of aluminium chelates in nutrient solution on the growth and
composition of ryegrass.,
Journal of Plant Nutrition, 1988, **11**(2), p117.

[Mur82] K. Murray,
A computer simulation of metal ion equilibria in soil solutions.,
PhD Thesis, University of Cape Town, 1982.

[Nic78] L. G. Nickell,
Plant growth regulators.,
Chemical and Engineering News, 1978, **56**(41), p18.

[Nic82] L. G. Nickell,
Plant growth regulators.
Springer-Verlag, Berlin Heidelberg, 1982.

[Nie76] N. E. Nielson,
The effects of plants on the copper concentration in the soil solution.,
Plant and Soil, 1976, **45**, p679.

[Nik74] L. V. Nikitina, L. D. Karmazina and N. M. Dyatlova,
The formation of transition metal complexes of glycine -
N,N-di(Methylenephosphonic) acid.,
Russian Journal of Inorganic Chemistry, 1974, **19**(11), p1671.

[Nob89] P. S. Nobel and J. A. Palta,
Soil O_2 and CO_2 effects on root respiration of cacti.,
Plant and Soil, 1989, **120**, p263.

[Nor69] W. A. Norvell and W. L. Lindsay,
Reactions of EDTA complexes of Fe, Zn, Mn and Cu in soils.,
Soil Science Society of America Proceedings, 1969, **33**, p86.

[Nor72a] W. A. Norvell,
Equilibria of metal chelates in soil solution.,
In Micronutrients in Agriculture.,edited by J. J. Mortvedt
*Soil Science Society of Amer*ica; Madison, Wisconsin, 1972, p115

[Nor72b] W. A. Norvell and W. L. Lindsay,
Reactions of DTPA chelates of iron, zinc, copper and manganese with soils.,
Soil Science Society of America Proceedings, 1972, **36**, p778.

[Nor79] D. K. Nordstrom, L. M. Plummer, T. M. L. Wigley, T. J. Wolery, J. W. Ball, E. A. Jenne, R. L. Bassett, D. A. Crerar, T. M. Florence, B. Fritz, M. Hoffman, G. R. Holdren, Jnr., G. M. Lafon, S. V. Mattigod, R. E. McDuff, F. Morel, M. M. Reddy, G. Sposito, and J. Thrailkill,
A comparison of computerised chemical models for equilibrium calculations in aqueous systems.
Chapter 38 *In* Chemical modeling in aqueous systems.,
edited by E. A. Jenne,
American Chemical Society Symposium Series 93, 1979.

[Oer74] J. J. Oertli and A. A. Opoku
Effect of macronutrient ions on the availability of iron from a chelated source.,
Soil Science Society of America Proceedings, 1974, **38**, p597.

[Ola85] G. A. Olah, G. K. S. Prakash and J. Sommer,
Superacids.,
Wiley, New York, 1985.

[Ole80] J. Oleksyszyn,
1 - N - Alkylaminoalkanephosphonic and 1 - N - Alkylaminoalkyl - phenylphosphinic acids.,
Synthesis, 1980, p722.

[Ols80a] R.A.Olsen and J.C.Brown,
Factors related to iron uptake by dicotyledonous and monocotyledonous plants. I. pH and reductant.,
Journal of Plant Nutrition, 1980, **2**(6), p629.

[Ols80b] R.A.Olsen and J.C.Brown,
Factors related to iron uptake by dicotyledonous and monocotyledonous plants. II. The reduction of Fe^{3+} as influenced by roots and inhibitors.,
Journal of Plant Nutrition, 1980, **2**(6), p647.

[Ols81] R.A.Olsen, J.H.Bennet, D.Blume and J.C.Brown,
Chemical aspects of the Fe stress response mechanism in tomatoes.,
Journal of Plant Nutrition, 1981, **3**(6), p905.

[Pau89] E. A. Paul and F. E. Clark,
Soil microbilogy and biochemistry.,
Academic Press, New York, 1989.

[Per67] D. D. Perrin and I. G. Sayce,
Computer calculation of equilibrium concentrations in mixtures of metal ions and complexing species.
Talanta, 1967, **14**, p833.

[Pre90] P. J. Pretorius,
A computer simulation of the protonation and metal complexation properties of fulvic acids.
M. Sc Thesis, University of Cape Town, 1990.

[Pyt79] R. M. Pytkowicz,
Activity coefficients in electrolyte solutions.,
CRC Press, Florida, 1979.

[Qui74] A. R. Quirt, J. R. Lyerla, I. R. Peat, J. S. Cohen, W. F. Reynolds and M. H. Freedman,
Carbon - 13 nuclear magnetic resonance titration shifts in amino acids.,
Journal of the American Chemical Society, 1974, **96**, p570.

*

[Ric74] B. N. Richards,
Introduction to the soil ecosystem.,
Longman Group Limited, Essex, 1974.

* [Ren 89] V. V. Rendig and H. M. Taylor,
Principles of Soil - Plant Interrelationships
McGraw - Hill Publishing company, New York 1989.

[Ril91] D. P. Riley, D. L. Fields and W. Rivers,
Homogeneous catalysts for selective molecular oxygen driven oxidative decarboxylations.,
Journal of the American Chemical Society, 1991, **113**(9), p3371.

[Roi74] U. Roisch and F. Lingens,
Effect of the herbicide N-Phosphonomethyl glycine on the biosynthesis of aromatic amino acids.,
Angewandte Chemie, International Edition, 1974, **13**(6), p400.

[Rom82] V.Romheld, H.Marshner and D.Kramer,
Responses to Fe deficiency in roots of "Fe-efficient" plant species.,
Journal of Plant Nutrition, 1982, **5**(4-7), p489.

[Ros61] F. C. Rossotti and H. Rossotti,
The determination of stability constants.,
McGraw Hill, New York, 1961.

[Ros78] H. Rossotti,
The study of ionic equilibria.,
Longman, London, 1978.

[Rue77] M. L. Rueppel, B. B. Brightwell, Jacob Schaefer and J. T. Marvel,
Metabolism and degradation of glyphosate in soil and water.,
Journal of Agriculture and Food Chemistry, 1977, **25**(3), p517.

[Rus73] E. W. Russell,
Soil conditions and plant growth, 10th edition.,
Longman, London, 1973.

[Sab74] A. Sabatini, A. Vacca and P. Gans,
MINIQUAD: - A general computer program for the computation of formation constants from potentiometric data.,
Talanta, 1974, **21**, p53.

[Sas63] K. Sasse,
Organische Phosphorverbindungen, Vol. XII/2,
Georg Thieme, Stuttgart, 1963.

[Say68] I. G. Sayce,
Computer calculations of equilibrium constants of
species present in mixtures of metal ions and
complexing agents.,
Talanta, 1968, **22**, p1397.

[Sch57] G. Schwarzenbach,
Complexometric titrations.,
Methuen and co. ltd., London, 1957.

[Sha87] S. A. Shaban, A. H. El-Hattab, E. A. Hassan and M. R. Abo-El Suoud,
Recovery of Faba bean (*Vicia faba L.*) plants as affected by glyphosate.,
Journal of Agronomy and Crop Science, 1987, **158**, p294.

[Shu83] L. M. Shukla, R. K. Rattan and B. K. Misra,
Role of cobalt in soil and plant nutrition - A review.,
International Journal of Tropical Agriculture, 1983, **1**(2), p111.

[Sil67] L. G. Sillen,
How have sea water and air got their present compositions?,
Chemistry in Britain, 1967, p291.

[Sim78] J. L. Sims and W. H. Patrick Jnr.,
The distribution of micronutrient cations in soil under conditions
of varying redox potential and pH.,
Soil Science Society of America Journal, 1978, **42**, p258.

[Sin89] S. P. Singh,
Reactions of fulvic acid complexes of Zn and Cu with alkaline soils.,
Agrochimica, 1989, **33**(6), p434.

[Sir87] M. S. Siraj-Ali, J. C. Peterson and H. K. Tayama,
Influence of nutrient solution pH on the uptake of plant nutrients and growth of *Chrysanthemum Morifolium*, " Bright Golden Anne", in hydroponic culture.,
Journal of Plant Nutrition, 1987, **10**(9-16), p2161.

[Sko86] D. A. Skoog and D. M. West,
Fundamentals of Analytical chemistry., 4th Ed.
Saunders College Publishing, Hong Kong, 1986.

[Smi74] L. R. Smith,
Herbicidal N - (Phosphonomethyl) glycine.,
German Patent, 2 314 134,
Chemical Abstracts, 1974, **80**, 3794z, p335.

[Smi83] G. S. Smith, C. M. Johnston and I. S. Cornforth,
Comparison of nutrient solutions for growth of plants in sand culture.,
New Phytology, 1983, **94**, p537.

[Som79] L. E. Sommers and W. L. Lindsay,
Effect of pH and redox on predicted heavy metal-chelate equilibria in soils.,
Soil Science Society of America Journal, 1979, **43**, p39.

[Spa86] D. L. Sparks,
Soil physical chemistry.,
CRC Press, Florida, 1986.

[Spo81] G.Sposito and F. T. Bingham,
Computer modelling of trace metal speciation in soil solutions : Correlations with trace metal uptake by higher plants.,
Journal of Plant Nutrition, 1981, **3**(1-4), p35.

[Spo84] G. Sposito and A. L. Page,
Cycling of metal ions in the soil environment.,
In Metal ions in biological systems. Volume 18,
Circulation of metals in the environment. edited by Helmut Sigel,
Marcel Decker, Inc., New York and Basel, 1984, p287.

[Spr75a] P. Sprankle, W. F. Meggitt and D. Penner,
Rapid inactivation of glyphosate in soil.,
Weed Science, 1975, **23**(3), p224.

[Spr75b] P. Sprankle, W. F. Meggitt and D. Penner,
Adsorption, mobility and microbial degradation of glyphosate in soil.,
Weed Science, 1975, **23**(3), p229.

[Spr75c] P. Sprankle, W. F. Meggitt and D. Penner,
Absorbtion, action and translocation of glyphosate.,
Weed Science, 1975, **23**(3), p235.

[Sta89] C. Starr and R. Taggart,
Biology:- The unity and diversity of life, 5th edition.,
Wadsworth Publishing Company, California, 1989.

[Ste86] F. J. Stevenson,
Cycles of soil.,
John Wiley and Sons, Toronto, 1986.

[Tel80] E. Teller,
The persuit of simplicity.,
Pepperdine University Press, 1980

[Thi74] K. V. Thimann,
Fifty years of plant hormone research.,
Plant Physiology, 1974, **54**, p450.

[Thi80] K. V. Thimann,
The development of plant hormone research in the last 60 years.,
In Plant Growth Substances 1979. Proceedings of the 10th International Conference on Plant Growth Substances., edited by F. Skoog,
Springer-Verlag, Berlin Heidelberg, 1980, p15.

[Tho88] B. M. Thomson, L. L. Barton and P. Jacobs,
Models of complexation which predict iron(II) availability.,
Journal of Plant Nutrition, 1988, 11(6-11), p1063.

[Tif60a] L. O. Tiffin, J. C. Barnes and R. W. Krauss,
Differential absorption of metal chelate components by plant roots.,
Plant Physiology, 1959, **35**, p362.

[Tif60b] L. O. Tiffin, J. C. Brown and R. S. Holmes,
Chelating agent and plant nutrient interactions affecting the iron nutrition of soybeans.,
Soil Science Society Proceedings, 1960, p120.

[Tif61] L. O. Tiffin and J. C. Brown,
Selective absorption of iron from iron chelates by soybean plants.,
Plant Physiology, 1961, **36**, p710.

[Tor77] N. T. L. Torstensson and A. Aamisepp,
Detoxification of glyphosate in soil.,
Weed Research, 1977, **17**, p209.

[Tru74] A. H. Truesdell and B. F. Jones,
WATEQ, a computer program for calculating chemical equilibria of natural waters.
Journal of Research, US Geological Survey, 1974, 2(2), p233.

[Ure84] N.C.Uren,
Forms, reactions and availability of iron in soils.,
Journal of Plant Nutrition, 1984, 7(1-5), p165.

[Van64] V.Vancura,
Root exudates of plants. I. Analysis of root exudates of barley and wheat in their initial stages of growth.,
Plant and Soil, 1964, **21**(2), p231.

[Van65] V.Vancura and A.Hovadik,
Root exudates of plants. II. Composition of root exudates of some vegetables.,
Plant and Soil, 1965, **22**(1), p21.

[Van67] V.Vancura,
Root exudates of plants. III. Effect of temperature and "cold shock" on the exudation of various compounds from seeds and seedlings of maize and cucumber.,
Plant and Soil, 1967, **27**(3), p319.

[Van72] V.Vancura and A.Hanzlikova,
Root exudates of Plants. IV. Differences in chemical composition of seed and seedlings exudates.,
Plant and Soil, 1972, **36**, p271.

[Voy85] A. G. Voye,
Chemical modelling of plant nutrient solutions.,
M.Sc Thesis, University of Cape Town, 1985.

[Wal55] A. Wallace, R. T. Mueller, O. R. Lunt, R. T. Ashcroft and L. M. Shannon,
Comparisons of five chelating agents in soils, in nutrient solutions, and in plant responces.,
Soil Science, 1955, **80**, p101.

[Wal57] A. Wallace, L. M. Shannon, O. R. Lunt and R. L. Impy,
Some aspects of the use of metal chelates as micronutrient fertilizer sources.,
Soil Science, 1957, **84**, p27.

[Wal74] A. Wallace, R. T. Mueller and G. V. Alexander,
Effect of high levels of nitrilotriacetate on metal uptake by plants grown in soil.,
Agronomy Journal, 1974, **66**, p707.

[Wal75] J. A. Wallwork,
The distribution and diversity of soil fauna.,
McGraw Hill, London, 1975.

[Wal80a] A. Wallace,
Effect of excess chelating agent on micronutrient concentrations in bush beans grown in solution culture.,
Journal of Plant Nutrition, 1980, **2**(1-2), p163.

[Wal80b] A. Wallace,
Effect of chelating agents on uptake of trace metals when chelating agents are applied to soil in contrast to when they are applied to solution cultures.,
Journal of Plant Nutrition, 1980, **2**(1-2), p171.

[Wal80c] A. Wallace, R. T. Mueller and J. W. Cha,
Will high usage of synthetic chelating agents eventually harm soils?,
Journal of Plant Nutrition, 1980, **2**(1-2), p177.

[Wal83a] A. Wallace,
General conclusions concerning chelating agents in plant nutrition in 1982.,
Journal of Plant Nutrition, 1983, **6**(6), p425.

[Wal83b] A. Wallace,
A one-decade update on chelated metals for supplying micronutrients to crops.,
Journal of Plant Nutrition, 1983, **6**(6), p429.

[Wal83c] A. Wallace and G. A. Wallace,
Studies on the use of DTPA and EDDHA chelates to supply micronutrients to plants in soils including simulated drip irrigation.,
Journal of Plant Nutrition, 1983, **6**(6), p457.

[Wal83d] A. Wallace, G. A. Wallace and G. V. Alexander,
Effect of excess chelating agent in nutrient solution at low levels of iron, zinc, copper and manganese.,
Journal of Plant Nutrition, 1983, **6**(6), p507

[Wal83e] A. Wallace and G. A. Wallace,
NTA (Nitriloacetate) as a source of iron for corn in hydroponic solution.,
Journal of Plant Nutrition, 1983, **6**(6), p527.

[Wal83f] A. Wallace and G. A. Wallace,
Iron uptake by plants from nutrient solutions with excess chelates in long term studies - relationship with pe + pH.,
Journal of Plant Nutrition, 1983, **6**(6), P541.

[Wal83g] A. Wallace, G. A. Wallace and M. A. AbouZamZam,
Use of more than one chelating agent simultaneously for different micronutrients in hydroponic nutrient cultures.,
Journal of Plant Nutrition, 1983, **6**(6), p545.

[Wal84a] G. A. Wallace and A. Wallace,
Maintenance of iron and other micronutrients in hydroponic nutrient solutions.,
Journal of Plant Nutrition, 1984, **7**(1-5), p575.

[Wal84b] A. Wallace, G. A. Wallace, R. A. Wood and A. M. AbouZamZam,
Uptake by plants of iron from iron chelates.,
Journal of Plant Nutrition, 1984, **7**(1-5), p695.

[Wal86] A.Wallace,
A multiplicity of mechanisms in the plant kingdom which can contribute to iron efficiency.,
Journal of Plant Nutrition, 1986, **9**(3-7), p781.

[Wea85] R. C. Weast, M. J. Astle and W. H. Beyer,
CRC Handbook of chemistry and physics.,
CRC Press, Florida, 1985.

[Wei54] L. H. Weinstein, W. R. Robbins and H. F. Perkins,
Chelating agents and plant nutrition.,
Science, 1954, **120**, p41.

[Wes65] S. Westerback, K. S. Rajan and A. E. Martell,
New multidentate ligands. III. Amino acids containing methylenephosphonate groups.,
Journal of American Chemical Society, 1965, 87(12), p2567.

[Wes76] J. C. Westall, J. L. Zachary and F. M. M. Morel,
MINEQL, a computer program for the calculation of chemical equilibrium composition of aqueous systems.,
Technical Note 18, Dept of Civil Engineering, Massachusetts Institute of Technology, 1976.

[Whi58] W. B. White, S. M. Johnson and G. B. Dantzig,
Chemical equilibrium in complex mixtures.,
Journal of Chemical Physics, 1958, **28**(5), p751

[Wit78] S. H. Wittwer,
The next generation of agricultural research.,
Science, 1978, **199**, editorial.

[Zel68] F. J. Zeleznik and S. Gordon,
Calculation of complex chemical equilibria.,
Industrial and Engineering Chemistry, 1968, **60**(6), p27.

APPENDICES

CONSISTING OF

APPENDIX A:- Database

APPENDIX B:- Results

APPENDIX C:- Results

APPENDIX D:- Results

APPENDIX E:- Results

APPENDIX F:- Results

APPENDIX A

A1 DEFINITION OF COMPONENTS

Listed below are the identity numbers (ID No), chemical names and abbreviations of components as used in MINEQL.

ID No		COMPONENT	ABBREVIATION
1	Ca^{2+}	Calcium	Ca+2
2	Mg^{2+}	Magnesium	Mg+2
4	K^{+}	Potassium	K +1
5	Na^{+}	Sodium	Na+1
6	Fe^{3+}	Iron(III)	Fe+3
7	Fe^{2+}	Iron(II)	Fe+2
8	Mn^{2+}	Manganese(II)	Mn+2
9	Cu^{2+}	Copper(II)	Cu+2
11	Cd^{2+}	Cadmium	Cd+2
12	Zn^{2+}	Zinc	Zn+2
13	Ni^{2+}	Nickel	Ni+2
16	Co^{2+}	Cobalt(II)	Co+2
17	Co^{3+}	Cobalt(III)	Co+3
20	Al^{3+}	Aluminium	Al+3
33	Cu^{+}	Copper(I)	Cu+1
34	Mn^{3+}	Manganese(III)	Mn+3
50	H^{+}	Protons	H +1
99	e^{-}	Electrons	E-
101	CO_3^{2-}	Carbonate	CO3
102	SO_4^{2-}	Sulphate	SO4
103	Cl^{-}	Chloride	Cl
107	NH_3	Ammonia	NH3
109	PO_4^{3-}	Phosphate	PO4
112	SiO_4^{4-}	Silicate	SiO4
148	$B(OH)_4^{-}$	Borate	BOH4
152	MoO_4^{2-}	Molybdate	MoO4
157	NO_3^{-}	Nitrate	NO3
161	$Caff^{2-}$	Caffeate	CAFF

162	BQA^-	Benzoquinone acrylate	BQA
175	Lig1	N - (Phosphonomethyl) glycinate	LIG1
178	Lig4	N -(Phosphonomethyl) iminodiacetate	LIG4
116	FA	Acetylacetone	ACAC
119	FA	Salicylic acid	SAL
132	FA	Phthalic acid	PHTH
163	FA	2 - Acetylphenol	ACPH
164	FA	Benzoic acid	BZA
165	FA	Phenol	PHEN
166	FA	Hydroxy - 1,4 benzoquinone	HBQN
167	FA	1,2-Dihydroxybenzene	DHBZ
168	FA	Hydroxy - 2 - methyl propanoic acid	HMPA
169	FA	3 - Hydroxy butanoic acid	HBA
170	FA	Diethyl malonic acid	DEMA
171	FA	Malic acid	MALI
172	FA	Succinic acid	SUCA
173	FA	2,3 - Dihydroxy - 2 - methyl butanoic acid	DMBA
174	FA	Propanoic acid	PROP

Components listed as "FA" above are the species used to model the binding of fulvic acids. Each species has been defined in its ionic form as required by the input of MINEQL.

A2 TERMINOLOGY

The database has been set up with all stability constants corrected to a temperature of 25 ^oC and an ionic strength of 0.0 $mol.dm^{-3}$. Each complex has its own identification number and is represented in terms of the identity numbers of its individual components, for example,

```
50004      -14.90     20   1    50   -3
```

The above coding implies that the soluble species, aluminium hydroxide, $Al(OH)_3$, with a complex code number of 50004 has a stability constant of $10^{-14.90}$ at a temperature of 25 ^oC and an ionic strength of 0.0 $mol.dm^{-3}$. It should be noted that hydroxl ions have not been defined in the list of components but are included implicitly as a result of the inclusion of the ionic product of water in the database.

The database consists of blocks seperating the various types of equilibria, viz.

Type I species:- Components

Type II species:- Soluble Complexes

Type III species:- Fixed Solids - Redox equilibria and soluble species of fixed concentration eg. pH and gases at fixed partial pressure.

Type IV species:- Precipitated Solids subject to dissolution if the activity is less than zero. Type IV species were not considered in this study and are therefore not included in the database, however the results include type IV species which are type V species whose solubility products have been exceeded.

Type V species:- Dissolved Solids subject to precipitation if the solubility products are exceeded.

The results presented in **appendices B** to **E** have also been seperated into blocks as described above. Each of the above appendices consist of the input concentrations (X and logX) of all the components in the model as well as the estimated equilibrium concentrations of each component represented by T. The output data consists of the equilibrium concentrations (C and logC) of all species (components and complexes) as well as logK, the log stability constant of each complex corrected to the ionic strength of the respective computation ie. 0.02 $mol.dm^{-3}$.

A3 LISTING OF DATABASE

```
00577      TYPE II COMPLEXES
50000    -5.02   20   1   50 -1
50002    -9.30   20   1   50 -2
50004   -14.90   20   1   50 -3
50006    -7.69   20   2   50 -2
50008    13.10  112   1   50  1
50010    22.97  112   1   50  2
50012    36.24  112   1   50  3
50014    45.95  112   1   50  4
50016     0.12   20   1  157  3
50018     5.88   20   1  102  1   50  1
50020     3.20   20   1  102  1
50022     1.90   20   1  102  2
50024    -1.88   20   2  102  3
50026     4.81    1   1  112  1
50028    14.88    1   1  112  1   50  1
50030     5.89    2   1  112  1
50032    15.13    2   1  112  1   50  1
50034    24.03    6   1  112  1   50  1
60000     1.27    5   1  101  1
60002    10.08    5   1  101  1   50  1
60004     4.18   11   1  101  1
60006     7.06   11   1  101  2
60008    12.69   11   1  101  1   50  1
60010     4.57   13   1  101  1
60012    12.92   13   1  101  1   50  1
60014     4.17   16   1  101  1
60016    12.72   16   1  101  1   50  1
60018     2.46   11   1  102  1
60020     2.34   13   1  102  1
60022     2.34   16   1  102  1
60024     0.64    2   1  103  1
60026     1.98   11   1  103  1
60028     2.60   11   1  103  2
60029     2.40   11   1  103  3
60030    -2.30   13   1  103  1
60032     0.54   16   1  103  1
60034     2.72   13   1  107  1
60036     4.89   13   1  107  2
60038     6.55   13   1  107  3
60040     7.67   13   1  107  4
60042     8.34   13   1  107  5
60044     8.31   13   1  107  6
60046     2.08   16   1  107  1
60048     3.50   16   1  107  2
60050     4.43   16   1  107  3
60052     5.07   16   1  107  4
60054     5.13   16   1  107  5
60056     4.39   16   1  107  6
60058    16.79   11   1  109  1   50  1
60060    20.17   11   1  109  1   50  2
60062    15.99   13   1  109  1   50  1
60064    22.18   13   1  109  1   50  2
60066    16.07   16   1  109  1   50  1
```

```
60068     0.50   11   1 157   1
60070     0.20   11   1 157   2
60072     0.40   13   1 157   1
60074    -2.24   13   1 157   2
60076     0.20   16   1 157   1
60078    -2.04   16   1 157   2
60092   -10.08   11   1  50  -1
60094   -20.35   11   1  50  -2
60096   -47.35   11   1  50  -4
60098    -9.39   11   2  50  -1
60100   -32.81   11   4  50  -4
60102    -9.86   13   1  50  -1
60104   -19.06   13   1  50  -2
60106   -30.00   13   1  50  -3
60108   -10.70   13   2  50  -1
60110   -27.74   13   4  50  -4
60112    -9.65   16   1  50  -1
60114   -18.80   16   1  50  -2
60116   -31.50   16   1  50  -3
60118   -46.3    16   1  50  -4
60120   -11.2    16   2  50  -1
60122   -30.53   16   4  50  -4
66124     3.83   11   1 116   1
60126     6.65   11   1 116   2
60128     5.99   13   1 116   1
60130    10.58   13   1 116   2
60132     5.40   16   1 116   1
60134     9.54   16   1 116   2
60136     6.50   11   1 119   1
60138    16.47   11   1 119   1  50   1
60140     7.90   13   1 119   1
60142    12.65   13   1 119   1  50   1
60144     7.67   16   1 119   1
60146    12.35   16   1 119   1  50   1
60148     0.70    4   1 132   1
60152     2.68   11   1 132   1
60154     3.75   11   1 132   2
60156     5.89   11   1 132   1  50   1
60158     7.96   11   1 132   2  50   1
60160     2.95   13   1 132   1
60162     6.38   13   1 132   1  50   1
60164     2.38   16   1 132   1
60166     6.96   16   1 132   1  50   1
60168     4.63   13   1 163   1
60170     7.69   13   1 163   2
60172     4.79   16   1 163   1
60174     7.85   16   1 163   2
60176     1.83   11   1 164   1
60178     2.26   11   1 164   2
60180     1.33   13   1 164   1
60182     1.10   16   1 164   1
60184    21.29    6   1 167   1
60186    36.46    6   1 167   2
60188    45.09    6   1 167   3
60190     9.07   11   1 167   1
60192     9.78   13   1 167   1
```

60194	15.26	13	1	167	2		
60196	9.46	16	1	167	1		
60198	15.86	16	1	167	2		
60200	1.67	11	1	168	1		
60202	2.81	11	1	168	2		
60204	3.14	11	1	168	3		
60206	2.10	13	1	168	1		
60208	3.44	13	1	168	2		
60210	3.85	13	1	168	3		
60212	1.88	16	1	168	1		
60214	3.08	16	1	168	2		
60216	3.34	16	1	168	3		
60218	1.17	11	1	169	1		
60220	0.97	13	1	169	1		
60222	0.80	16	1	169	1		
60224	0.94	4	1	170	1		
60226	3.40	11	1	170	1		
60228	3.23	13	1	170	1		
60230	3.11	16	1	170	1		
60232	3.21	11	1	171	1		
60234	7.29	11	1	171	1	50	1
60236	4.02	13	1	171	1		
60238	7.78	13	1	171	1	50	1
60240	3.71	16	1	171	1		
60242	7.59	16	1	171	1	50	1
60243	0.50	4	1	172	1		
60244	2.72	11	1	172	1		
60245	2.34	13	1	172	1		
60246	1.30	13	1	172	1	50	1
60248	2.32	16	1	172	1		
60250	2.05	11	1	173	1		
60252	2.24	13	1	173	1		
60254	2.02	16	1	173	1		
60256	1.60	11	1	174	1		
60258	2.47	11	1	174	2		
60260	1.19	13	1	174	1		
60262	1.82	13	1	174	2		
60264	1.13	16	1	174	1		
70000	2.31	1	1	102	1		
70002	0.11	1	1	103	1		
70004	6.46	1	1	109	1		
70006	14.75	1	1	109	1	50	1
70008	20.54	1	1	109	1	50	2
70010	28.44	1	1	109	2	50	2
70012	33.75	1	1	109	2	50	3
70014	30.06	1	2	109	2	50	2
70016	12.28	1	1	128	1		
70018	15.79	1	1	128	1	50	1
70020	-12.70	1	1	50	-1		
70022	3.15	1	1	101	1		
70024	11.33	1	1	101	1	50	1
70026	-0.29	1	1	107	1		
70028	-1.09	1	1	107	2		
70030	-2.09	1	1	107	3		
70032	0.70	1	1	157	1		
70034	0.60	1	1	157	2		

70054	2.23	2	1	102	1		
70056	6.59	2	1	109	1		
70058	15.25	2	1	109	1	50	1
70060	21.05	2	1	109	1	50	2
70062	34.23	2	1	109	2	50	3
70064	28.41	2	1	109	2	50	2
70066	30.64	2	2	109	2	50	2
70072	-11.42	2	1	50	-1		
70074	-39.70	2	4	50	-4		
70076	3.90	2	1	101	1		
70078	11.88	2	1	101	1	50	1
70080	0.80	2	1	107	1		
70082	-0.27	2	1	107	2		
70084	-0.85	2	1	107	3		
70086	-1.75	2	1	107	4		
70112	-14.50	4	1	50	-1		
70114	0.80	4	1	102	1		
70116	13.43	4	1	109	1	50	1
70118	-0.76	4	1	103	1		
70120	-0.15	4	1	157	1		
70124	0.70	5	1	102	1		
70126	1.51	5	1	102	2		
70132	13.54	5	1	109	1	50	1
70134	2.13	5	1	148	1		
70136	-13.90	5	1	50	-1		
70138	-0.51	5	1	157	1		
70140	4.04	6	1	102	1		
70142	5.38	6	1	102	2		
70144	1.48	6	1	103	1		
70146	2.13	6	1	103	2		
70148	1.13	6	1	103	3		
70150	22.44	6	1	109	1	50	1
70152	23.53	6	1	109	1	50	2
70154	29.24	6	2	109	1	50	1
70168	9.05	6	1	148	1		
70170	16.41	6	1	148	2		
70172	21.50	6	1	148	3		
70174	8.73	6	1	152	1		
70176	17.33	6	1	152	3		
70178	-2.19	6	1	50	-1		
70180	-5.70	6	1	50	-2		
70200	-9.51	6	1	50	-3		
70202	-21.60	6	1	50	-4		
70204	-2.90	6	2	50	-2		
70206	-6.30	6	3	50	-4		
70208	1.00	6	1	157	1		
70220	2.20	7	1	102	1		
70222	2.70	7	1	102	1	50	1
70224	-9.50	7	1	50	-1		
70226	-20.60	7	1	50	-2		
70228	-32.00	7	1	50	-3		
70230	-46.40	7	1	50	-4		
70240	15.94	7	1	109	1	50	1
70242	22.24	7	1	109	1	50	2
70244	29.52	7	1	109	2	50	2
70266	15.91	8	1	109	1	50	1

```
70268    22.24    8   1 109   1   50   2
70270    29.27    8   1 109   2   50   2
70272     2.26    8   1 102   1
70274   -10.60    8   1  50  -1
70276   -22.31    8   1  50  -2
70278   -34.20    8   1  50  -3
70280   -48.30    8   1  50  -4
70282   -10.60    8   2  50  -1
70284   -23.90    8   2  50  -3
70286    12.13    8   1  50   1 101   1
70294     0.86    8   1 107   1
70296     1.49    8   1 107   2
70298     1.75    8   1 107   3
70300     1.32    8   1 107   4
70302     0.20    8   1 157   1
70304     0.60    8   1 157   2
70318    16.35    9   1 109   1   50   1
70320    21.06    9   1 109   1   50   2
70322    33.44    9   1 109   2   50   3
70324    33.08    9   2 109   2   50   2
70326    29.81    9   1 109   2   50   2
70328     2.36    9   1 102   1
70330     3.76    9   1 102   2
70332     2.55    9   1 102   3
70334     7.53    9   1 148   1
70336    13.08    9   1 148   2
70338    15.81    9   1 148   3
70340    -7.70    9   1  50  -1
70342   -14.80    9   1  50  -2
70344   -27.58    9   1  50  -3
70346   -39.60    9   1  50  -4
70348   -10.90    9   2  50  -2
70350   -21.60    9   3  50  -4
70352   -20.90    9   4  50  -3
70364     6.75    9   1 101   1
70366     9.83    9   1 101   2
70368     0.40    9   1 103   1
70370     4.06    9   1 107   1
70372     7.36    9   1 107   2
70374    10.10    9   1 107   3
70376    11.99    9   1 107   4
70378    11.43    9   1 107   5
70380    -2.80    9   1 107   1   50  -1
70382    -0.80    9   1 107   3   50  -1
70384   -15.70    9   1 107   2   50  -2
70386     0.50    9   1 157   1
70388     0.42    9   1 157   2
70424    15.55   12   1 109   1   50   1
70426    21.12   12   1 109   1   50   2
71208    34.40   12   1 109   2   50   3
71210    31.65   12   2 109   2   50   2
71212    29.21   12   1 109   2   50   2
71214     2.38   12   1 102   1
71216     3.72   12   1 102   2
71218     3.17   12   1 102   3
71220     2.38   12   1 102   4
```

71222	-9.00	12	1	50	-1			
71224	-15.08	12	1	50	-2			
71226	-28.40	12	1	50	-3			
71228	-41.20	12	1	50	-4			
71230	-9.00	12	2	50	-1			
71242	4.70	12	1	101	1			
71243	12.13	12	1	50	1	101	1	
71244	0.43	12	1	103	1			
71246	1.04	12	1	103	2			
71248	1.54	12	1	103	3			
71250	1.74	12	1	103	4			
71252	2.21	12	1	107	1			
71254	4.50	12	1	107	2			
71256	6.86	12	1	107	3			
71258	8.89	12	1	107	4			
71260	-4.39	12	1	107	1	50	-1	
71262	-2.83	12	1	107	2	50	-1	
71264	-1.64	12	1	107	3	50	-1	
71266	-14.36	12	1	107	1	50	-2	
71268	-13.77	12	1	107	2	50	-2	
71270	-26.92	12	1	107	1	50	-3	
71300	0.40	12	1	157	1			
71302	0.64	12	1	157	2			
77300	10.18	33	1	107	2			
77400	3.44	34	1	102	1			
77402	0.81	34	1	50	-1			
78600	10.33	50	1	101	1			
78602	16.68	50	2	101	1			
78604	1.99	50	1	102	1			
78606	-5.40	50	2	102	1			
78610	12.34	50	1	109	1			
78612	19.54	50	2	109	1			
78614	21.68	50	3	109	1			
78616	30.79	50	3	109	2			
78618	38.75	50	4	109	2			
78620	41.77	50	5	109	2			
78634	-14.00	50	-1					
78636	9.34	50	1	148	1			
78638	9.94	50	1	148	3			
78640	20.02	50	2	148	3			
78642	20.44	50	2	148	4			
78644	29.96	50	3	148	4			
78646	38.92	50	4	148	5			
78648	4.04	50	1	152	1			
78650	8.03	50	2	152	1			
78652	8.89	50	3	152	1			
78654	-6.20	50	1	103	1			
78656	9.24	50	1	107	1			
78700	10.74	50	1	107	1	103	1	
78702	10.35	50	1	107	1	102	1	
78708	-1.42	50	1	157	1			
78710	8.75	20	1	116	1			
78712	16.79	20	1	116	2			
78714	22.70	20	1	116	3			
78716	15.09	20	1	119	1			
78718	4.47	20	1	132	1			

```
78720     8.04   20   1 132   1
78722    -1.64   20   1 164   1   50 -1
90100    13.3   167   1  50   1
90102    22.7   167   1  50   2
90104     6.5     2   1 167   1
90106     5.1     1   1 167   1
90108     8.5     8   1 167   1
90110    16.7     8   1 167   1   50  1
90112     9.2     7   1 167   1
90114    17.4     7   1 167   1   50  1
90116    14.7     9   1 167   1
90118    10.7    12   1 167   1
90120     4.0   168   1  50   1
90122     1.5     1   1 168   1
90124     1.4     2   1 168   1
90126     1.4     8   1 168   1
90128     1.9     7   1 168   1
90130     3.2     9   1 168   1
90132     2.2    12   1 168   1
90134     3.5     6   1 168   1
90136     2.6     6   1 168   1   50 -1
90138    13.7   119   1  50   1
90140    16.7   119   1  50   2
90141     6.1     2   1 119   1
90142     5.2     1   1 119   1
90144    14.1     1   1 119   1   50  1
90146     6.7     8   1 119   1
90148     7.4     7   1 119   1
90150    11.4     9   1 119   1
90152     7.7    12   1 119   1
90154    17.4     6   1 119   1
90156    18.5     6   1 119   1   50  1
90158    10.5     2   1 119   2
90160     8.5     1   1 119   2
90162    10.7     8   1 119   2
90164    12.1     7   1 119   2
90166    31.3     6   1 119   2
90168    19.3     9   1 119   2
90170     6.1    12   1 119   2
90172    10.1   163   1  50   1
90174     1.5     1   1 163   1
90176     2.7     8   1 163   1
90178     7.1     9   1 163   1
90180     3.5    12   1 163   1
90182    10.9     6   1 163   1
90184     4.5   169   1  50   1
90186     1.0     2   1 169   1
90188     0.8     1   1 169   1
90190     2.5     9   1 169   1
90192     1.5    12   1 169   1
90194     7.4   170   1  50   1
90196     9.6   170   1  50   2
90198     0.8     5   1 170   1
90200     2.3     2   1 170   1
90202     8.2     2   1 170   1   50  1
90204     2.3     1   1 170   1
```

90206	8.4	1	1	170	1	50	1
90208	2.6	8	1	170	1		
90210	5.7	9	1	170	1		
90212	8.7	9	1	170	1	50	1
90214	3.2	12	1	170	1		
90216	8.8	12	1	170	1	50	1
90218	9.8	6	1	170	1		
90220	10.7	6	1	170	1	50	1
90222	9.0	116	1	50	1		
90224	3.7	2	1	116	1		
90226	3.1	1	1	116	1		
90228	4.2	8	1	116	1		
90230	5.1	7	1	116	1		
90232	8.3	9	1	116	1		
90234	5.1	12	1	116	1		
90236	10.5	6	1	116	1		
90238	5.4	132	1	50	1		
90240	8.4	132	1	50	2		
90242	0.7	5	1	132	1		
90244	2.4	1	1	132	1		
90246	2.7	8	1	132	1		
90248	4.0	9	1	132	1		
90250	2.9	12	1	132	1		
90252	8.5	6	1	132	1		
90254	5.3	9	1	132	2		
90256	4.2	12	1	132	2		
90258	5.1	171	1	50	1		
90260	8.6	171	1	50	2		
90262	0.7	5	1	171	1		
90264	0.6	4	1	171	1		
90266	2.5	2	1	171	1		
90268	6.5	2	1	171	1	50	1
90270	2.7	1	1	171	1		
90272	6.6	1	1	171	1	50	1
90274	3.1	8	1	171	1		
90276	3.4	7	1	171	1		
90278	4.2	9	1	171	1		
90280	6.6	9	1	171	1		
90282	3.3	12	1	171	1		
90284	7.1	12	1	171	1	50	1
90286	8.5	6	1	171	1		
90288	5.6	172	1	50	1		
90290	9.8	172	1	50	2		
90292	0.3	5	1	172	1		
90294	2.0	2	1	172	1		
90296	6.5	2	1	172	1	50	1
90298	2.0	1	1	172	1		
90300	6.5	1	1	172	1	50	1
90302	2.3	8	1	172	1		
90304	3.5	8	1	172	1	50	1
90306	2.2	7	1	172	1		
90308	3.3	9	1	172	1		
90310	2.5	12	1	172	1		
90312	6.9	12	1	172	1	50	1
90314	8.3	6	1	172	1		
90316	3.7	173	1	50	1		

90318	1.3	2	1	173	1		
90320	1.6	1	1	173	1		
90322	3.0	9	1	173	1		
90324	2.1	12	1	173	1		
90326	4.2	164	1	50	1		
90328	0.5	2	1	164	1		
90330	0.7	1	1	164	1		
90332	1.2	8	1	164	1		
90334	2.0	9	1	164	1		
90336	1.3	12	1	164	1		
90338	5.8	6	1	164	1		
90340	10.0	165	1	50	1		
90342	8.2	6	1	165	1		
90344	4.9	174	1	50	1		
90346	0.9	2	1	174	1		
90348	1.0	1	1	174	1		
90350	2.2	9	1	174	1		
90352	1.3	12	1	174	1		
90354	4.0	6	1	174	1		
90356	2.8	166	1	50	1		
90358	2.0	2	1	166	1		
90360	1.6	1	1	166	1		
90362	2.6	8	1	166	1		
90364	5.2	9	1	166	1		
90366	4.5	12	1	166	1		
90368	7.8	6	1	166	1		
90370	3.3	2	1	166	2		
90372	2.8	1	1	166	2		
90374	4.0	8	1	166	2		
90376	13.9	6	1	166	2		
90378	9.0	9	1	166	2		
90380	6.1	12	1	166	2		
90382	10.97	178	1	50	1		
90384	17.17	178	1	50	2		
90386	19.90	178	1	50	3		
90388	21.58	178	1	50	4		
90390	8.77	1	1	178	1		
90392	15.21	1	1	178	1	50	1
90394	7.87	2	1	178	1		
90396	14.75	2	1	178	1	50	1
90398	19.96	6	1	178	1		
90400	0.40	7	1	178	1	50	-1
90402	11.63	7	1	178	1		
90404	13.25	7	1	178	2		
90406	17.47	7	1	178	1	50	1
90408	30.91	7	1	178	2	50	2
90410	9.87	8	1	178	1		
90412	15.96	8	1	178	1	50	1
90414	5.42	9	1	178	1	50	-1
90416	15.77	9	1	178	1		
90418	20.91	9	1	178	1	50	1
90420	2.52	12	1	178	1	50	-1
90422	13.27	12	1	178	1	50	
90424	18.43	12	1	178	1	50	1
90426	17.28	20	1	178	1		
90428	20.26	20	1	178	1	50	1

```
90430     12.42   11   1 178   1
90432     12.99   13   1 178   1
90434     14.41   13   1 178   2
90436     19.08   13   1 178   1  50   1
90438     12.54   16   1 178   1
90440     18.03   16   1 178   1  50   1
90500      9.08   50   1 161   1
90502     13.67   50   2 161   1
90504      5.04    7   1 161   1
90506      7.64    7   2 161   1
90508     -3.95    7   1 161   1  50  -1
90510      0.13    7   1 161   2  50  -1
90512     -7.49    7   1 161   3  50  -2
90514     -4.30    8   1 161   1  50  -1
90516    -15.31    8   1 161   1  50  -2
90518      6.80    9   1 161   1
90520     11.21    9   1 161   1  50   1
90522      0.79    9   1 161   1  50  -1
90524      4.47    9   2 161   1  50  -1
90526      0.44    9   2 161   3  50  -3
90528      8.89    9   3 161   2  50  -2
90530     -4.16   11   1 161   1  50  -1
90532    -12.50   11   1 161   2  50  -2
90534    -21.50   11   1 161   3  50  -3
90536      3.78   12   1 161   1
90538     -2.48   12   1 161   1  50  -1
90540     -0.20   12   1 161   2  50  -1
90542     -8.63   12   1 161   2  50  -2
90544     -6.98   12   1 161   3  50  -2
90546     -2.90   13   1 161   1  50  -1
90548    -12.93   13   1 161   1  50  -2
90550     -0.51   13   2 161   1  50  -1
90552     -0.80   13   3 161   2  50  -2
90554     -3.39   16   1 161   1  50  -1
90556     -0.58   16   2 161   1  50  -1
90600     10.71  175   1  50   1
90602     16.56  175   1  50   2
90604     18.88  175   1  50   3
90606     12.94  175   1   1   1  50   1
90608      4.54  175   1   1   1
90610      6.52  175   2   1   1
90612     13.55  175   1   2   1  50   1
90614      4.57  175   1   2   1
90616      6.11  175   2   2   1
90618     13.79  175   1   8   1  50   1
90620      6.79  175   1   8   1
90622      8.45  175   2   8   1
90624     14.25  175   1   7   1  50   1
90626      8.16  175   1   7   1
90628     11.83  175   2   7   1
90630     14.05  175   1  16   1  50   1
90632      8.52  175   1  16   1
90634     11.77  175   2  16   1
90636     14.82  175   1  13   1  50   1
90638      9.39  175   1  13   1
90640     12.90  175   2  13   1
```

```
90642    17.31 175  1   9  1  50  1
90644    13.22 175  1   9  1
90646    16.67 175  2   9  1
90648     3.16 175  1   9  1  50 -1
90650    19.57 175  1   6  1  50  1
90652    18.03 175  1   6  1
90654    24.94 175  2   6  1
90656    12.25 175  1   6  1  50 -1
90658     3.12 175  1   6  1  50 -2
90660    10.03 175  1  12  1
90662    12.34 175  2  12  1
90664     0.09 175  1  12  1  50 -1
90666    14.10 175  1  11  1  50  1
90668     8.58 175  1  11  1
90670    11.56 175  2  11  1
90672    -2.38 175  1  11  1  50 -1
90674    29.48 175  2  20  1  50  1
90676    18.12 175  1  20  1  50  1
90678    15.64 175  1  20  1
90680    23.99 175  2  20  1
00006     TYPE III SPECIES
80000    13.03   6  1   7 -1  99  1
80002    26.06  34  1   8 -1  99  1
80004     2.59   9  1  33 -1  99  1
80006    30.93  17  1  16 -1  99  1
80008    17.73 162  1 161 -1  99  2  50  1
80010    21.65  50  2 101  1
00000     TYPE IV SPECIES (None)
00065     TYPE V SPECIES
80090    -0.19   5  1 103  1
80096    -9.52  16  1 101  1
80098    -4.50  13  1 101  1
80100     4.60   1  1 102  1
80102    43.75   1  5 109  3  50 -1
80104    46.90   1  4 109  3  50  1
80106    19.24   1  1 109  1  50  1
80110   -22.97   1  1  50 -2
80112    28.92   1  3 109  2
80114    18.94   1  1 109  1  50  1
80116     8.49   1  1 101  1
80200    25.20   2  3 109  2
80202    18.16   2  1 109  1  50  1
80204   -16.85   2  1  50 -2
80206     8.09   2  1 101  1
80208     4.67   2  1 101  1
80210    17.00   2  1   1  1 101  2
80211    29.97   2  3   1  1 101  4
80212    21.35   2  1 107  1 109  1  50  1
80214    10.62   2  1   4  1 109  1
80600    -3.20   6  1  50 -3
80602    26.40   6  1 109  1
80606   -17.67   6  2   7  1  50 -8
80608    -9.60   6  2   7  1  50 -8
80700   -12.90   7  1  50 -2
80702    10.24   7  1 101  1
80704    36.00   7  3 109  2
```

80701	2.46	7	1	102	1				
80800	-15.20	8	1	50	-2				
80802	9.30	8	1	101	1				
80900	-8.68	9	1	50	-2				
80904	37.70	9	3	109	2				
80906	9.63	9	1	101	1				
80908	5.16	9	2	101	1	50	-2		
80910	16.88	9	3	101	2	50	-2		
80912	15.12	9	1	148	2				
81200	35.30	12	3	109	2				
81202	10.80	12	1	101	1				
81204	-12.48	12	1	50	-2				
83302	6.73	33	1	103	1				
83304	-13.40	33	1	50	-1				
84000	6.33	1	2	112	1				
84002	8.13	1	2	112	1				
84004	68.57	1	1	20	2	112	2		
84006	17.08	2	2	112	1				
84008	34.70	5	1	20	1	112	1		
84010	32.90	4	1	20	1	112	1		
84012	26.19	7	2	112	1				
84014	32.80	12	2	112	1				
84016	21.50	8	2	112	1				
84018	-9.66	20	1	50	-3				
84020	-8.51	20	1	50	-3				
84022	-8.40	20	1	50	-3				
84024	-20.84	20	2	102	3				
84026	-3.04	20	3	4	1	102	2	50	-6
84028	19.05	20	1	109	1				
84030	11.99	11	1	101	1				
84032	0.04	11	1	102	1				
84034	38.10	11	3	109	2				
84036	8.36	1	1	152	1				
84038	0.62	2	1	152	1				
84040	6.48	9	1	152	1				
84042	7.70	7	1	152	1				
84044	4.13	8	1	152	1				
84046	4.94	12	1	152	1				
00000	**TYPE VI SPECIES** (None)								

APPENDIX B

SOIL SOLUTION MODEL IN THE PRESENCE OF DISSOLVED OXYGEN (See chapter 5.4.1).

INPUT

IONIC STRENGTH = 2.00E-02

ID	X	LOGX	T	COMPONENTS
50	3.16E-07	-6.50	0.00E+00	H +1
1	1.00E-03	-3.00	2.50E-03	Ca+2
2	1.00E-03	-3.00	1.00E-03	Mg+2
4	1.00E-03	-3.00	5.00E-03	K +1
5	1.00E-05	-5.00	2.00E-03	Na+1
6	1.00E-05	-5.00	2.00E-05	Fe+3
7	1.00E-09	-9.00	0.00E+00	Fe+2
8	1.00E-05	-5.00	1.00E-05	Mn+2
9	1.00E-06	-6.00	1.00E-06	Cu+2
11	1.00E-06	-6.00	1.00E-06	Cd+2
12	1.00E-06	-6.00	5.00E-06	Zn+2
13	1.00E-06	-6.00	1.00E-06	Ni+2
16	1.00E-07	-7.00	1.00E-06	Co+2
17	1.00E-09	-9.00	0.00E+00	Co+3
20	1.00E-07	-7.00	1.50E-06	Al+3
33	1.00E-09	-9.00	0.00E+00	Cu+1
34	1.00E-09	-9.00	0.00E+00	Mn+3
99	1.00E-09	-9.00	0.00E+00	E-
101	1.00E-08	-8.00	0.00E+00	CO3
102	1.00E-03	-3.00	3.00E-03	SO4
103	1.00E-03	-3.00	2.00E-03	Cl
107	1.00E-03	-3.00	1.00E-03	NH3
109	1.00E-03	-3.00	1.00E-03	PO4
112	1.00E-04	-4.00	3.50E-03	SiO4
148	1.00E-06	-6.00	5.00E-05	BOH4
152	1.00E-08	-8.00	3.00E-08	MoO4
157	1.00E-03	-3.00	6.00E-03	NO3

167	1.00E-05	-5.00	1.90E-05	DHBZ
119	1.00E-05	-5.00	3.10E-05	SAL
168	1.00E-05	-5.00	4.90E-06	HMPA
163	1.00E-05	-5.00	1.70E-05	ACPH
169	1.00E-05	-5.00	7.00E-05	HBA
170	1.00E-05	-5.00	4.20E-05	DEMA
116	1.00E-05	-5.00	1.30E-05	ACAC
132	1.00E-05	-5.00	8.00E-06	PHTH
171	1.00E-05	-5.00	2.40E-05	MALI
172	1.00E-05	-5.00	3.20E-05	SUCA
173	1.00E-05	-5.00	2.60E-05	DMBA
164	1.00E-05	-5.00	7.30E-05	BZA
165	1.00E-05	-5.00	1.20E-04	PHEN
174	1.00E-05	-5.00	9.20E-05	PROP
166	1.00E-05	-5.00	2.70E-05	HBQN

OUTPUT

ID	C	LOGC	LOGK	SPECIES:	TYPE I - COMPONENTS
166	2.40E-05	-4.62	0.00	HBQN	1
1	7.35E-04	-3.13	0.00	Ca+2	1
2	8.59E-04	-3.07	0.00	Mg+2	1
4	4.93E-03	-2.31	0.00	K +1	1
5	1.98E-03	-2.70	0.00	Na+1	1
6	1.15E-16	-15.94	0.00	Fe+3	1
7	5.25E-18	-17.28	0.00	Fe+2	1
8	8.33E-06	-5.08	0.00	Mn+2	1
9	2.54E-08	-7.59	0.00	Cu+2	1
11	6.73E-07	-6.17	0.00	Cd+2	1
12	2.91E-06	-5.54	0.00	Zn+2	1
13	7.51E-07	-6.12	0.00	Ni+2	1
16	7.89E-07	-6.10	0.00	Co+2	1
17	1.52E-25	-24.82	0.00	Co+3	1
20	1.82E-11	-10.74	0.00	Al+3	1
33	7.96E-18	-17.10	0.00	Cu+1	1
34	1.19E-19	-18.92	0.00	Mn+3	1

99	1.40E-12	-11.85	0.00	E-	1
101	5.13E-09	-8.29	0.00	CO3	1
102	2.65E-03	-2.58	0.00	SO4	1
103	1.95E-03	-2.71	0.00	Cl	1
107	1.70E-06	-5.77	0.00	NH3	1
109	2.47E-11	-10.61	0.00	PO4	1
112	6.20E-22	-21.21	0.00	SiO4	1
148	9.49E-08	-7.02	0.00	BOH4	1
152	2.99E-08	-7.52	0.00	MoO4	1
157	5.97E-03	-2.22	0.00	NO3	1
167	8.64E-15	-14.06	0.00	DHBZ	1
119	3.39E-12	-11.47	0.00	SAL	1
168	4.76E-06	-5.32	0.00	HMPA	1
163	5.63E-09	-8.25	0.00	ACPH	1
169	6.89E-05	-4.16	0.00	HBA	1
170	7.30E-06	-5.14	0.00	DEMA	1
116	5.25E-08	-7.28	0.00	ACAC	1
132	7.08E-06	-5.15	0.00	PHTH	1
171	1.85E-05	-4.73	0.00	MALI	1
172	2.81E-05	-4.55	0.00	SUCA	1
173	2.53E-05	-4.60	0.00	DMBA	1
164	7.24E-05	-4.14	0.00	BZA	1
165	5.00E-08	-7.30	0.00	PHEN	1
174	8.96E-05	-4.05	0.00	PROP	1

ID	C	LOGC	LOGK	SPECIES:	TYPE II - COMPLEXES	
90380	9.23E-10	-9.03	5.74	Zn+2	1	HBQN 2
50000	3.16E-10	-9.50	-5.26	Al+3	1	H +1 -1
50002	3.98E-08	-7.40	-9.66	Al+3	1	H +1 -2
50004	3.16E-07	-6.50	-15.26	Al+3	1	H +1 -3
50006	6.75E-17	-16.17	-7.69	Al+3	2	H +1 -2
50008	8.19E-16	-15.09	12.62	SiO4	1	H +1 1
50010	8.38E-13	-12.08	22.13	SiO4	1	H +1 2
50012	2.84E-06	-5.55	35.16	SiO4	1	H +1 3
50014	3.50E-03	-2.46	44.75	SiO4	1	H +1 4
50016	9.73E-19	-18.01	-0.60	NO3	3	Al+3 1

```
50020    1.46E-11  -10.84    2.48    SO4    1    Al+3    1
50022    1.12E-15  -14.95    0.94    SO4    2    Al+3    1
50024    1.30E-33  -32.89   -3.68    SO4    3    Al+3    2
50026    3.23E-21  -20.49    3.85    Ca+2   1    SiO4    1
50028    6.92E-18  -17.16   13.68    Ca+2   1    SiO4    1
H +1    1
50030    4.55E-20  -19.34    4.93    Mg+2   1    SiO4    1
50032    1.44E-17  -16.84   13.93    Mg+2   1    SiO4    1
H +1    1
50034    6.66E-22  -21.18   22.47    SiO4   1    Fe+3    1
H +1    1
60000    1.09E-10   -9.96    1.03    Na+1   1    CO3     1
60002    1.69E-08   -7.77    9.72    Na+1   1    CO3     1
H +1    1
60004    1.73E-11  -10.76    3.70    Cd+2   1    CO3     1
60006    6.73E-17  -16.17    6.58    Cd+2   1    CO3     2
60008    1.77E-09   -8.75   12.21    Cd+2   1    CO3     1
H +1    1
60010    4.74E-11  -10.32    4.09    Ni+2   1    CO3     1
60012    3.36E-09   -8.47   12.44    Ni+2   1    CO3     1
H +1    1
60014    1.98E-11  -10.70    3.69    Co+2   1    CO3     1
60016    2.23E-09   -8.65   12.24    Co+2   1    CO3     1
H +1    1
60018    1.71E-07   -6.77    1.98    Cd+2   1    SO4     1
60020    1.45E-07   -6.84    1.86    Ni+2   1    SO4     1
60022    1.52E-07   -6.82    1.86    Co+2   1    SO4     1
60024    4.21E-06   -5.38    0.40    Mg+2   1    Cl      1
60026    7.22E-08   -7.14    1.74    Cd+2   1    Cl      1
60028    4.45E-10   -9.35    2.24    Cd+2   1    Cl      2
60029    5.48E-13  -12.26    2.04    Cd+2   1    Cl      3
60030    4.23E-12  -11.37   -2.54    Ni+2   1    Cl      1
60032    3.07E-09   -8.51    0.30    Co+2   1    Cl      1
60034    6.72E-10   -9.17    2.72    Ni+2   1    NH3     1
60036    1.69E-13  -12.77    4.89    Ni+2   1    NH3     2
60038    1.32E-17  -16.88    6.55    Ni+2   1    NH3     3
60040    2.96E-22  -21.53    7.67    Ni+2   1    NH3     4
```

60042	2.36E-27	-26.63	8.34	Ni+2	1	NH3	5
60044	3.75E-33	-32.43	8.31	Ni+2	1	NH3	6
60046	1.62E-10	-9.79	2.08	Co+2	1	NH3	1
60048	7.24E-15	-14.14	3.50	Co+2	1	NH3	2
60050	1.05E-19	-18.98	4.43	Co+2	1	NH3	3
60052	7.81E-25	-24.11	5.07	Co+2	1	NH3	4
60054	1.53E-30	-29.82	5.13	Co+2	1	NH3	5
60056	4.73E-37	-36.32	4.39	Co+2	1	NH3	6
60058	4.69E-08	-7.33	15.95	Cd+2	1	PO4	1
H +1	1						
60060	3.56E-11	-10.45	19.33	Cd+2	1	PO4	1
H +1	2						
60062	8.29E-09	-8.08	15.15	Ni+2	1	PO4	1
H +1	1						
60064	4.06E-09	-8.39	21.34	Ni+2	1	PO4	1
H +1	2						
60066	1.05E-08	-7.98	15.23	Co+2	1	PO4	1
H +1	1						
60068	7.32E-09	-8.14	0.26	Cd+2	1	NO3	1
60070	1.66E-11	-10.78	-0.16	Cd+2	1	NO3	2
60072	6.49E-09	-8.19	0.16	Ni+2	1	NO3	1
60074	6.73E-14	-13.17	-2.60	Ni+2	1	NO3	2
60076	4.30E-09	-8.37	-0.04	Co+2	1	NO3	1
60078	1.12E-13	-12.95	-2.40	Co+2	1	NO3	2
60092	1.34E-10	-9.87	-10.20	Cd+2	1	H +1	-1
60094	2.28E-14	-13.64	-20.47	Cd+2	1	H +1	-2
60096	5.22E-28	-27.28	-47.11	Cd+2	1	H +1	-4
60098	7.70E-16	-15.11	-9.27	Cd+2	2	H +1	-1
60100	5.53E-32	-31.26	-32.57	Cd+2	4	H +1	-4
60102	2.49E-10	-9.60	-9.98	Ni+2	1	H +1	-1
60104	4.97E-13	-12.30	-19.18	Ni+2	1	H +1	-2
60106	2.38E-17	-16.62	-30.00	Ni+2	1	H +1	-3
60108	4.70E-17	-16.33	-10.58	Ni+2	2	H +1	-1
60110	1.01E-26	-26.00	-27.50	Ni+2	4	H +1	-4
60112	4.24E-10	-9.37	-9.77	Co+2	1	H +1	-1
60114	9.49E-13	-12.02	-18.92	Co+2	1	H +1	-2
60116	7.89E-19	-18.10	-31.50	Co+2	1	H +1	-3

60118	6.87E-27	-26.16	-46.06	Co+2	1	H +1	-4
60120	1.64E-17	-16.79	-11.08	Co+2	2	H +1	-1
60122	1.99E-29	-28.70	-30.29	Co+2	4	H +1	-4
66124	1.38E-10	-9.86	3.59	Cd+2	1	ACAC	1
60126	3.62E-15	-14.44	6.29	Cd+2	1	ACAC	2
60128	2.22E-08	-7.65	5.75	Ni+2	1	ACAC	1
60130	3.44E-11	-10.46	10.22	Ni+2	1	ACAC	2
60132	5.99E-09	-8.22	5.16	Co+2	1	ACAC	1
60134	3.29E-12	-11.48	9.18	Co+2	1	ACAC	2
60136	2.39E-12	-11.62	6.02	Cd+2	1	SAL	1
60138	7.06E-09	-8.15	15.99	Cd+2	1	SAL	1
H +1	1						
60140	6.71E-11	-10.17	7.42	Ni+2	1	SAL	1
60142	1.19E-12	-11.92	12.17	Ni+2	1	SAL	1
H +1	1						
60144	4.15E-11	-10.38	7.19	Co+2	1	SAL	1
60146	6.28E-13	-12.20	11.87	Co+2	1	SAL	1
H +1	1						
60148	1.01E-07	-7.00	0.46	K +1	1	PHTH	1
60152	7.56E-10	-9.12	2.20	PHTH	1	Cd+2	1
60154	6.29E-14	-13.20	3.27	PHTH	2	Cd+2	1
60156	3.88E-13	-12.41	5.41	PHTH	1	Cd+2	1
H +1	1						
60158	1.86E-16	-15.73	7.24	PHTH	2	Cd+2	1
H +1	1						
60160	1.57E-09	-8.80	2.47	PHTH	1	Ni+2	1
60162	1.34E-12	-11.87	5.90	PHTH	1	Ni+2	1
H +1	1						
60164	4.44E-10	-9.35	1.90	PHTH	1	Co+2	1
60166	5.34E-12	-11.27	6.48	PHTH	1	Co+2	1
H +1	1						
60168	1.04E-10	-9.98	4.39	Ni+2	1	ACPH	1
60170	5.09E-16	-15.29	7.33	Ni+2	1	ACPH	2
60172	1.58E-10	-9.80	4.55	Co+2	1	ACPH	1
60174	7.72E-16	-15.11	7.49	Co+2	1	ACPH	2
60176	1.90E-09	-8.72	1.59	Cd+2	1	BZA	1
60178	2.81E-13	-12.55	1.90	Cd+2	1	BZA	2

60180	6.70E-10	-9.17	1.09	Ni+2	1	BZA	1
60182	4.14E-10	-9.38	0.86	Co+2	1	BZA	1
60184	3.69E-10	-9.43	20.57	DHBZ	1	Fe+3	1
60186	2.72E-09	-8.57	35.50	DHBZ	2	Fe+3	1
60188	1.74E-14	-13.76	44.37	DHBZ	3	Fe+3	1
60190	2.27E-12	-11.64	8.59	Cd+2	1	DHBZ	1
60192	1.30E-11	-10.89	9.30	Ni+2	1	DHBZ	1
60194	3.39E-20	-19.47	14.78	Ni+2	1	DHBZ	2
60196	6.52E-12	-11.19	8.98	Co+2	1	DHBZ	1
60198	1.42E-19	-18.85	15.38	Co+2	1	DHBZ	2
60200	8.64E-11	-10.06	1.43	Cd+2	1	HMPA	1
60202	4.31E-15	-14.37	2.45	Cd+2	1	HMPA	2
60204	4.39E-20	-19.36	2.78	Cd+2	1	HMPA	3
60206	2.59E-10	-9.59	1.86	Ni+2	1	HMPA	1
60208	2.05E-14	-13.69	3.08	Ni+2	1	HMPA	2
60210	2.51E-19	-18.60	3.49	Ni+2	1	HMPA	3
60212	1.64E-10	-9.78	1.64	Co+2	1	HMPA	1
60214	9.40E-15	-14.03	2.72	Co+2	1	HMPA	2
60216	8.15E-20	-19.09	2.98	Co+2	1	HMPA	3
60218	3.95E-10	-9.40	0.93	Cd+2	1	HBA	1
60220	2.78E-10	-9.56	0.73	Ni+2	1	HBA	1
60222	1.98E-10	-9.70	0.56	Co+2	1	HBA	1
60224	1.81E-07	-6.74	0.70	K +1	1	DEMA	1
60226	4.09E-09	-8.39	2.92	Cd+2	1	DEMA	1
60228	3.09E-09	-8.51	2.75	Ni+2	1	DEMA	1
60230	2.46E-09	-8.61	2.63	Co+2	1	DEMA	1
60232	6.70E-09	-8.17	2.73	Cd+2	1	MALI	1
60234	2.55E-11	-10.59	6.81	Cd+2	1	MALI	1
H +1	1						
60236	4.83E-08	-7.32	3.54	Ni+2	1	MALI	1
60238	8.79E-11	-10.06	7.30	Ni+2	1	MALI	1
H +1	1						
60240	2.48E-08	-7.60	3.23	Co+2	1	MALI	1
60242	5.96E-11	-10.22	7.11	Co+2	1	MALI	1
H +1	1						
60243	2.52E-07	-6.60	0.26	SUCA	1	K +1	1
60244	3.29E-09	-8.48	2.24	SUCA	1	Cd+2	1

60245	1.53E-09	-8.81	1.86	SUCA	1	Ni+2	1
60246	4.42E-17	-16.35	0.82	SUCA	1	Ni+2	1
H +1	1						
60248	1.54E-09	-8.81	1.84	SUCA	1	Co+2	1
60250	1.10E-09	-8.96	1.81	DMBA	1	Cd+2	1
60252	1.90E-09	-8.72	2.00	DMBA	1	Ni+2	1
60254	1.20E-09	-8.92	1.78	DMBA	1	Co+2	1
60256	1.38E-09	-8.86	1.36	Cd+2	1	PROP	1
60258	6.96E-13	-12.16	2.11	Cd+2	1	PROP	2
60260	6.00E-10	-9.22	0.95	Ni+2	1	PROP	1
60262	1.74E-13	-12.76	1.46	Ni+2	1	PROP	2
60264	5.49E-10	-9.26	0.89	Co+2	1	PROP	1
70000	1.32E-04	-3.88	1.83	Ca+2	1	SO4	1
70002	1.06E-06	-5.97	-0.13	Ca+2	1	Cl	1
70004	9.98E-09	-8.00	5.74	Ca+2	1	PO4	1
70006	4.67E-07	-6.33	13.91	Ca+2	1	PO4	1
H +1	1						
70008	9.10E-08	-7.04	19.70	Ca+2	1	PO4	1
H +1	2						
70010	7.79E-11	-10.11	27.24	Ca+2	1	PO4	2
H +1	2						
70012	2.90E-12	-11.54	32.31	Ca+2	1	PO4	2
H +1	3						
70014	7.91E-13	-12.10	28.38	Ca+2	2	PO4	2
H +1	2						
70020	3.52E-10	-9.45	-12.82	Ca+2	1	H +1	-1
70022	1.76E-09	-8.75	2.67	Ca+2	1	CO3	1
70024	8.44E-08	-7.07	10.85	Ca+2	1	CO3	1
H +1	1						
70026	6.42E-10	-9.19	-0.29	Ca+2	1	NH3	1
70028	1.73E-16	-15.76	-1.09	Ca+2	1	NH3	2
70030	2.95E-23	-22.53	-2.09	Ca+2	1	NH3	3
70032	1.27E-05	-4.90	0.46	Ca+2	1	NO3	1
70034	4.55E-08	-7.34	0.24	Ca+2	1	NO3	2
70054	1.28E-04	-3.89	1.75	Mg+2	1	SO4	1
70056	1.57E-08	-7.80	5.87	Mg+2	1	PO4	1

70058	1.73E-06	-5.76	14.41	Mg+2	1	PO4	1
H +1	1						
70060	3.44E-07	-6.46	20.21	Mg+2	1	PO4	1
H +1	2						
70062	1.02E-11	-10.99	32.79	Mg+2	1	PO4	2
H +1	3						
70064	8.50E-11	-10.07	27.21	Mg+2	1	PO4	2
H +1	2						
70066	4.11E-12	-11.39	28.96	Mg+2	2	PO4	2
H +1	2						
70072	7.84E-09	-8.11	-11.54	Mg+2	1	H +1	-1
70074	1.89E-26	-25.72	-39.46	Mg+2	4	H +1	-4
70076	1.16E-08	-7.94	3.42	Mg+2	1	CO3	1
70078	3.50E-07	-6.46	11.40	Mg+2	1	CO3	1
H +1	1						
70080	9.24E-09	-8.03	0.80	Mg+2	1	NH3	1
70082	1.34E-15	-14.87	-0.27	Mg+2	1	NH3	2
70084	6.00E-22	-21.22	-0.85	Mg+2	1	NH3	3
70086	1.29E-28	-27.89	-1.75	Mg+2	1	NH3	4
70112	4.93E-11	-10.31	-14.50	K +1	1	H +1	-1
70114	4.76E-05	-4.32	0.56	K +1	1	SO4	1
70116	2.60E-07	-6.58	12.83	K +1	1	PO4	1
H +1	1						
70118	1.27E-06	-5.90	-0.88	K +1	1	Cl	1
70120	1.58E-05	-4.80	-0.27	K +1	1	NO3	1
70124	1.52E-05	-4.82	0.46	Na+1	1	SO4	1
70126	4.52E-07	-6.34	1.51	Na+1	1	SO4	2
70132	1.35E-07	-6.87	12.94	Na+1	1	PO4	1
H +1	1						
70134	1.93E-08	-7.72	2.01	Na+1	1	BOH4	1
70136	7.89E-11	-10.10	-13.90	Na+1	1	H +1	-1
70138	2.77E-06	-5.56	-0.63	Na+1	1	NO3	1
70140	6.37E-16	-15.20	3.32	SO4	1	Fe+3	1
70142	2.13E-17	-16.67	4.42	SO4	2	Fe+3	1
70144	2.95E-18	-17.53	1.12	Cl	1	Fe+3	1
70146	1.48E-20	-19.83	1.53	Cl	2	Fe+3	1
70148	2.19E-24	-23.66	0.41	Cl	3	Fe+3	1

```
70150   2.05E-12  -11.69   21.36     PO4    1    Fe+3   1
H +1   1
70152   1.05E-17  -16.98   22.57     PO4    1    Fe+3   1
H +1   2
70154   3.40E-21  -20.47   28.52     PO4    1    Fe+3   1
H +1   1
70168   5.34E-15  -14.27    8.69     BOH4   1    Fe+3   1
70170   6.68E-15  -14.17   15.81     BOH4   2    Fe+3   1
70172   5.92E-17  -16.23   20.78     BOH4   3    Fe+3   1
70174   3.52E-16  -15.45    8.01     MoO4   1    Fe+3   1
70176   1.26E-22  -21.90   16.61     MoO4   3    Fe+3   1
70178   1.35E-12  -11.87   -2.43     Fe+3   1    H +1   -1
70180   1.00E-09   -9.00   -6.06     Fe+3   1    H +1   -2
70200   4.90E-07   -6.31   -9.87     Fe+3   1    H +1   -3
70202   1.66E-12  -11.78  -21.84     Fe+3   1    H +1   -4
70204   1.66E-22  -21.78   -2.90     Fe+3   2    H +1   -2
70206   9.98E-29  -28.00   -6.18     Fe+3   3    H +1   -4
70208   2.99E-18  -17.52    0.64     NO3    1    Fe+3   1
70220   7.32E-19  -18.14    1.72     SO4    1    Fe+2   1
70222   7.32E-25  -24.14    2.22     SO4    1    Fe+2   1
H +1   1
70224   3.98E-21  -20.40   -9.62     Fe+2   1    H +1   -1
70226   1.00E-25  -25.00  -20.72     Fe+2   1    H +1   -2
70228   1.66E-30  -29.78  -32.00     Fe+2   1    H +1   -3
70230   3.63E-38  -37.44  -46.16     Fe+2   1    H +1   -4
70240   5.16E-20  -19.29   15.10     Fe+2   1    PO4    1
H +1   1
70242   3.26E-20  -19.49   21.40     Fe+2   1    PO4    1
H +1   2
70244   6.68E-24  -23.17   28.32     Fe+2   1    PO4    2
H +1   2
70266   7.65E-08   -7.12   15.07     Mn+2   1    PO4    1
H +1   1
70268   5.17E-08   -7.29   21.40     Mn+2   1    PO4    1
H +1   2
```

70270	5.97E-12	-11.22	28.07	Mn+2	1	PO4	2
H +1	2						
70272	1.33E-06	-5.87	1.78	Mn+2	1	SO4	1
70274	5.02E-10	-9.30	-10.72	Mn+2	1	H +1	-1
70276	3.10E-15	-14.51	-22.43	Mn+2	1	H +1	-2
70278	1.66E-20	-19.78	-34.20	Mn+2	1	H +1	-3
70280	7.25E-28	-27.14	-48.06	Mn+2	1	H +1	-4
70282	7.27E-15	-14.14	-10.48	Mn+2	2	H +1	-1
70284	1.59E-15	-14.80	-24.14	Mn+2	2	H +1	-3
70286	6.04E-09	-8.22	11.65	Mn+2	1	CO3	1
H +1	1						
70294	1.03E-10	-9.99	0.86	Mn+2	1	NH3	1
70296	7.47E-16	-15.13	1.49	Mn+2	1	NH3	2
70298	2.32E-21	-20.64	1.75	Mn+2	1	NH3	3
70300	1.47E-27	-26.83	1.32	Mn+2	1	NH3	4
70302	4.54E-08	-7.34	-0.04	Mn+2	1	NO3	1
70304	5.16E-10	-9.29	0.24	Mn+2	1	NO3	2
70318	6.43E-10	-9.19	15.51	Cu+2	1	PO4	1
H +1	1						
70320	1.04E-11	-10.98	20.22	Cu+2	1	PO4	1
H +1	2						
70322	4.91E-17	-16.31	32.00	Cu+2	1	PO4	2
H +1	3						
70324	9.92E-19	-18.00	31.40	Cu+2	2	PO4	2
H +1	2						
70326	6.32E-14	-13.20	28.61	Cu+2	1	PO4	2
H +1	2						
70328	5.13E-09	-8.29	1.88	Cu+2	1	SO4	1
70330	3.42E-10	-9.47	3.28	Cu+2	1	SO4	2
70332	1.69E-13	-12.77	2.55	Cu+2	1	SO4	3
70334	4.71E-08	-7.33	7.29	Cu+2	1	BOH4	1
70336	1.20E-09	-8.92	12.72	Cu+2	1	BOH4	2
70338	6.14E-14	-13.21	15.45	Cu+2	1	BOH4	3
70340	1.22E-09	-8.91	-7.82	Cu+2	1	H +1	-1
70342	3.06E-10	-9.51	-14.92	Cu+2	1	H +1	-2
70344	2.12E-16	-15.67	-27.58	Cu+2	1	H +1	-3
70346	1.11E-21	-20.95	-39.36	Cu+2	1	H +1	-4

```
70348   6.18E-14  -13.21  -11.02    Cu+2  2    H +1  -2
70350   2.38E-19  -18.62  -21.84    Cu+2  3    H +1  -4
70352   8.74E-32  -31.06  -20.18    Cu+2  4    H +1  -3
70364   2.43E-10   -9.61    6.27    Cu+2  1    CO3    1
70366   1.50E-15  -14.82    9.35    Cu+2  1    CO3    2
70368   7.17E-11  -10.14    0.16    Cu+2  1    Cl     1
70370   4.98E-10   -9.30    4.06    Cu+2  1    NH3    1
70372   1.69E-12  -11.77    7.36    Cu+2  1    NH3    2
70374   1.58E-15  -14.80   10.10    Cu+2  1    NH3    3
70376   2.09E-19  -18.68   11.99    Cu+2  1    NH3    4
70378   9.82E-26  -25.01   11.43    Cu+2  1    NH3    5
70380   1.65E-10   -9.78   -2.92    Cu+2  1    NH3    1
H +1  -1
70382   4.78E-20  -19.32   -0.92    Cu+2  1    NH3    3
H +1  -1
70384   1.12E-22  -21.95  -15.82    Cu+2  1    NH3    2
H +1  -2
70386   2.76E-10   -9.56    0.26    Cu+2  1    NO3    1
70388   1.04E-12  -11.98    0.06    Cu+2  1    NO3    2
70424   1.17E-08   -7.93   14.71    Zn+2  1    PO4    1
H +1   1
70426   1.37E-09   -8.86   20.28    Zn+2  1    PO4    1
H +1   2
71208   5.12E-14  -13.29   32.96    Zn+2  1    PO4    2
H +1   3
71210   4.83E-16  -15.32   29.97    Zn+2  2    PO4    2
H +1   2
71212   1.82E-12  -11.74   28.01    Zn+2  1    PO4    2
H +1   2
71214   6.14E-07   -6.21    1.90    Zn+2  1    SO4    1
71216   3.57E-08   -7.45    3.24    Zn+2  1    SO4    2
71218   8.06E-11  -10.09    3.17    Zn+2  1    SO4    3
71220   3.16E-13  -12.50    3.34    Zn+2  1    SO4    4
71222   6.98E-09   -8.16   -9.12    Zn+2  1    H +1  -1
71224   1.84E-08   -7.74  -15.20    Zn+2  1    H +1  -2
71226   3.66E-15  -14.44  -28.40    Zn+2  1    H +1  -3
71228   3.19E-21  -20.50  -40.96    Zn+2  1    H +1  -4
```

71230	3.53E-14	-13.45	-8.88	Zn+2	2	H +1	-1
71242	2.48E-10	-9.61	4.22	Zn+2	1	CO3	1
71243	2.11E-09	-8.68	11.65	Zn+2	1	CO3	1
H +1	1						
71244	8.79E-09	-8.06	0.19	Zn+2	1	Cl	1
71246	5.30E-11	-10.28	0.68	Zn+2	1	Cl	2
71248	3.27E-13	-12.49	1.18	Zn+2	1	Cl	3
71250	1.33E-15	-14.88	1.50	Zn+2	1	Cl	4
71252	8.04E-10	-9.09	2.21	Zn+2	1	NH3	1
71254	2.67E-13	-12.57	4.50	Zn+2	1	NH3	2
71256	1.04E-16	-15.98	6.86	Zn+2	1	NH3	3
71258	1.90E-20	-19.72	8.89	Zn+2	1	NH3	4
71260	4.85E-10	-9.31	-4.51	Zn+2	1	NH3	1
H +1	-1						
71262	3.00E-14	-13.52	-2.95	Zn+2	1	NH3	2
H +1	-1						
71264	7.91E-19	-18.10	-1.76	Zn+2	1	NH3	3
H +1	-1						
71266	1.64E-13	-12.78	-14.48	Zn+2	1	NH3	1
H +1	-2						
71268	1.09E-18	-17.96	-13.89	Zn+2	1	NH3	2
H +1	-2						
71270	1.88E-19	-18.72	-26.92	Zn+2	1	NH3	1
H +1	-3						
71300	2.51E-08	-7.60	0.16	Zn+2	1	NO3	1
71302	1.98E-10	-9.70	0.28	Zn+2	1	NO3	2
77300	3.50E-19	-18.46	10.18	NH3	2	Cu+1	1
77400	1.66E-19	-18.78	2.72	SO4	1	Mn+3	1
77402	1.40E-12	-11.85	0.57	Mn+3	1	H +1	-1
78600	1.99E-05	-4.70	10.09	CO3	1	H +1	1
78602	1.07E-05	-4.97	16.32	CO3	1	H +1	2
78604	4.72E-08	-7.33	1.75	SO4	1	H +1	1
78606	4.62E-22	-21.34	-5.76	SO4	1	H +1	2
78610	7.45E-06	-5.13	11.98	PO4	1	H +1	1
78612	2.15E-05	-4.67	18.94	PO4	1	H +1	2
78614	7.12E-10	-9.15	20.96	PO4	1	H +1	3
78616	2.26E-11	-10.65	30.07	PO4	2	H +1	3

78618	2.85E-10	-9.54	37.67	PO4	2	H +1	4
78620	5.44E-14	-13.26	40.45	PO4	2	H +1	5
78634	4.17E-08	-7.38	-13.88	H +1	-1		
78636	4.98E-05	-4.30	9.22	BOH4	1	H +1	1
78638	2.36E-18	-17.63	9.94	BOH4	3	H +1	1
78640	5.16E-15	-14.29	19.78	BOH4	3	H +1	2
78642	1.70E-21	-20.77	20.32	BOH4	4	H +1	2
78644	1.02E-18	-17.99	29.60	BOH4	4	H +1	3
78646	2.13E-23	-22.67	38.44	BOH4	5	H +1	4
78648	5.98E-11	-10.22	3.80	MoO4	1	H +1	1
78650	1.40E-13	-12.85	7.67	MoO4	1	H +1	2
78652	3.21E-19	-18.49	8.53	MoO4	1	H +1	3
78654	2.95E-16	-15.53	-6.32	Cl	1	H +1	1
78656	9.36E-04	-3.03	9.24	NH3	1	H +1	1
78700	4.38E-05	-4.36	10.62	Cl	1	NH3	1
H +1	1						
78702	1.84E-05	-4.73	10.11	SO4	1	NH3	1
H +1	1						
78708	5.44E-11	-10.26	-1.54	NO3	1	H +1	1
78710	2.34E-10	-9.63	8.39	ACAC	1	Al+3	1
78712	7.76E-10	-9.11	16.19	ACAC	2	Al+3	1
78714	2.51E-11	-10.60	21.98	ACAC	3	Al+3	1
78716	1.45E-08	-7.84	14.37	SAL	1	Al+3	1
78718	7.25E-13	-12.14	3.75	PHTH	1	Al+3	1
78720	2.69E-09	-8.57	7.32	PHTH	1	Al+3	1
78722	3.16E-11	-10.50	-2.12	BZA	1	Al+3	1
H +1	-1						
90100	3.14E-08	-7.50	13.06	DHBZ	1	H +1	1
90102	1.89E-05	-4.72	22.34	DHBZ	1	H +1	2
90104	7.79E-12	-11.11	6.02	Mg+2	1	DHBZ	1
90106	2.65E-13	-12.58	4.62	Ca+2	1	DHBZ	1
90108	7.55E-12	-11.12	8.02	Mn+2	1	DHBZ	1
90110	3.78E-10	-9.42	16.22	Mn+2	1	DHBZ	1
H +1	1						
90112	2.38E-23	-22.62	8.72	DHBZ	1	Fe+2	1
90114	1.19E-21	-20.92	16.92	DHBZ	1	Fe+2	1
H +1	1						

90116	3.65E-08	-7.44	14.22	Cu+2	1	DHBZ	1
90118	4.18E-10	-9.38	10.22	Zn+2	1	DHBZ	1
90120	1.14E-08	-7.94	3.88	HMPA	1	H +1	1
90122	6.37E-08	-7.20	1.26	Ca+2	1	HMPA	1
90124	5.92E-08	-7.23	1.16	Mg+2	1	HMPA	1
90126	5.74E-10	-9.24	1.16	Mn+2	1	HMPA	1
90128	1.14E-21	-20.94	1.66	HMPA	1	Fe+2	1
90130	1.11E-10	-9.96	2.96	Cu+2	1	HMPA	1
90132	1.26E-09	-8.90	1.96	Zn+2	1	HMPA	1
90134	7.55E-19	-18.12	3.14	HMPA	1	Fe+3	1
90136	2.28E-13	-12.64	2.12	HMPA	1	Fe+3	1
H +1	-1						
90138	3.09E-05	-4.51	13.46	SAL	1	H +1	1
90140	7.42E-09	-8.13	16.34	SAL	1	H +1	2
90141	1.22E-09	-8.92	5.62	Mg+2	1	SAL	1
90142	1.31E-10	-9.88	4.72	Ca+2	1	SAL	1
90144	3.29E-08	-7.48	13.62	Ca+2	1	SAL	1
H +1	1						
90146	4.69E-11	-10.33	6.22	Mn+2	1	SAL	1
90148	1.48E-22	-21.83	6.92	SAL	1	Fe+2	1
90150	7.18E-09	-8.14	10.92	Cu+2	1	SAL	1
90152	1.64E-10	-9.79	7.22	Zn+2	1	SAL	1
90154	1.86E-11	-10.73	16.68	SAL	1	Fe+3	1
90156	9.78E-17	-16.01	17.90	SAL	1	Fe+3	1
H +1	1						
90158	1.03E-16	-15.99	10.02	Mg+2	1	SAL	2
90160	8.85E-19	-18.05	8.02	Ca+2	1	SAL	2
90162	1.59E-18	-17.80	10.22	Mn+2	1	SAL	2
90164	2.51E-29	-28.60	11.62	SAL	2	Fe+2	1
90166	2.89E-09	-8.54	30.34	SAL	2	Fe+3	1
90168	1.93E-12	-11.71	18.82	Cu+2	1	SAL	2
90170	1.39E-23	-22.86	5.62	Zn+2	1	SAL	2
90172	1.70E-05	-4.77	9.98	ACPH	1	H +1	1
90174	7.53E-11	-10.12	1.26	Ca+2	1	ACPH	1
90176	1.35E-11	-10.87	2.46	Mn+2	1	ACPH	1
90178	1.04E-09	-8.98	6.86	Cu+2	1	ACPH	1
90180	2.98E-11	-10.53	3.26	Zn+2	1	ACPH	1

90182	2.24E-14	-13.65	10.54	ACPH	1	Fe+3	1
90184	5.23E-07	-6.28	4.38	HBA	1	H +1	1
90186	3.41E-07	-6.47	0.76	Mg+2	1	HBA	1
90188	1.84E-07	-6.73	0.56	Ca+2	1	HBA	1
90190	3.19E-10	-9.50	2.26	Cu+2	1	HBA	1
90192	3.65E-09	-8.44	1.26	Zn+2	1	HBA	1
90194	3.34E-05	-4.48	7.16	DEMA	1	H +1	1
90196	1.27E-09	-8.90	9.24	DEMA	1	H +1	2
90198	5.25E-08	-7.28	0.56	Na+1	1	DEMA	1
90200	4.15E-07	-6.38	1.82	Mg+2	1	DEMA	1
90202	1.04E-07	-6.98	7.72	Mg+2	1	DEMA	1
H +1	1						
90204	3.55E-07	-6.45	1.82	Ca+2	1	DEMA	1
90206	1.41E-07	-6.85	7.92	Ca+2	1	DEMA	1
H +1	1						
90208	8.03E-09	-8.10	2.12	Mn+2	1	DEMA	1
90210	3.09E-08	-7.51	5.22	Cu+2	1	DEMA	1
90212	9.76E-12	-11.01	8.22	Cu+2	1	DEMA	1
H +1	1						
90214	1.12E-08	-7.95	2.72	Zn+2	1	DEMA	1
90216	1.41E-09	-8.85	8.32	Zn+2	1	DEMA	1
H +1	1						
90218	1.01E-12	-12.00	9.08	DEMA	1	Fe+3	1
90220	3.34E-18	-17.48	10.10	DEMA	1	Fe+3	1
H +1	1						
90222	1.26E-05	-4.90	8.88	ACAC	1	H +1	1
90224	1.30E-07	-6.89	3.46	Mg+2	1	ACAC	1
90226	2.80E-08	-7.55	2.86	Ca+2	1	ACAC	1
90228	3.99E-09	-8.40	3.96	Mn+2	1	ACAC	1
90230	2.00E-20	-19.70	4.86	ACAC	1	Fe+2	1
90232	1.53E-07	-6.81	8.06	Cu+2	1	ACAC	1
90234	1.11E-08	-7.96	4.86	Zn+2	1	ACAC	1
90236	8.32E-14	-13.08	10.14	ACAC	1	Fe+3	1
90238	3.24E-07	-6.49	5.16	PHTH	1	H +1	1
90240	7.77E-11	-10.11	8.04	PHTH	1	H +1	2
90242	4.05E-08	-7.39	0.46	Na+1	1	PHTH	1
90244	4.33E-07	-6.36	1.92	Ca+2	1	PHTH	1

90246	9.80E-09	-8.01	2.22	PHTH	1	Mn+2	1
90248	5.97E-10	-9.22	3.52	PHTH	1	Cu+2	1
90250	5.43E-09	-8.27	2.42	PHTH	1	Zn+2	1
90252	4.90E-14	-13.31	7.78	PHTH	1	Fe+3	1
90254	8.43E-14	-13.07	4.82	PHTH	2	Cu+2	1
90256	7.66E-13	-12.12	3.72	PHTH	2	Zn+2	1
90258	4.24E-07	-6.37	4.86	MALI	1	H +1	1
90260	3.22E-10	-9.49	8.24	MALI	1	H +1	2
90262	1.06E-07	-6.98	0.46	Na+1	1	MALI	1
90264	2.09E-07	-6.68	0.36	K +1	1	MALI	1
90266	1.67E-06	-5.78	2.02	Mg+2	1	MALI	1
90268	5.27E-09	-8.28	6.02	Mg+2	1	MALI	1
H +1	1						
90270	2.26E-06	-5.65	2.22	Ca+2	1	MALI	1
90272	5.68E-09	-8.25	6.12	Ca+2	1	MALI	1
H +1	1						
90274	6.44E-08	-7.19	2.62	Mn+2	1	MALI	1
90276	8.09E-20	-19.09	2.92	MALI	1	Fe+2	1
90278	2.47E-09	-8.61	3.72	Cu+2	1	MALI	1
90280	6.22E-07	-6.21	6.12	Cu+2	1	MALI	1
90282	3.56E-08	-7.45	2.82	Zn+2	1	MALI	1
90284	7.11E-11	-10.15	6.62	Zn+2	1	MALI	1
H +1	1						
90286	1.28E-13	-12.89	7.78	MALI	1	Fe+3	1
90288	2.04E-06	-5.69	5.36	SUCA	1	H +1	1
90290	7.75E-09	-8.11	9.44	SUCA	1	H +1	2
90292	6.40E-08	-7.19	0.06	SUCA	1	Na+1	1
90294	8.01E-07	-6.10	1.52	SUCA	1	Mg+2	1
90296	8.01E-09	-8.10	6.02	SUCA	1	Mg+2	1
H +1	1						
90298	6.85E-07	-6.16	1.52	SUCA	1	Ca+2	1
90300	6.85E-09	-8.16	6.02	SUCA	1	Ca+2	1
H +1	1						
90302	1.55E-08	-7.81	1.82	SUCA	1	Mn+2	1
90304	7.76E-14	-13.11	3.02	SUCA	1	Mn+2	1
H +1	1						
90306	7.75E-21	-20.11	1.72	SUCA	1	Fe+2	1

90308	4.73E-10	-9.33	2.82	SUCA	1	Cu+2	1
90310	8.57E-09	-8.07	2.02	SUCA	1	Zn+2	1
90312	6.81E-11	-10.17	6.42	SUCA	1	Zn+2	1
H +1	1						
90314	1.23E-13	-12.91	7.58	SUCA	1	Fe+3	1
90316	3.04E-08	-7.52	3.58	DMBA	1	H +1	1
90318	2.50E-07	-6.60	1.06	Mg+2	1	DMBA	1
90320	4.26E-07	-6.37	1.36	Ca+2	1	DMBA	1
90322	3.70E-10	-9.43	2.76	DMBA	1	Cu+2	1
90324	5.33E-09	-8.27	1.86	DMBA	1	Zn+2	1
90326	2.75E-07	-6.56	4.08	BZA	1	H +1	1
90328	1.13E-07	-6.95	0.26	Mg+2	1	BZA	1
90330	1.54E-07	-6.81	0.46	Ca+2	1	BZA	1
90332	5.51E-09	-8.26	0.96	Mn+2	1	BZA	1
90334	1.06E-10	-9.97	1.76	Cu+2	1	BZA	1
90336	2.42E-09	-8.62	1.06	Zn+2	1	BZA	1
90338	2.29E-15	-14.64	5.44	BZA	1	Fe+3	1
90340	1.20E-04	-3.92	9.88	PHEN	1	H +1	1
90342	3.97E-16	-15.40	7.84	PHEN	1	Fe+3	1
90344	1.71E-06	-5.77	4.78	PROP	1	H +1	1
90346	3.52E-07	-6.45	0.66	Mg+2	1	PROP	1
90348	3.79E-07	-6.42	0.76	Ca+2	1	PROP	1
90350	2.08E-10	-9.68	1.96	Cu+2	1	PROP	1
90352	2.99E-09	-8.52	1.06	Zn+2	1	PROP	1
90354	4.49E-17	-16.35	3.64	PROP	1	Fe+3	1
90356	3.64E-09	-8.44	2.68	HBQN	1	H +1	1
90358	1.19E-06	-5.93	1.76	Mg+2	1	HBQN	1
90360	4.05E-07	-6.39	1.36	Ca+2	1	HBQN	1
90362	4.59E-08	-7.34	2.36	Mn+2	1	HBQN	1
90364	5.57E-08	-7.25	4.96	Cu+2	1	HBQN	1
90366	1.27E-06	-5.90	4.26	Zn+2	1	HBQN	1
90368	7.59E-14	-13.12	7.44	HBQN	1	Fe+3	1
90370	4.32E-10	-9.36	2.94	Mg+2	1	HBQN	2
90372	1.17E-10	-9.93	2.44	Ca+2	1	HBQN	2
90374	2.10E-11	-10.68	3.64	Mn+2	1	HBQN	2
90376	1.32E-12	-11.88	13.30	HBQN	2	Fe+3	1
90378	6.41E-09	-8.19	8.64	Cu+2	1	HBQN	2

90374	2.10E-11	-10.68	3.64	Mn+2	1	HBQN	2
90376	1.32E-12	-11.88	13.30	HBQN	2	Fe+3	1
90378	6.41E-09	-8.19	8.64	Cu+2	1	HBQN	2

ID	C	LOGC	LOGK	SPECIES:	TYPE III - FIXED SOLIDS		
50	-1.49E-02	-1.83	6.50	H +1	1		
80000	-6.18E-18	-17.21	7.84	Fe+2	1	Fe+3	-1
H +1	1						
80002	-1.40E-12	-11.85	25.70	Mn+2	-1	Mn+3	1
E-	1						
80004	8.31E-18	-17.08	2.35	Cu+2	1	Cu+1	-1
E-	1						
80006	-1.11E-17	-16.95	30.57	Co+2	-1	Co+3	1
E-	1						
80010	-3.11E-05	-4.51	21.29	CO3	1	H +1	2

ID	C	LOGC	LOGK	SPECIES:	TYPE IV - PRECIPITATED SOLIDS		
80102	3.23E-04	-3.49	40.99	Ca+2	5	PO4	3
H +1	-1						
80600	1.95E-05	-4.71	-3.56	Fe+3	1	H +1	-3
84022	1.13E-06	-5.95	-8.76	Al+3	1	H +1	-3

ID	C	LOGC	LOGK	SPECIES:	TYPE V - DISSOLVED SOLIDS		
80100	2.57E-02	-1.59	4.12	Ca+2	1	SO4	1
80090	1.89E-06	-5.72	-0.31	Na+1	1	Cl	1
80104	2.53E-07	-6.60	44.26	Ca+2	4	PO4	3
H +1	1						
80106	1.44E-02	-1.84	18.40	Ca+2	1	PO4	1
H +1	1						
80110	5.98E-14	-13.22	-23.09	Ca+2	1	H +1	-2
80112	3.20E-04	-3.50	27.12	Ca+2	3	PO4	2
80114	7.23E-03	-2.14	18.10	Ca+2	1	PO4	1
H +1	1						
80116	3.86E-04	-3.41	8.01	Ca+2	1	CO3	1

80200	9.73E-08	-7.01	23.40	Mg+2	3	PO4	2
80202	1.40E-03	-2.85	17.32	Mg+2	1	PO4	1
H +1	1						
80204	9.21E-08	-7.04	-16.97	Mg+2	1	H +1	-2
80206	1.80E-04	-3.75	7.61	Mg+2	1	CO3	1
80208	6.83E-08	-7.17	4.19	Mg+2	1	CO3	1
80210	1.82E-07	-6.74	16.04	Ca+2	1	Mg+2	1
CO3	2						
80211	3.63E-18	-17.44	28.05	Ca+2	1	Mg+2	3
CO3	4						
80212	3.70E-06	-5.43	20.51	Mg+2	1	NH3	1
PO4	1	H +1	1				
80214	6.31E-07	-6.20	9.78	Mg+2	1	K +1	1
PO4	1						
80096	4.05E-25	-24.39	-10.00	Co+2	1	CO3	1
80602	5.92E-02	-1.23	25.32	PO4	1	Fe+3	1
80606	2.14E-16	-15.67	-18.51	Fe+2	1	Fe+3	2
H +1	-8						
80608	2.51E-08	-7.60	-10.44	Fe+2	1	Fe+3	2
H +1	-8						
80700	5.01E-18	-17.30	-13.02	Fe+2	1	H +1	-2
80702	1.55E-16	-15.81	9.76	Fe+2	1	CO3	1
80704	0.00E+00	-38.85	34.20	Fe+2	3	PO4	2
80701	1.33E-18	-17.88	1.98	SO4	1	Fe+2	1
80800	3.99E-08	-7.40	-15.32	Mn+2	1	H +1	-2
80802	2.82E-05	-4.55	8.82	Mn+2	1	CO3	1
80900	4.03E-04	-3.39	-8.80	Cu+2	1	H +1	-2
80904	7.98E-09	-8.10	35.90	Cu+2	3	PO4	2
80906	1.84E-07	-6.73	9.15	Cu+2	1	CO3	1
80908	1.21E-06	-5.92	4.56	Cu+2	2	CO3	1
H +1	-2						
80910	2.73E-11	-10.56	15.80	Cu+2	3	CO3	2
H +1	-2						
80912	1.32E-07	-6.88	14.76	Cu+2	1	BOH4	2
81200	4.76E-05	-4.32	33.50	Zn+2	3	PO4	2
81202	3.12E-04	-3.51	10.32	Zn+2	1	CO3	1
81204	7.31E-06	-5.14	-12.60	Zn+2	1	H +1	-2

83302	6.33E-14	-13.20	6.61	Cl	1	Cu+1	1
83304	1.00E-24	-24.00	-13.40	Cu+1	1	H +1	-1
84000	2.61E-23	-22.58	4.89	Ca+2	2	SiO4	1
84002	1.65E-21	-20.78	6.69	Ca+2	2	SiO4	1
84004	2.01E-02	-1.70	65.33	Ca+2	1	SiO4	2
Al+3	2						
84006	2.01E-12	-11.70	15.64	Mg+2	2	SiO4	1
84008	3.09E-02	-1.51	33.14	Na+1	1	SiO4	1
Al+3	1						
84010	1.22E-03	-2.91	31.34	K +1	1	SiO4	1
Al+3	1						
84012	9.63E-32	-31.02	24.75	SiO4	1	Fe+2	2
84014	1.21E-01	-0.92	31.36	Zn+2	2	SiO4	1
84016	4.96E-12	-11.30	20.06	Mn+2	2	SiO4	1
84018	5.50E-02	-1.26	-10.02	Al+3	1	H +1	-3
84020	7.76E-01	-0.11	-8.87	Al+3	1	H +1	-3
80098	4.04E-20	-19.39	-4.98	Ni+2	1	CO3	1
84024	0.00E+00	-51.85	-22.64	SO4	3	Al+3	2
84026	3.03E-06	-5.52	-4.84	K +1	1	SO4	2
Al+3	3	H +1	-6				
84028	4.19E-04	-3.38	17.97	Al+3	1	PO4	1
84030	1.12E-03	-2.95	11.51	Cd+2	1	CO3	1
84032	6.50E-10	-9.19	-0.44	Cd+2	1	SO4	1
84034	3.72E-04	-3.43	36.30	Cd+2	3	PO4	2
84036	1.67E-03	-2.78	7.88	Ca+2	1	MoO4	1
84038	3.56E-11	-10.45	0.14	Mg+2	1	MoO4	1
84040	7.62E-10	-9.12	6.00	Cu+2	1	MoO4	1
84042	2.61E-18	-17.58	7.22	MoO4	1	Fe+2	1
84044	1.12E-09	-8.95	3.65	Mn+2	1	MoO4	1
84046	2.52E-09	-8.60	4.46	Zn+2	1	MoO4	1

PERCENTAGE DISTRIBUTION OF COMPONENTS

SUCA

87.8	PERCENT BOUND IN SPECIES # 172	SUCA	1
6.4	PERCENT BOUND IN SPECIES #90288	SUCA	1

H +1 1

```
          2.5     PERCENT BOUND IN SPECIES #90294   SUCA    1
Mg+2    1
          2.1     PERCENT BOUND IN SPECIES #90298   SUCA    1
Ca+2    1

Ca+2
         29.4     PERCENT BOUND IN SPECIES #    1   Ca+2    1
          5.3     PERCENT BOUND IN SPECIES #70000   Ca+2    1
SO4     1
         64.5     PERCENT BOUND IN SPECIES #80102   Ca+2    5
PO4     3    H +1   -1

Mg+2
         85.9     PERCENT BOUND IN SPECIES #    2   Mg+2    1
         12.8     PERCENT BOUND IN SPECIES #70054   Mg+2    1
SO4     1

K +1
         98.7     PERCENT BOUND IN SPECIES #    4   K +1    1

Na+1
         99.1     PERCENT BOUND IN SPECIES #    5   Na+1    1

PHTH
         88.5     PERCENT BOUND IN SPECIES #  132   PHTH    1
          1.3     PERCENT BOUND IN SPECIES #60148   K +1    1
PHTH    1
          4.0     PERCENT BOUND IN SPECIES #90238   PHTH    1
H +1    1
          5.4     PERCENT BOUND IN SPECIES #90244   Ca+2    1
PHTH    1

DMBA
         97.2     PERCENT BOUND IN SPECIES #  173   DMBA    1
          1.6     PERCENT BOUND IN SPECIES #90320   Ca+2    1
DMBA    1
```

```
Mn+2
          83.3      PERCENT BOUND IN SPECIES #    8    Mn+2    1
          13.3      PERCENT BOUND IN SPECIES #70272    Mn+2    1
SO4     1

Cu+2
           2.5      PERCENT BOUND IN SPECIES #    9    Cu+2    1
           4.7      PERCENT BOUND IN SPECIES #70334    Cu+2    1
BOH4    1
           3.7      PERCENT BOUND IN SPECIES #90116    Cu+2    1
DHBZ    1
           3.1      PERCENT BOUND IN SPECIES #90210    Cu+2    1
DEMA    1
          15.3      PERCENT BOUND IN SPECIES #90232    Cu+2    1
ACAC    1
          62.2      PERCENT BOUND IN SPECIES #90280    Cu+2    1
MALI    1
           5.6      PERCENT BOUND IN SPECIES #90364    Cu+2    1
HBQN    1

Cd+2
          67.3      PERCENT BOUND IN SPECIES #   11    Cd+2    1
          17.1      PERCENT BOUND IN SPECIES #60018    Cd+2    1
SO4     1
           7.2      PERCENT BOUND IN SPECIES #60026    Cd+2    1
Cl      1
           4.7      PERCENT BOUND IN SPECIES #60058    Cd+2    1
PO4     1    H +1    1

Zn+2
          58.2      PERCENT BOUND IN SPECIES #   12    Zn+2    1
          12.3      PERCENT BOUND IN SPECIES #71214    Zn+2    1
SO4     1
          25.4      PERCENT BOUND IN SPECIES #90366    Zn+2    1
HBQN    1

Ni+2
```

```
          75.1     PERCENT BOUND IN SPECIES #   13   Ni+2   1
          14.5     PERCENT BOUND IN SPECIES #60020   Ni+2   1
SO4    1
           2.2     PERCENT BOUND IN SPECIES #60128   Ni+2   1
ACAC   1
           4.8     PERCENT BOUND IN SPECIES #60236   Ni+2   1
MALI   1

Co+2
          78.9     PERCENT BOUND IN SPECIES #   16   Co+2   1
          15.2     PERCENT BOUND IN SPECIES #60022   Co+2   1
SO4    1
           1.0     PERCENT BOUND IN SPECIES #60066   Co+2   1
PO4    1    H +1   1
           2.5     PERCENT BOUND IN SPECIES #60240   Co+2   1
MALI   1

Co+3

ACAC
          96.9     PERCENT BOUND IN SPECIES #90222   ACAC   1
H +1   1
           1.0     PERCENT BOUND IN SPECIES #90224   Mg+2   1
ACAC   1
           1.2     PERCENT BOUND IN SPECIES #90232   Cu+2   1
ACAC   1

PHEN
         100.0     PERCENT BOUND IN SPECIES #90340   PHEN   1
H +1   1

BZA
          99.2     PERCENT BOUND IN SPECIES #  164   BZA    1

PROP
          97.3     PERCENT BOUND IN SPECIES #  174   PROP   1
```

```
            1.9     PERCENT BOUND IN SPECIES #90344   PROP   1
H +1   1

HBQN
           88.9     PERCENT BOUND IN SPECIES #  166   HBQN   1
            4.4     PERCENT BOUND IN SPECIES #90358   Mg+2   1
HBQN   1
            1.5     PERCENT BOUND IN SPECIES #90360   Ca+2   1
HBQN   1
            4.7     PERCENT BOUND IN SPECIES #90366   Zn+2   1
HBQN   1

SO4
           88.5     PERCENT BOUND IN SPECIES #  102   SO4    1
            4.4     PERCENT BOUND IN SPECIES #70000   Ca+2   1
SO4    1
            4.3     PERCENT BOUND IN SPECIES #70054   Mg+2   1
SO4    1
            1.6     PERCENT BOUND IN SPECIES #70114   K +1   1
SO4    1

Cl
           97.5     PERCENT BOUND IN SPECIES #  103   Cl     1
            2.2     PERCENT BOUND IN SPECIES #78700   Cl     1
NH3    1    H +1   1

NH3
           93.6     PERCENT BOUND IN SPECIES #78656   NH3    1
H +1   1
            4.4     PERCENT BOUND IN SPECIES #78700   Cl     1
NH3    1    H +1   1
            1.8     PERCENT BOUND IN SPECIES #78702   SO4    1
NH3    1    H +1   1

MALI
           77.2     PERCENT BOUND IN SPECIES #  171   MALI   1
```

```
            1.8     PERCENT BOUND IN SPECIES #90258   MALI    1
H +1    1
            6.9     PERCENT BOUND IN SPECIES #90266   Mg+2    1
MALI    1
            9.4     PERCENT BOUND IN SPECIES #90270   Ca+2    1
MALI    1
            2.6     PERCENT BOUND IN SPECIES #90280   Cu+2    1
MALI    1

SiO4
           99.9     PERCENT BOUND IN SPECIES #50014   SiO4    1
H +1    4

BOH4
           99.7     PERCENT BOUND IN SPECIES #78636   BOH4    1
H +1    1

MoO4
           99.8     PERCENT BOUND IN SPECIES #  152   MoO4    1

NO3
           99.5     PERCENT BOUND IN SPECIES #  157   NO3     1

DHBZ
           99.6     PERCENT BOUND IN SPECIES #90102   DHBZ    1
H +1    2

SAL
           99.8     PERCENT BOUND IN SPECIES #90138   SAL     1
H +1    1

HMPA
           97.2     PERCENT BOUND IN SPECIES #  168   HMPA    1
            1.3     PERCENT BOUND IN SPECIES #90122   Ca+2    1
HMPA    1
            1.2     PERCENT BOUND IN SPECIES #90124   Mg+2    1
HMPA    1
```

```
ACPH
        100.0     PERCENT BOUND IN SPECIES #90172   ACPH    1
H +1    1

HBA
         98.5     PERCENT BOUND IN SPECIES #  169   HBA     1

DEMA
         17.4     PERCENT BOUND IN SPECIES #  170   DEMA    1
         79.5     PERCENT BOUND IN SPECIES #90194   DEMA    1
H +1    1

Al+3
          2.7     PERCENT BOUND IN SPECIES #50002   Al+3    1
H +1   -2
         21.1     PERCENT BOUND IN SPECIES #50004   Al+3    1
H +1   -3
         75.0     PERCENT BOUND IN SPECIES #84022   Al+3    1
H +1   -3

Fe+2
         84.9     PERCENT BOUND IN SPECIES #    7   Fe+2    1
         11.8     PERCENT BOUND IN SPECIES #70220   SO4     1
Fe+2    1
          1.3     PERCENT BOUND IN SPECIES #90276   MALI    1
Fe+2    1

Mn+3
        100.0     PERCENT BOUND IN SPECIES #77402   Mn+3    1
H +1   -1

Cu+1
         95.8     PERCENT BOUND IN SPECIES #   33   Cu+1    1
          4.2     PERCENT BOUND IN SPECIES #77300   NH3     2
Cu+1    1
```

```
E-
        100.0     PERCENT BOUND IN SPECIES #   99   E-      1

CO3
          1.1     PERCENT BOUND IN SPECIES #70078   Mg+2    1
CO3     1    H +1   1
         64.0     PERCENT BOUND IN SPECIES #78600   CO3     1
H +1    1
         34.4     PERCENT BOUND IN SPECIES #78602   CO3     1
H +1    2

PO4
          2.2     PERCENT BOUND IN SPECIES #78612   PO4     1
H +1    2
         96.8     PERCENT BOUND IN SPECIES #80102   Ca+2    5
PO4     3    H +1  -1

Fe+3
          2.4     PERCENT BOUND IN SPECIES #70200   Fe+3    1
H +1   -3
         97.5     PERCENT BOUND IN SPECIES #80600   Fe+3    1
H +1   -3

H +1
         93.2     PERCENT BOUND IN SPECIES #50014   SiO4    1
H +1    4
          6.2     PERCENT BOUND IN SPECIES #78656   NH3     1
H +1    1
```

APPENDIX C

SOIL SOLUTION MODEL IN THE ABSENCE OF DISSOLVED OXYGEN (See chapter 5.4.2).

INPUT

IONIC STRENGTH = 2.00E-02

ID	X	LOGX	T	COMPONENTS
50	3.16E-07	-6.50	0.00E+00	H +1
1	1.00E-03	-3.00	2.50E-03	Ca+2
2	1.00E-03	-3.00	1.00E-03	Mg+2
4	1.00E-03	-3.00	5.00E-03	K +1
5	1.00E-05	-5.00	2.00E-03	Na+1
6	1.00E-05	-5.00	2.00E-05	Fe+3
7	1.00E-09	-9.00	0.00E+00	Fe+2
8	1.00E-05	-5.00	1.00E-05	Mn+2
9	1.00E-06	-6.00	1.00E-06	Cu+2
11	1.00E-06	-6.00	1.00E-06	Cd+2
12	1.00E-06	-6.00	5.00E-06	Zn+2
13	1.00E-06	-6.00	1.00E-06	Ni+2
16	1.00E-07	-7.00	1.00E-06	Co+2
17	1.00E-09	-9.00	0.00E+00	Co+3
20	1.00E-07	-7.00	1.50E-06	Al+3
33	1.00E-09	-9.00	0.00E+00	Cu+1
34	1.00E-09	-9.00	0.00E+00	Mn+3
99	1.00E-07	-7.00	0.00E+00	E-
101	1.00E-08	-8.00	0.00E+00	CO3
102	1.00E-03	-3.00	3.00E-03	SO4
103	1.00E-03	-3.00	2.00E-03	Cl
107	1.00E-03	-3.00	1.00E-03	NH3
109	1.00E-03	-3.00	1.00E-03	PO4
112	1.00E-04	-4.00	3.50E-03	SiO4
148	1.00E-06	-6.00	5.00E-05	BOH4
152	1.00E-08	-8.00	3.00E-08	MoO4
157	1.00E-03	-3.00	6.00E-03	NO3

167	1.00E-05	-5.00	1.90E-05	DHBZ
119	1.00E-05	-5.00	3.10E-05	SAL
168	1.00E-05	-5.00	4.90E-06	HMPA
163	1.00E-05	-5.00	1.70E-05	ACPH
169	1.00E-05	-5.00	7.00E-05	HBA
170	1.00E-05	-5.00	4.20E-05	DEMA
116	1.00E-05	-5.00	1.30E-05	ACAC
132	1.00E-05	-5.00	8.00E-06	PHTH
171	1.00E-05	-5.00	2.40E-05	MALI
172	1.00E-05	-5.00	3.20E-05	SUCA
173	1.00E-05	-5.00	2.60E-05	DMBA
164	1.00E-05	-5.00	7.30E-05	BZA
165	1.00E-05	-5.00	1.20E-04	PHEN
174	1.00E-05	-5.00	9.20E-05	PROP
166	1.00E-05	-5.00	2.70E-05	HBQN

OUTPUT

ID	C	LOGC	LOGK	SPECIES:	TYPE I - COMPONENTS
166	2.40E-05	-4.62	0.00	HBQN	1
1	7.35E-04	-3.13	0.00	Ca+2	1
2	8.59E-04	-3.07	0.00	Mg+2	1
4	4.93E-03	-2.31	0.00	K +1	1
5	1.98E-03	-2.70	0.00	Na+1	1
6	1.15E-16	-15.94	0.00	Fe+3	1
7	7.50E-16	-15.12	0.00	Fe+2	1
8	8.33E-06	-5.08	0.00	Mn+2	1
9	2.54E-08	-7.59	0.00	Cu+2	1
11	6.73E-07	-6.17	0.00	Cd+2	1
12	2.91E-06	-5.54	0.00	Zn+2	1
13	7.51E-07	-6.12	0.00	Ni+2	1
16	7.89E-07	-6.10	0.00	Co+2	1
17	1.52E-25	-24.82	0.00	Co+3	1
20	1.82E-11	-10.74	0.00	Al+3	1
33	7.96E-18	-17.10	0.00	Cu+1	1
34	1.19E-19	-18.92	0.00	Mn+3	1
99	1.40E-12	-11.85	0.00	E-	1

101	5.13E-09	-8.29	0.00	CO3	1
102	2.65E-03	-2.58	0.00	SO4	1
103	1.95E-03	-2.71	0.00	Cl	1
107	1.70E-06	-5.77	0.00	NH3	1
109	2.47E-11	-10.61	0.00	PO4	1
112	6.20E-22	-21.21	0.00	SiO4	1
148	9.49E-08	-7.02	0.00	BOH4	1
152	2.99E-08	-7.52	0.00	MoO4	1
157	5.97E-03	-2.22	0.00	NO3	1
167	8.64E-15	-14.06	0.00	DHBZ	1
119	3.39E-12	-11.47	0.00	SAL	1
168	4.76E-06	-5.32	0.00	HMPA	1
163	5.63E-09	-8.25	0.00	ACPH	1
169	6.89E-05	-4.16	0.00	HBA	1
170	7.30E-06	-5.14	0.00	DEMA	1
116	5.25E-08	-7.28	0.00	ACAC	1
132	7.08E-06	-5.15	0.00	PHTH	1
171	1.85E-05	-4.73	0.00	MALI	1
172	2.81E-05	-4.55	0.00	SUCA	1
173	2.53E-05	-4.60	0.00	DMBA	1
164	7.24E-05	-4.14	0.00	BZA	1
165	5.00E-08	-7.30	0.00	PHEN	1
174	8.96E-05	-4.05	0.00	PROP	1

ID	C	LOGC	LOGK	SPECIES:	TYPE II - COMPLEXES	
90380	9.23E-10	-9.03	5.74	Zn+2	1	HBQN 2
50000	3.16E-10	-9.50	-5.26	Al+3	1	H +1 -1
50002	3.98E-08	-7.40	-9.66	Al+3	1	H +1 -2
50004	3.16E-07	-6.50	-15.26	Al+3	1	H +1 -3
50006	6.75E-17	-16.17	-7.69	Al+3	2	H +1 -2
50008	8.19E-16	-15.09	12.62	SiO4	1	H +1 1
50010	8.38E-13	-12.08	22.13	SiO4	1	H +1 2
50012	2.84E-06	-5.55	35.16	SiO4	1	H +1 3
50014	3.50E-03	-2.46	44.75	SiO4	1	H +1 4
50016	9.73E-19	-18.01	-0.60	NO3	3	Al+3 1

50018	2.91E-15	-14.54	5.28	SO4	1	Al+3	1
H +1	1						
50020	1.46E-11	-10.84	2.48	SO4	1	Al+3	1
50022	1.12E-15	-14.95	0.94	SO4	2	Al+3	1
50024	1.30E-33	-32.89	-3.68	SO4	3	Al+3	2
50026	3.23E-21	-20.49	3.85	Ca+2	1	SiO4	1
50028	6.92E-18	-17.16	13.68	Ca+2	1	SiO4	1
H +1	1						
50030	4.55E-20	-19.34	4.93	Mg+2	1	SiO4	1
50032	1.44E-17	-16.84	13.93	Mg+2	1	SiO4	1
H +1	1						
50034	6.66E-22	-21.18	22.47	SiO4	1	Fe+3	1
H +1	1						
60000	1.09E-10	-9.96	1.03	Na+1	1	CO3	1
60002	1.69E-08	-7.77	9.72	Na+1	1	CO3	1
H +1	1						
60004	1.73E-11	-10.76	3.70	Cd+2	1	CO3	1
60006	6.73E-17	-16.17	6.58	Cd+2	1	CO3	2
60008	1.77E-09	-8.75	12.21	Cd+2	1	CO3	1
H +1	1						
60010	4.74E-11	-10.32	4.09	Ni+2	1	CO3	1
60012	3.36E-09	-8.47	12.44	Ni+2	1	CO3	1
H +1	1						
60014	1.98E-11	-10.70	3.69	Co+2	1	CO3	1
60016	2.23E-09	-8.65	12.24	Co+2	1	CO3	1
H +1	1						
60018	1.71E-07	-6.77	1.98	Cd+2	1	SO4	1
60020	1.45E-07	-6.84	1.86	Ni+2	1	SO4	1
60022	1.52E-07	-6.82	1.86	Co+2	1	SO4	1
60024	4.21E-06	-5.38	0.40	Mg+2	1	Cl	1
60026	7.22E-08	-7.14	1.74	Cd+2	1	Cl	1
60028	4.45E-10	-9.35	2.24	Cd+2	1	Cl	2
60029	5.48E-13	-12.26	2.04	Cd+2	1	Cl	3
60030	4.23E-12	-11.37	-2.54	Ni+2	1	Cl	1
60032	3.07E-09	-8.51	0.30	Co+2	1	Cl	1
60034	6.72E-10	-9.17	2.72	Ni+2	1	NH3	1
60036	1.69E-13	-12.77	4.89	Ni+2	1	NH3	2

60038	1.32E-17	-16.88	6.55	Ni+2	1	NH3	3
60040	2.96E-22	-21.53	7.67	Ni+2	1	NH3	4
60042	2.36E-27	-26.63	8.34	Ni+2	1	NH3	5
60044	3.75E-33	-32.43	8.31	Ni+2	1	NH3	6
60046	1.62E-10	-9.79	2.08	Co+2	1	NH3	1
60048	7.24E-15	-14.14	3.50	Co+2	1	NH3	2
60050	1.05E-19	-18.98	4.43	Co+2	1	NH3	3
60052	7.81E-25	-24.11	5.07	Co+2	1	NH3	4
60054	1.53E-30	-29.82	5.13	Co+2	1	NH3	5
60056	4.73E-37	-36.32	4.39	Co+2	1	NH3	6
60058	4.69E-08	-7.33	15.95	Cd+2	1	PO4	1
H +1	1						
60060	3.56E-11	-10.45	19.33	Cd+2	1	PO4	1
H +1	2						
60062	8.29E-09	-8.08	15.15	Ni+2	1	PO4	1
H +1	1						
60064	4.06E-09	-8.39	21.34	Ni+2	1	PO4	1
H +1	2						
60066	1.05E-08	-7.98	15.23	Co+2	1	PO4	1
H +1	1						
60068	7.32E-09	-8.14	0.26	Cd+2	1	NO3	1
60070	1.66E-11	-10.78	-0.16	Cd+2	1	NO3	2
60072	6.49E-09	-8.19	0.16	Ni+2	1	NO3	1
60074	6.73E-14	-13.17	-2.60	Ni+2	1	NO3	2
60076	4.30E-09	-8.37	-0.04	Co+2	1	NO3	1
60078	1.12E-13	-12.95	-2.40	Co+2	1	NO3	2
60092	1.34E-10	-9.87	-10.20	Cd+2	1	H +1	-1
60094	2.28E-14	-13.64	-20.47	Cd+2	1	H +1	-2
60096	5.22E-28	-27.28	-47.11	Cd+2	1	H +1	-4
60098	7.70E-16	-15.11	-9.27	Cd+2	2	H +1	-1
60100	5.53E-32	-31.26	-32.57	Cd+2	4	H +1	-4
60102	2.49E-10	-9.60	-9.98	Ni+2	1	H +1	-1
60104	4.97E-13	-12.30	-19.18	Ni+2	1	H +1	-2
60106	2.38E-17	-16.62	-30.00	Ni+2	1	H +1	-3
60108	4.70E-17	-16.33	-10.58	Ni+2	2	H +1	-1
60110	1.01E-26	-26.00	-27.50	Ni+2	4	H +1	-4
60112	4.24E-10	-9.37	-9.77	Co+2	1	H +1	-1

60114	9.49E-13	-12.02	-18.92	Co+2	1	H +1	-2
60116	7.89E-19	-18.10	-31.50	Co+2	1	H +1	-3
60118	6.87E-27	-26.16	-46.06	Co+2	1	H +1	-4
60120	1.64E-17	-16.79	-11.08	Co+2	2	H +1	-1
60122	1.99E-29	-28.70	-30.29	Co+2	4	H +1	-4
66124	1.38E-10	-9.86	3.59	Cd+2	1	ACAC	1
60126	3.62E-15	-14.44	6.29	Cd+2	1	ACAC	2
60128	2.22E-08	-7.65	5.75	Ni+2	1	ACAC	1
60130	3.44E-11	-10.46	10.22	Ni+2	1	ACAC	2
60132	5.99E-09	-8.22	5.16	Co+2	1	ACAC	1
60134	3.29E-12	-11.48	9.18	Co+2	1	ACAC	2
60136	2.39E-12	-11.62	6.02	Cd+2	1	SAL	1
60138	7.06E-09	-8.15	15.99	Cd+2	1	SAL	1
H +1	1						
60140	6.71E-11	-10.17	7.42	Ni+2	1	SAL	1
60142	1.19E-12	-11.92	12.17	Ni+2	1	SAL	1
H +1	1						
60144	4.15E-11	-10.38	7.19	Co+2	1	SAL	1
60146	6.28E-13	-12.20	11.87	Co+2	1	SAL	1
H +1	1						
60148	1.01E-07	-7.00	0.46	K +1	1	PHTH	1
60152	7.56E-10	-9.12	2.20	PHTH	1	Cd+2	1
60154	6.29E-14	-13.20	3.27	PHTH	2	Cd+2	1
60156	3.88E-13	-12.41	5.41	PHTH	1	Cd+2	1
H +1	1						
60158	1.86E-16	-15.73	7.24	PHTH	2	Cd+2	1
H +1	1						
60160	1.57E-09	-8.80	2.47	PHTH	1	Ni+2	1
60162	1.34E-12	-11.87	5.90	PHTH	1	Ni+2	1
H +1	1						
60164	4.44E-10	-9.35	1.90	PHTH	1	Co+2	1
60166	5.34E-12	-11.27	6.48	PHTH	1	Co+2	1
H +1	1						
60168	1.04E-10	-9.98	4.39	Ni+2	1	ACPH	1
60170	5.09E-16	-15.29	7.33	Ni+2	1	ACPH	2
60172	1.58E-10	-9.80	4.55	Co+2	1	ACPH	1
60174	7.72E-16	-15.11	7.49	Co+2	1	ACPH	2

60176	1.90E-09	-8.72	1.59	Cd+2	1	BZA	1
60178	2.81E-13	-12.55	1.90	Cd+2	1	BZA	2
60180	6.70E-10	-9.17	1.09	Ni+2	1	BZA	1
60182	4.14E-10	-9.38	0.86	Co+2	1	BZA	1
60184	3.69E-10	-9.43	20.57	DHBZ	1	Fe+3	1
60186	2.72E-09	-8.57	35.50	DHBZ	2	Fe+3	1
60188	1.74E-14	-13.76	44.37	DHBZ	3	Fe+3	1
60190	2.27E-12	-11.64	8.59	Cd+2	1	DHBZ	1
60192	1.30E-11	-10.89	9.30	Ni+2	1	DHBZ	1
60194	3.39E-20	-19.47	14.78	Ni+2	1	DHBZ	2
60196	6.52E-12	-11.19	8.98	Co+2	1	DHBZ	1
60198	1.42E-19	-18.85	15.38	Co+2	1	DHBZ	2
60200	8.64E-11	-10.06	1.43	Cd+2	1	HMPA	1
60202	4.31E-15	-14.37	2.45	Cd+2	1	HMPA	2
60204	4.39E-20	-19.36	2.78	Cd+2	1	HMPA	3
60206	2.59E-10	-9.59	1.86	Ni+2	1	HMPA	1
60208	2.05E-14	-13.69	3.08	Ni+2	1	HMPA	2
60210	2.51E-19	-18.60	3.49	Ni+2	1	HMPA	3
60212	1.64E-10	-9.78	1.64	Co+2	1	HMPA	1
60214	9.40E-15	-14.03	2.72	Co+2	1	HMPA	2
60216	8.15E-20	-19.09	2.98	Co+2	1	HMPA	3
60218	3.95E-10	-9.40	0.93	Cd+2	1	HBA	1
60220	2.78E-10	-9.56	0.73	Ni+2	1	HBA	1
60222	1.98E-10	-9.70	0.56	Co+2	1	HBA	1
60224	1.81E-07	-6.74	0.70	K +1	1	DEMA	1
60226	4.09E-09	-8.39	2.92	Cd+2	1	DEMA	1
60228	3.09E-09	-8.51	2.75	Ni+2	1	DEMA	1
60230	2.46E-09	-8.61	2.63	Co+2	1	DEMA	1
60232	6.70E-09	-8.17	2.73	Cd+2	1	MALI	1
60234	2.55E-11	-10.59	6.81	Cd+2	1	MALI	1
H +1	1						
60236	4.83E-08	-7.32	3.54	Ni+2	1	MALI	1
60238	8.79E-11	-10.06	7.30	Ni+2	1	MALI	1
H +1	1						
60240	2.48E-08	-7.60	3.23	Co+2	1	MALI	1
60242	5.96E-11	-10.22	7.11	Co+2	1	MALI	1
H +1	1						

60243	2.52E-07	-6.60	0.26	SUCA	1	K +1	1
60244	3.29E-09	-8.48	2.24	SUCA	1	Cd+2	1
60245	1.53E-09	-8.81	1.86	SUCA	1	Ni+2	1
60246	4.42E-17	-16.35	0.82	SUCA	1	Ni+2	1
H +1	1						
60248	1.54E-09	-8.81	1.84	SUCA	1	Co+2	1
60250	1.10E-09	-8.96	1.81	Cd+2	1	DMBA	1
60252	1.90E-09	-8.72	2.00	Ni+2	1	DMBA	1
60254	1.20E-09	-8.92	1.78	Co+2	1	DMBA	1
60256	1.38E-09	-8.86	1.36	Cd+2	1	PROP	1
60258	6.96E-13	-12.16	2.11	Cd+2	1	PROP	2
60260	6.00E-10	-9.22	0.95	Ni+2	1	PROP	1
60262	1.74E-13	-12.76	1.46	Ni+2	1	PROP	2
60264	5.49E-10	-9.26	0.89	Co+2	1	PROP	1
70000	1.32E-04	-3.88	1.83	Ca+2	1	SO4	1
70002	1.06E-06	-5.97	-0.13	Ca+2	1	Cl	1
70004	9.98E-09	-8.00	5.74	Ca+2	1	PO4	1
70006	4.67E-07	-6.33	13.91	Ca+2	1	PO4	1
H +1	1						
70008	9.10E-08	-7.04	19.70	Ca+2	1	PO4	1
H +1	2						
70010	7.79E-11	-10.11	27.24	Ca+2	1	PO4	2
H +1	2						
70012	2.90E-12	-11.54	32.31	Ca+2	1	PO4	2
H +1	3						
70014	7.91E-13	-12.10	28.38	Ca+2	2	PO4	2
H +1	2						
70020	3.52E-10	-9.45	-12.82	Ca+2	1	H +1	-1
70022	1.76E-09	-8.75	2.67	Ca+2	1	CO3	1
70024	8.44E-08	-7.07	10.85	Ca+2	1	CO3	1
H +1	1						
70026	6.42E-10	-9.19	-0.29	Ca+2	1	NH3	1
70028	1.73E-16	-15.76	-1.09	Ca+2	1	NH3	2
70030	2.95E-23	-22.53	-2.09	Ca+2	1	NH3	3
70032	1.27E-05	-4.90	0.46	Ca+2	1	NO3	1
70034	4.55E-08	-7.34	0.24	Ca+2	1	NO3	2
70054	1.28E-04	-3.89	1.75	Mg+2	1	SO4	1

70056	1.57E-08	-7.80	5.87	Mg+2	1	PO4	1
70058	1.73E-06	-5.76	14.41	Mg+2	1	PO4	1
H +1	1						
70060	3.44E-07	-6.46	20.21	Mg+2	1	PO4	1
H +1	2						
70062	1.02E-11	-10.99	32.79	Mg+2	1	PO4	2
H +1	3						
70064	8.50E-11	-10.07	27.21	Mg+2	1	PO4	2
H +1	2						
70066	4.11E-12	-11.39	28.96	Mg+2	2	PO4	2
H +1	2						
70072	7.84E-09	-8.11	-11.54	Mg+2	1	H +1	-1
70074	1.89E-26	-25.72	-39.46	Mg+2	4	H +1	-4
70076	1.16E-08	-7.94	3.42	Mg+2	1	CO3	1
70078	3.50E-07	-6.46	11.40	Mg+2	1	CO3	1
H +1	1						
70080	9.24E-09	-8.03	0.80	Mg+2	1	NH3	1
70082	1.34E-15	-14.87	-0.27	Mg+2	1	NH3	2
70084	6.00E-22	-21.22	-0.85	Mg+2	1	NH3	3
70086	1.29E-28	-27.89	-1.75	Mg+2	1	NH3	4
70112	4.93E-11	-10.31	-14.50	K +1	1	H +1	-1
70114	4.76E-05	-4.32	0.56	K +1	1	SO4	1
70116	2.60E-07	-6.58	12.83	K +1	1	PO4	1
H +1	1						
70118	1.27E-06	-5.90	-0.88	K +1	1	Cl	1
70120	1.58E-05	-4.80	-0.27	K +1	1	NO3	1
70124	1.52E-05	-4.82	0.46	Na+1	1	SO4	1
70126	4.52E-07	-6.34	1.51	Na+1	1	SO4	2
70132	1.35E-07	-6.87	12.94	Na+1	1	PO4	1
H +1	1						
70134	1.93E-08	-7.72	2.01	Na+1	1	BOH4	1
70136	7.89E-11	-10.10	-13.90	Na+1	1	H +1	-1
70138	2.77E-06	-5.56	-0.63	Na+1	1	NO3	1
70140	6.37E-16	-15.20	3.32	SO4	1	Fe+3	1
70142	2.13E-17	-16.67	4.42	SO4	2	Fe+3	1
70144	2.95E-18	-17.53	1.12	Cl	1	Fe+3	1
70146	1.48E-20	-19.83	1.53	Cl	2	Fe+3	1

```
70148   2.19E-24  -23.66    0.41     Cl     3    Fe+3   1
70150   2.05E-12  -11.69   21.36     PO4    1    Fe+3   1
H +1   1
70152   1.05E-17  -16.98   22.57     PO4    1    Fe+3   1
H +1   2
70154   3.40E-21  -20.47   28.52     PO4    1    Fe+3   1
H +1   1
70168   5.34E-15  -14.27    8.69     BOH4   1    Fe+3   1
70170   6.68E-15  -14.17   15.81     BOH4   2    Fe+3   1
70172   5.92E-17  -16.23   20.78     BOH4   3    Fe+3   1
70174   3.52E-16  -15.45    8.01     MoO4   1    Fe+3   1
70176   1.26E-22  -21.90   16.61     MoO4   3    Fe+3   1
70178   1.35E-12  -11.87   -2.43     Fe+3   1    H +1  -1
70180   1.00E-09   -9.00   -6.06     Fe+3   1    H +1  -2
70200   4.90E-07   -6.31   -9.87     Fe+3   1    H +1  -3
70202   1.66E-12  -11.78  -21.84     Fe+3   1    H +1  -4
70204   1.66E-22  -21.78   -2.90     Fe+3   2    H +1  -2
70206   9.98E-29  -28.00   -6.18     Fe+3   3    H +1  -4
70208   2.99E-18  -17.52    0.64     NO3    1    Fe+3   1
70220   1.05E-16  -15.98    1.72     Fe+2   1    SO4    1
70222   1.05E-22  -21.98    2.22     Fe+2   1    SO4    1
H +1   1
70224   5.69E-19  -18.24   -9.62     Fe+2   1    H +1  -1
70226   1.43E-23  -22.84  -20.72     Fe+2   1    H +1  -2
70228   2.37E-28  -27.62  -32.00     Fe+2   1    H +1  -3
70230   5.19E-36  -35.29  -46.16     Fe+2   1    H +1  -4
70240   7.38E-18  -17.13   15.10     Fe+2   1    PO4    1
H +1   1
70242   4.66E-18  -17.33   21.40     Fe+2   1    PO4    1
H +1   2
70244   9.56E-22  -21.02   28.32     Fe+2   1    PO4    2
H +1   2
70266   7.65E-08   -7.12   15.07     Mn+2   1    PO4    1
H +1   1
```

70268	5.17E-08	-7.29	21.40	Mn+2	1	PO4	1
H +1	2						
70270	5.97E-12	-11.22	28.07	Mn+2	1	PO4	2
H +1	2						
70272	1.33E-06	-5.87	1.78	Mn+2	1	SO4	1
70274	5.02E-10	-9.30	-10.72	Mn+2	1	H +1	-1
70276	3.10E-15	-14.51	-22.43	Mn+2	1	H +1	-2
70278	1.66E-20	-19.78	-34.20	Mn+2	1	H +1	-3
70280	7.25E-28	-27.14	-48.06	Mn+2	1	H +1	-4
70282	7.27E-15	-14.14	-10.48	Mn+2	2	H +1	-1
70284	1.59E-15	-14.80	-24.14	Mn+2	2	H +1	-3
70286	6.04E-09	-8.22	11.65	Mn+2	1	CO3	1
H +1	1						
70294	1.03E-10	-9.99	0.86	Mn+2	1	NH3	1
70296	7.47E-16	-15.13	1.49	Mn+2	1	NH3	2
70298	2.32E-21	-20.64	1.75	Mn+2	1	NH3	3
70300	1.47E-27	-26.83	1.32	Mn+2	1	NH3	4
70302	4.54E-08	-7.34	-0.04	Mn+2	1	NO3	1
70304	5.16E-10	-9.29	0.24	Mn+2	1	NO3	2
70318	6.43E-10	-9.19	15.51	Cu+2	1	PO4	1
H +1	1						
70320	1.04E-11	-10.98	20.22	Cu+2	1	PO4	1
H +1	2						
70322	4.91E-17	-16.31	32.00	Cu+2	1	PO4	2
H +1	3						
70324	9.92E-19	-18.00	31.40	Cu+2	2	PO4	2
H +1	2						
70326	6.32E-14	-13.20	28.61	Cu+2	1	PO4	2
H +1	2						
70328	5.13E-09	-8.29	1.88	Cu+2	1	SO4	1
70330	3.42E-10	-9.47	3.28	Cu+2	1	SO4	2
70332	1.69E-13	-12.77	2.55	Cu+2	1	SO4	3
70334	4.71E-08	-7.33	7.29	Cu+2	1	BOH4	1
70336	1.20E-09	-8.92	12.72	Cu+2	1	BOH4	2
70338	6.14E-14	-13.21	15.45	Cu+2	1	BOH4	3
70340	1.22E-09	-8.91	-7.82	Cu+2	1	H +1	-1
70342	3.06E-10	-9.51	-14.92	Cu+2	1	H +1	-2

70344	2.12E-16	-15.67	-27.58	Cu+2	1	H +1	-3
70346	1.11E-21	-20.95	-39.36	Cu+2	1	H +1	-4
70348	6.18E-14	-13.21	-11.02	Cu+2	2	H +1	-2
70350	2.38E-19	-18.62	-21.84	Cu+2	3	H +1	-4
70352	8.74E-32	-31.06	-20.18	Cu+2	4	H +1	-3
70364	2.43E-10	-9.61	6.27	Cu+2	1	CO3	1
70366	1.50E-15	-14.82	9.35	Cu+2	1	CO3	2
70368	7.17E-11	-10.14	0.16	Cu+2	1	Cl	1
70370	4.98E-10	-9.30	4.06	Cu+2	1	NH3	1
70372	1.69E-12	-11.77	7.36	Cu+2	1	NH3	2
70374	1.58E-15	-14.80	10.10	Cu+2	1	NH3	3
70376	2.09E-19	-18.68	11.99	Cu+2	1	NH3	4
70378	9.82E-26	-25.01	11.43	Cu+2	1	NH3	5
70380	1.65E-10	-9.78	-2.92	Cu+2	1	NH3	1
H +1	-1						
70382	4.78E-20	-19.32	-0.92	Cu+2	1	NH3	3
H +1	-1						
70384	1.12E-22	-21.95	-15.82	Cu+2	1	NH3	2
H +1	-2						
70386	2.76E-10	-9.56	0.26	Cu+2	1	NO3	1
70388	1.04E-12	-11.98	0.06	Cu+2	1	NO3	2
70424	1.17E-08	-7.93	14.71	Zn+2	1	PO4	1
H +1	1						
70426	1.37E-09	-8.86	20.28	Zn+2	1	PO4	1
H +1	2						
71208	5.12E-14	-13.29	32.96	Zn+2	1	PO4	2
H +1	3						
71210	4.83E-16	-15.32	29.97	Zn+2	2	PO4	2
H +1	2						
71212	1.82E-12	-11.74	28.01	Zn+2	1	PO4	2
H +1	2						
71214	6.14E-07	-6.21	1.90	Zn+2	1	SO4	1
71216	3.57E-08	-7.45	3.24	Zn+2	1	SO4	2
71218	8.06E-11	-10.09	3.17	Zn+2	1	SO4	3
71220	3.16E-13	-12.50	3.34	Zn+2	1	SO4	4
71222	6.98E-09	-8.16	-9.12	Zn+2	1	H +1	-1
71224	1.84E-08	-7.74	-15.20	Zn+2	1	H +1	-2

71226	3.66E-15	-14.44	-28.40	Zn+2	1	H +1	-3
71228	3.19E-21	-20.50	-40.96	Zn+2	1	H +1	-4
71230	3.53E-14	-13.45	-8.88	Zn+2	2	H +1	-1
71242	2.48E-10	-9.61	4.22	Zn+2	1	CO3	1
71243	2.11E-09	-8.68	11.65	Zn+2	1	CO3	1
H +1	1						
71244	8.79E-09	-8.06	0.19	Zn+2	1	Cl	1
71246	5.30E-11	-10.28	0.68	Zn+2	1	Cl	2
71248	3.27E-13	-12.49	1.18	Zn+2	1	Cl	3
71250	1.33E-15	-14.88	1.50	Zn+2	1	Cl	4
71252	8.04E-10	-9.09	2.21	Zn+2	1	NH3	1
71254	2.67E-13	-12.57	4.50	Zn+2	1	NH3	2
71256	1.04E-16	-15.98	6.86	Zn+2	1	NH3	3
71258	1.90E-20	-19.72	8.89	Zn+2	1	NH3	4
71260	4.85E-10	-9.31	-4.51	Zn+2	1	NH3	1
H +1	-1						
71262	3.00E-14	-13.52	-2.95	Zn+2	1	NH3	2
H +1	-1						
71264	7.91E-19	-18.10	-1.76	Zn+2	1	NH3	3
H +1	-1						
71266	1.64E-13	-12.78	-14.48	Zn+2	1	NH3	1
H +1	-2						
71268	1.09E-18	-17.96	-13.89	Zn+2	1	NH3	2
H +1	-2						
71270	1.88E-19	-18.72	-26.92	Zn+2	1	NH3	1
H +1	-3						
71300	2.51E-08	-7.60	0.16	Zn+2	1	NO3	1
71302	1.98E-10	-9.70	0.28	Zn+2	1	NO3	2
77300	3.50E-19	-18.46	10.18	NH3	2	Cu+1	1
77400	1.66E-19	-18.78	2.72	SO4	1	Mn+3	1
77402	1.40E-12	-11.85	0.57	Mn+3	1	H +1	-1
78600	1.99E-05	-4.70	10.09	CO3	1	H +1	1
78602	1.07E-05	-4.97	16.32	CO3	1	H +1	2
78604	4.72E-08	-7.33	1.75	SO4	1	H +1	1
78606	4.62E-22	-21.34	-5.76	SO4	1	H +1	2
78610	7.45E-06	-5.13	11.98	PO4	1	H +1	1

```
78612   2.15E-05   -4.67    18.94    PO4    1    H +1    2
78614   7.12E-10   -9.15    20.96    PO4    1    H +1    3
78616   2.26E-11  -10.65    30.07    PO4    2    H +1    3
78618   2.85E-10   -9.54    37.67    PO4    2    H +1    4
78620   5.44E-14  -13.26    40.45    PO4    2    H +1    5
78634   4.17E-08   -7.38   -13.88    H +1  -1
78636   4.98E-05   -4.30     9.22    BOH4   1    H +1    1
78638   2.36E-18  -17.63     9.94    BOH4   3    H +1    1
78640   5.16E-15  -14.29    19.78    BOH4   3    H +1    2
78642   1.70E-21  -20.77    20.32    BOH4   4    H +1    2
78644   1.02E-18  -17.99    29.60    BOH4   4    H +1    3
78646   2.13E-23  -22.67    38.44    BOH4   5    H +1    4
78648   5.98E-11  -10.22     3.80    MoO4   1    H +1    1
78650   1.40E-13  -12.85     7.67    MoO4   1    H +1    2
78652   3.21E-19  -18.49     8.53    MoO4   1    H +1    3
78654   2.95E-16  -15.53    -6.32    Cl     1    H +1    1
78656   9.36E-04   -3.03     9.24    NH3    1    H +1    1
78700   4.38E-05   -4.36    10.62    Cl     1    NH3     1
H +1    1
78702   1.84E-05   -4.73    10.11    SO4    1    NH3     1
H +1    1
78708   5.44E-11  -10.26    -1.54    NO3    1    H +1    1
78710   2.34E-10   -9.63     8.39    ACAC   1    Al+3    1
78712   7.76E-10   -9.11    16.19    ACAC   2    Al+3    1
78714   2.51E-11  -10.60    21.98    ACAC   3    Al+3    1
78716   1.45E-08   -7.84    14.37    SAL    1    Al+3    1
78718   7.25E-13  -12.14     3.75    PHTH   1    Al+3    1
78720   2.69E-09   -8.57     7.32    PHTH   1    Al+3    1
78722   3.16E-11  -10.50    -2.12    BZA    1    Al+3    1
H +1   -1
90100   3.14E-08   -7.50    13.06    DHBZ   1    H +1    1
90102   1.89E-05   -4.72    22.34    DHBZ   1    H +1    2
90104   7.79E-12  -11.11     6.02    Mg+2   1    DHBZ    1
90106   2.65E-13  -12.58     4.62    Ca+2   1    DHBZ    1
90108   7.55E-12  -11.12     8.02    Mn+2   1    DHBZ    1
90110   3.78E-10   -9.42    16.22    Mn+2   1    DHBZ    1
H +1    1
```

90112	3.41E-21	-20.47	8.72	Fe+2	1	DHBZ	1
90114	1.71E-19	-18.77	16.92	Fe+2	1	DHBZ	1
H +1	1						
90116	3.65E-08	-7.44	14.22	Cu+2	1	DHBZ	1
90118	4.18E-10	-9.38	10.22	Zn+2	1	DHBZ	1
90120	1.14E-08	-7.94	3.88	HMPA	1	H +1	1
90122	6.37E-08	-7.20	1.26	Ca+2	1	HMPA	1
90124	5.92E-08	-7.23	1.16	Mg+2	1	HMPA	1
90126	5.74E-10	-9.24	1.16	Mn+2	1	HMPA	1
90128	1.63E-19	-18.79	1.66	Fe+2	1	HMPA	1
90130	1.11E-10	-9.96	2.96	Cu+2	1	HMPA	1
90132	1.26E-09	-8.90	1.96	Zn+2	1	HMPA	1
90134	7.55E-19	-18.12	3.14	HMPA	1	Fe+3	1
90136	2.28E-13	-12.64	2.12	HMPA	1	Fe+3	1
H +1	-1						
90138	3.09E-05	-4.51	13.46	SAL	1	H +1	1
90140	7.42E-09	-8.13	16.34	SAL	1	H +1	2
90141	1.22E-09	-8.92	5.62	Mg+2	1	SAL	1
90142	1.31E-10	-9.88	4.72	Ca+2	1	SAL	1
90144	3.29E-08	-7.48	13.62	Ca+2	1	SAL	1
H +1	1						
90146	4.69E-11	-10.33	6.22	Mn+2	1	SAL	1
90148	2.12E-20	-19.67	6.92	Fe+2	1	SAL	1
90150	7.18E-09	-8.14	10.92	Cu+2	1	SAL	1
90152	1.64E-10	-9.79	7.22	Zn+2	1	SAL	1
90154	1.86E-11	-10.73	16.68	SAL	1	Fe+3	1
90156	9.78E-17	-16.01	17.90	SAL	1	Fe+3	1
H +1	1						
90158	1.03E-16	-15.99	10.02	Mg+2	1	SAL	2
90160	8.85E-19	-18.05	8.02	Ca+2	1	SAL	2
90162	1.59E-18	-17.80	10.22	Mn+2	1	SAL	2
90164	3.60E-27	-26.44	11.62	Fe+2	1	SAL	2
90166	2.89E-09	-8.54	30.34	SAL	2	Fe+3	1
90168	1.93E-12	-11.71	18.82	Cu+2	1	SAL	2
90170	1.39E-23	-22.86	5.62	Zn+2	1	SAL	2
90172	1.70E-05	-4.77	9.98	ACPH	1	H +1	1
90174	7.53E-11	-10.12	1.26	Ca+2	1	ACPH	1

90176	1.35E-11	-10.87	2.46	Mn+2	1	ACPH	1
90178	1.04E-09	-8.98	6.86	Cu+2	1	ACPH	1
90180	2.98E-11	-10.53	3.26	Zn+2	1	ACPH	1
90182	2.24E-14	-13.65	10.54	ACPH	1	Fe+3	1
90184	5.23E-07	-6.28	4.38	HBA	1	H +1	1
90186	3.41E-07	-6.47	0.76	Mg+2	1	HBA	1
90188	1.84E-07	-6.73	0.56	Ca+2	1	HBA	1
90190	3.19E-10	-9.50	2.26	Cu+2	1	HBA	1
90192	3.65E-09	-8.44	1.26	Zn+2	1	HBA	1
90194	3.34E-05	-4.48	7.16	DEMA	1	H +1	1
90196	1.27E-09	-8.90	9.24	DEMA	1	H +1	2
90198	5.25E-08	-7.28	0.56	Na+1	1	DEMA	1
90200	4.15E-07	-6.38	1.82	Mg+2	1	DEMA	1
90202	1.04E-07	-6.98	7.72	Mg+2	1	DEMA	1
H +1	1						
90204	3.55E-07	-6.45	1.82	Ca+2	1	DEMA	1
90206	1.41E-07	-6.85	7.92	Ca+2	1	DEMA	1
H +1	1						
90208	8.03E-09	-8.10	2.12	Mn+2	1	DEMA	1
90210	3.09E-08	-7.51	5.22	Cu+2	1	DEMA	1
90212	9.76E-12	-11.01	8.22	Cu+2	1	DEMA	1
H +1	1						
90214	1.12E-08	-7.95	2.72	Zn+2	1	DEMA	1
90216	1.41E-09	-8.85	8.32	Zn+2	1	DEMA	1
H +1	1						
90218	1.01E-12	-12.00	9.08	DEMA	1	Fe+3	1
90220	3.34E-18	-17.48	10.10	DEMA	1	Fe+3	1
H +1	1						
90222	1.26E-05	-4.90	8.88	ACAC	1	H +1	1
90224	1.30E-07	-6.89	3.46	Mg+2	1	ACAC	1
90226	2.80E-08	-7.55	2.86	Ca+2	1	ACAC	1
90228	3.99E-09	-8.40	3.96	Mn+2	1	ACAC	1
90230	2.85E-18	-17.54	4.86	Fe+2	1	ACAC	1
90232	1.53E-07	-6.81	8.06	Cu+2	1	ACAC	1
90234	1.11E-08	-7.96	4.86	Zn+2	1	ACAC	1
90236	8.32E-14	-13.08	10.14	ACAC	1	Fe+3	1
90238	3.24E-07	-6.49	5.16	PHTH	1	H +1	1

90240	7.77E-11	-10.11	8.04	PHTH	1	H +1	2
90242	4.05E-08	-7.39	0.46	Na+1	1	PHTH	1
90244	4.33E-07	-6.36	1.92	Ca+2	1	PHTH	1
90246	9.80E-09	-8.01	2.22	PHTH	1	Mn+2	1
90248	5.97E-10	-9.22	3.52	PHTH	1	Cu+2	1
90250	5.43E-09	-8.27	2.42	PHTH	1	Zn+2	1
90252	4.90E-14	-13.31	7.78	PHTH	1	Fe+3	1
90254	8.43E-14	-13.07	4.82	PHTH	2	Cu+2	1
90256	7.66E-13	-12.12	3.72	PHTH	2	Zn+2	1
90258	4.24E-07	-6.37	4.86	MALI	1	H +1	1
90260	3.22E-10	-9.49	8.24	MALI	1	H +1	2
90262	1.06E-07	-6.98	0.46	Na+1	1	MALI	1
90264	2.09E-07	-6.68	0.36	K +1	1	MALI	1
90266	1.67E-06	-5.78	2.02	Mg+2	1	MALI	1
90268	5.27E-09	-8.28	6.02	Mg+2	1	MALI	1
H +1	1						
90270	2.26E-06	-5.65	2.22	Ca+2	1	MALI	1
90272	5.68E-09	-8.25	6.12	Ca+2	1	MALI	1
H +1	1						
90274	6.44E-08	-7.19	2.62	Mn+2	1	MALI	1
90276	1.16E-17	-16.94	2.92	Fe+2	1	MALI	1
90278	2.47E-09	-8.61	3.72	Cu+2	1	MALI	1
90280	6.22E-07	-6.21	6.12	Cu+2	1	MALI	1
90282	3.56E-08	-7.45	2.82	Zn+2	1	MALI	1
90284	7.11E-11	-10.15	6.62	Zn+2	1	MALI	1
H +1	1						
90286	1.28E-13	-12.89	7.78	MALI	1	Fe+3	1
90288	2.04E-06	-5.69	5.36	SUCA	1	H +1	1
90290	7.75E-09	-8.11	9.44	SUCA	1	H +1	2
90292	6.40E-08	-7.19	0.06	SUCA	1	Na+1	1
90294	8.01E-07	-6.10	1.52	SUCA	1	Mg+2	1
90296	8.01E-09	-8.10	6.02	SUCA	1	Mg+2	1
H +1	1						
90298	6.85E-07	-6.16	1.52	SUCA	1	Ca+2	1
90300	6.85E-09	-8.16	6.02	SUCA	1	Ca+2	1
H +1	1						
90302	1.55E-08	-7.81	1.82	SUCA	1	Mn+2	1

90304	7.76E-14	-13.11	3.02	SUCA	1	Mn+2	1
H +1	1						
90306	1.11E-18	-17.96	1.72	SUCA	1	Fe+2	1
90308	4.73E-10	-9.33	2.82	SUCA	1	Cu+2	1
90310	8.57E-09	-8.07	2.02	SUCA	1	Zn+2	1
90312	6.81E-11	-10.17	6.42	SUCA	1	Zn+2	1
H +1	1						
90314	1.23E-13	-12.91	7.58	SUCA	1	Fe+3	1
90316	3.04E-08	-7.52	3.58	DMBA	1	H +1	1
90318	2.50E-07	-6.60	1.06	Mg+2	1	DMBA	1
90320	4.26E-07	-6.37	1.36	Ca+2	1	DMBA	1
90322	3.70E-10	-9.43	2.76	Cu+2	1	DMBA	1
90324	5.33E-09	-8.27	1.86	Zn+2	1	DMBA	1
90326	2.75E-07	-6.56	4.08	BZA	1	H +1	1
90328	1.13E-07	-6.95	0.26	Mg+2	1	BZA	1
90330	1.54E-07	-6.81	0.46	Ca+2	1	BZA	1
90332	5.51E-09	-8.26	0.96	Mn+2	1	BZA	1
90334	1.06E-10	-9.97	1.76	Cu+2	1	BZA	1
90336	2.42E-09	-8.62	1.06	Zn+2	1	BZA	1
90338	2.29E-15	-14.64	5.44	BZA	1	Fe+3	1
90340	1.20E-04	-3.92	9.88	PHEN	1	H +1	1
90342	3.97E-16	-15.40	7.84	PHEN	1	Fe+3	1
90344	1.71E-06	-5.77	4.78	PROP	1	H +1	1
90346	3.52E-07	-6.45	0.66	Mg+2	1	PROP	1
90348	3.79E-07	-6.42	0.76	Ca+2	1	PROP	1
90350	2.08E-10	-9.68	1.96	Cu+2	1	PROP	1
90352	2.99E-09	-8.52	1.06	Zn+2	1	PROP	1
90354	4.49E-17	-16.35	3.64	PROP	1	Fe+3	1
90356	3.64E-09	-8.44	2.68	HBQN	1	H +1	1
90358	1.19E-06	-5.93	1.76	Mg+2	1	HBQN	1
90360	4.05E-07	-6.39	1.36	Ca+2	1	HBQN	1
90362	4.59E-08	-7.34	2.36	Mn+2	1	HBQN	1
90364	5.57E-08	-7.25	4.96	Cu+2	1	HBQN	1
90366	1.27E-06	-5.90	4.26	Zn+2	1	HBQN	1
90368	7.59E-14	-13.12	7.44	HBQN	1	Fe+3	1
90370	4.32E-10	-9.36	2.94	Mg+2	1	HBQN	2
90372	1.17E-10	-9.93	2.44	Ca+2	1	HBQN	2

90374	2.10E-11	-10.68	3.64	Mn+2	1	HBQN	2
90376	1.32E-12	-11.88	13.30	HBQN	2	Fe+3	1
90378	6.41E-09	-8.19	8.64	Cu+2	1	HBQN	2

ID	C	LOGC	LOGK	SPECIES:		TYPE III -	
FIXED SOLIDS							
50	-1.49E-02	-1.83	6.50	H +1	1		
80000	8.79E-16	-15.06	12.67	Fe+2	-1	E-	1
Fe+3	1						
80002	-1.40E-12	-11.85	25.70	Mn+2	-1	E-	1
Mn+3	1						
80004	8.31E-18	-17.08	2.35	Cu+2	1	E-	1
Cu+1	-1						
80006	-1.52E-25	-24.82	30.57	Co+2	-1	E-	1
Co+3	1						
80010	-3.11E-05	-4.51	21.29	CO3	1	H +1	2

ID	C	LOGC	LOGK	SPECIES:		TYPE IV -	
PRECIPITATED SOLIDS							
80102	3.23E-04	-3.49	40.99	Ca+2	5	PO4	3
H +1	-1						
80600	1.95E-05	-4.71	-3.56	Fe+3	1	H +1	-3
84022	1.13E-06	-5.95	-8.76	Al+3	1	H +1	-3

ID	C	LOGC	LOGK	SPECIES:		TYPE V -	
DISSOLVED SOLIDS							
80100	2.57E-02	-1.59	4.12	Ca+2	1	SO4	1
80090	1.89E-06	-5.72	-0.31	Na+1	1	Cl	1
80104	2.53E-07	-6.60	44.26	Ca+2	4	PO4	3
H +1	1						
80106	1.44E-02	-1.84	18.40	Ca+2	1	PO4	1
H +1	1						
80110	5.98E-14	-13.22	-23.09	Ca+2	1	H +1	-2
80112	3.20E-04	-3.50	27.12	Ca+2	3	PO4	2
80114	7.23E-03	-2.14	18.10	Ca+2	1	PO4	1
H +1	1						
80116	3.86E-04	-3.41	8.01	Ca+2	1	CO3	1

```
80200    9.73E-08   -7.01    23.40     Mg+2   3    PO4    2
80202    1.40E-03   -2.85    17.32     Mg+2   1    PO4    1
H +1   1
80204    9.21E-08   -7.04   -16.97     Mg+2   1    H +1  -2
80206    1.80E-04   -3.75     7.61     Mg+2   1    CO3    1
80208    6.83E-08   -7.17     4.19     Mg+2   1    CO3    1
80210    1.82E-07   -6.74    16.04     Ca+2   1    Mg+2   1
CO3    2
80211    3.63E-18  -17.44    28.05     Ca+2   1    Mg+2   3
CO3    4
80212    3.70E-06   -5.43    20.51     Mg+2   1    NH3    1
PO4    1    H +1   1
80214    6.31E-07   -6.20     9.78     Mg+2   1    K +1   1
PO4    1
80096    4.05E-25  -24.39   -10.00     Co+2   1    CO3    1
80602    5.92E-02   -1.23    25.32     PO4    1    Fe+3   1
80606    3.06E-14  -13.51   -18.51     Fe+2   1    Fe+3   2
H +1  -8
80608    3.59E-06   -5.44   -10.44     Fe+2   1    Fe+3   2
H +1  -8
80700    7.17E-16  -15.14   -13.02     Fe+2   1    H +1  -2
80702    2.21E-14  -13.65     9.76     Fe+2   1    CO3    1
80704    4.08E-33  -32.39    34.20     Fe+2   3    PO4    2
80701    1.90E-16  -15.72     1.98     Fe+2   1    SO4    1
80800    3.99E-08   -7.40   -15.32     Mn+2   1    H +1  -2
80802    2.82E-05   -4.55     8.82     Mn+2   1    CO3    1
80900    4.03E-04   -3.39    -8.80     Cu+2   1    H +1  -2
80904    7.98E-09   -8.10    35.90     Cu+2   3    PO4    2
80906    1.84E-07   -6.73     9.15     Cu+2   1    CO3    1
80908    1.21E-06   -5.92     4.56     Cu+2   2    CO3    1
H +1  -2
80910    2.73E-11  -10.56    15.80     Cu+2   3    CO3    2
H +1  -2
80912    1.32E-07   -6.88    14.76     Cu+2   1    BOH4   2
81200    4.76E-05   -4.32    33.50     Zn+2   3    PO4    2
81202    3.12E-04   -3.51    10.32     Zn+2   1    CO3    1
81204    7.31E-06   -5.14   -12.60     Zn+2   1    H +1  -2
```

83302	6.32E-14	-13.20	6.61	Cl	1	Cu+1	1
83304	1.00E-24	-24.00	-13.40	Cu+1	1	H +1	-1
84000	2.61E-23	-22.58	4.89	Ca+2	2	SiO4	1
84002	1.65E-21	-20.78	6.69	Ca+2	2	SiO4	1
84004	2.01E-02	-1.70	65.33	Ca+2	1	SiO4	2
Al+3	2						
84006	2.01E-12	-11.70	15.64	Mg+2	2	SiO4	1
84008	3.09E-02	-1.51	33.14	Na+1	1	SiO4	1
Al+3	1						
84010	1.22E-03	-2.91	31.34	K +1	1	SiO4	1
Al+3	1						
84012	1.97E-27	-26.71	24.75	Fe+2	2	SiO4	1
84014	1.21E-01	-0.92	31.36	Zn+2	2	SiO4	1
84016	4.96E-12	-11.30	20.06	Mn+2	2	SiO4	1
84018	5.50E-02	-1.26	-10.02	Al+3	1	H +1	-3
84020	7.76E-01	-0.11	-8.87	Al+3	1	H +1	-3
80098	4.04E-20	-19.39	-4.98	Ni+2	1	CO3	1
84024	0.00E+00	-51.85	-22.64	SO4	3	Al+3	2
84026	3.03E-06	-5.52	-4.84	K +1	1	SO4	2
Al+3	3	H +1	-6				
84028	4.19E-04	-3.38	17.97	Al+3	1	PO4	1
84030	1.12E-03	-2.95	11.51	Cd+2	1	CO3	1
84032	6.50E-10	-9.19	-0.44	Cd+2	1	SO4	1
84034	3.72E-04	-3.43	36.30	Cd+2	3	PO4	2
84036	1.67E-03	-2.78	7.88	Ca+2	1	MoO4	1
84038	3.56E-11	-10.45	0.14	Mg+2	1	MoO4	1
84040	7.62E-10	-9.12	6.00	Cu+2	1	MoO4	1
84042	3.73E-16	-15.43	7.22	Fe+2	1	MoO4	1
84044	1.12E-09	-8.95	3.65	Mn+2	1	MoO4	1
84046	2.52E-09	-8.60	4.46	Zn+2	1	MoO4	1

PERCENTAGE DISTRIBUTION OF COMPONENTS

SUCA

87.8	PERCENT BOUND IN SPECIES #	172	SUCA	1
6.4	PERCENT BOUND IN SPECIES #	90288	SUCA	1

H +1 1

```
          2.5     PERCENT BOUND IN SPECIES #90294    SUCA    1
Mg+2    1
          2.1     PERCENT BOUND IN SPECIES #90298    SUCA    1
Ca+2    1

Ca+2
         29.4     PERCENT BOUND IN SPECIES #     1    Ca+2    1
          5.3     PERCENT BOUND IN SPECIES #70000    Ca+2    1
SO4     1
         64.5     PERCENT BOUND IN SPECIES #80102    Ca+2    5
PO4     3    H +1   -1

Mg+2
         85.9     PERCENT BOUND IN SPECIES #     2    Mg+2    1
         12.8     PERCENT BOUND IN SPECIES #70054    Mg+2    1
SO4     1

K +1
         98.7     PERCENT BOUND IN SPECIES #     4    K +1    1

Na+1
         99.1     PERCENT BOUND IN SPECIES #     5    Na+1    1

PHTH
         88.5     PERCENT BOUND IN SPECIES #   132    PHTH    1
          1.3     PERCENT BOUND IN SPECIES #60148    K +1    1
PHTH    1
          4.0     PERCENT BOUND IN SPECIES #90238    PHTH    1
H +1    1
          5.4     PERCENT BOUND IN SPECIES #90244    Ca+2    1
PHTH    1

Fe+2
         85.4     PERCENT BOUND IN SPECIES #     7    Fe+2    1
         11.9     PERCENT BOUND IN SPECIES #70220    Fe+2    1
SO4     1
```

```
          1.3     PERCENT BOUND IN SPECIES #90276    Fe+2    1
MALI    1

Mn+2
         83.3     PERCENT BOUND IN SPECIES #    8    Mn+2    1
         13.3     PERCENT BOUND IN SPECIES #70272    Mn+2    1
SO4     1

Cu+2
          2.5     PERCENT BOUND IN SPECIES #    9    Cu+2    1
          4.7     PERCENT BOUND IN SPECIES #70334    Cu+2    1
BOH4    1
          3.7     PERCENT BOUND IN SPECIES #90116    Cu+2    1
DHBZ    1
          3.1     PERCENT BOUND IN SPECIES #90210    Cu+2    1
DEMA    1
         15.3     PERCENT BOUND IN SPECIES #90232    Cu+2    1
ACAC    1
         62.2     PERCENT BOUND IN SPECIES #90280    Cu+2    1
MALI    1
          5.6     PERCENT BOUND IN SPECIES #90364    Cu+2    1
HBQN    1

Cd+2
         67.3     PERCENT BOUND IN SPECIES #   11    Cd+2    1
         17.1     PERCENT BOUND IN SPECIES #60018    Cd+2    1
SO4     1
          7.2     PERCENT BOUND IN SPECIES #60026    Cd+2    1
Cl      1
          4.7     PERCENT BOUND IN SPECIES #60058    Cd+2    1
PO4     1    H +1    1

Zn+2
         58.2     PERCENT BOUND IN SPECIES #   12    Zn+2    1
         12.3     PERCENT BOUND IN SPECIES #71214    Zn+2    1
SO4     1
```

```
          25.4      PERCENT BOUND IN SPECIES #90366    Zn+2    1
HBQN    1

Ni+2
          75.1      PERCENT BOUND IN SPECIES #   13    Ni+2    1
          14.5      PERCENT BOUND IN SPECIES #60020    Ni+2    1
SO4     1
           2.2      PERCENT BOUND IN SPECIES #60128    Ni+2    1
ACAC    1
           4.8      PERCENT BOUND IN SPECIES #60236    Ni+2    1
MALI    1

Co+2
          78.9      PERCENT BOUND IN SPECIES #   16    Co+2    1
          15.2      PERCENT BOUND IN SPECIES #60022    Co+2    1
SO4     1
           1.0      PERCENT BOUND IN SPECIES #60066    Co+2    1
PO4     1    H +1    1
           2.5      PERCENT BOUND IN SPECIES #60240    Co+2    1
MALI    1

DMBA
          97.2      PERCENT BOUND IN SPECIES #  173    DMBA    1
           1.6      PERCENT BOUND IN SPECIES #90320    Ca+2    1
DMBA    1

ACAC
          96.9      PERCENT BOUND IN SPECIES #90222    ACAC    1
H +1    1
           1.0      PERCENT BOUND IN SPECIES #90224    Mg+2    1
ACAC    1
           1.2      PERCENT BOUND IN SPECIES #90232    Cu+2    1
ACAC    1

PHEN
         100.0      PERCENT BOUND IN SPECIES #90340    PHEN    1
H +1    1
```

```
BZA
          99.2      PERCENT BOUND IN SPECIES #  164    BZA     1

PROP
          97.3      PERCENT BOUND IN SPECIES #  174    PROP    1
           1.9      PERCENT BOUND IN SPECIES #90344    PROP    1
H +1    1

HBQN
          88.9      PERCENT BOUND IN SPECIES #  166    HBQN    1
           4.4      PERCENT BOUND IN SPECIES #90358    Mg+2    1
HBQN    1
           1.5      PERCENT BOUND IN SPECIES #90360    Ca+2    1
HBQN    1
           4.7      PERCENT BOUND IN SPECIES #90366    Zn+2    1
HBQN    1

SO4
          88.5      PERCENT BOUND IN SPECIES #  102    SO4     1
           4.4      PERCENT BOUND IN SPECIES #70000    Ca+2    1
SO4     1
           4.3      PERCENT BOUND IN SPECIES #70054    Mg+2    1
SO4     1
           1.6      PERCENT BOUND IN SPECIES #70114    K +1    1
SO4     1

Cl
          97.5      PERCENT BOUND IN SPECIES #  103    Cl      1
           2.2      PERCENT BOUND IN SPECIES #78700    Cl      1
NH3     1    H +1    1

NH3
          93.6      PERCENT BOUND IN SPECIES #78656    NH3     1
H +1    1
           4.4      PERCENT BOUND IN SPECIES #78700    Cl      1
NH3     1    H +1    1
```

```
          1.8     PERCENT BOUND IN SPECIES #78702    SO4     1
NH3     1    H +1    1

MALI
         77.2     PERCENT BOUND IN SPECIES #  171    MALI    1
          1.8     PERCENT BOUND IN SPECIES #90258    MALI    1
H +1    1
          6.9     PERCENT BOUND IN SPECIES #90266    Mg+2    1
MALI    1
          9.4     PERCENT BOUND IN SPECIES #90270    Ca+2    1
MALI    1
          2.6     PERCENT BOUND IN SPECIES #90280    Cu+2    1
MALI    1

SiO4
         99.9     PERCENT BOUND IN SPECIES #50014    SiO4    1
H +1    4

BOH4
         99.7     PERCENT BOUND IN SPECIES #78636    BOH4    1
H +1    1

MoO4
         99.8     PERCENT BOUND IN SPECIES #  152    MoO4    1

NO3
         99.5     PERCENT BOUND IN SPECIES #  157    NO3     1

DHBZ
         99.6     PERCENT BOUND IN SPECIES #90102    DHBZ    1
H +1    2

SAL
         99.8     PERCENT BOUND IN SPECIES #90138    SAL     1
H +1    1

HMPA
```

```
          97.2      PERCENT BOUND IN SPECIES #  168    HMPA    1
           1.3      PERCENT BOUND IN SPECIES #90122    Ca+2    1
HMPA    1
           1.2      PERCENT BOUND IN SPECIES #90124    Mg+2    1
HMPA    1

ACPH
         100.0      PERCENT BOUND IN SPECIES #90172    ACPH    1
H +1    1

HBA
          98.5      PERCENT BOUND IN SPECIES #  169    HBA     1

DEMA
          17.4      PERCENT BOUND IN SPECIES #  170    DEMA    1
          79.5      PERCENT BOUND IN SPECIES #90194    DEMA    1
H +1    1

Al+3
           2.7      PERCENT BOUND IN SPECIES #50002    Al+3    1
H +1   -2
          21.1      PERCENT BOUND IN SPECIES #50004    Al+3    1
H +1   -3
          75.0      PERCENT BOUND IN SPECIES #84022    Al+3    1
H +1   -3

E-
         100.0      PERCENT BOUND IN SPECIES #   99    E-      1

Mn+3
         100.0      PERCENT BOUND IN SPECIES #77402    Mn+3    1
Fe+3    0     H +1   -1

Cu+1
          95.8      PERCENT BOUND IN SPECIES #   33    Cu+1    1
           4.2      PERCENT BOUND IN SPECIES #77300    NH3     2
Cu+1    1
```

```
Co+3
        100.0     PERCENT BOUND IN SPECIES #   17   Co+3    1

CO3
          1.1     PERCENT BOUND IN SPECIES #70078   Mg+2    1
CO3     1    H +1   1
         64.0     PERCENT BOUND IN SPECIES #78600   CO3     1
H +1    1
         34.4     PERCENT BOUND IN SPECIES #78602   CO3     1
H +1    2

PO4
          2.2     PERCENT BOUND IN SPECIES #78612   PO4     1
H +1    2
         96.8     PERCENT BOUND IN SPECIES #80102   Ca+2    5
PO4     3    H +1  -1

Fe+3
          2.4     PERCENT BOUND IN SPECIES #70200   Fe+3    1
H +1   -3
         97.5     PERCENT BOUND IN SPECIES #80600   Fe+3    1
H +1   -3

H +1
         93.2     PERCENT BOUND IN SPECIES #50014   SiO4    1
H +1    4
          6.2     PERCENT BOUND IN SPECIES #78656   NH3     1
H +1    1
```

APPENDIX D

SOIL SOLUTION MODEL INCLUDING THE CAFFEIC ACID / BENZOQUINONE ACRYLATE, $Caff^{2-}$ / BQA^{-} COUPLE (See chapter 5.4.3).

INPUT

IONIC STRENGTH = 2.00E-02

ID	X	LOGX	T	COMPONENTS
50	3.16E-07	-6.50	0.00E+00	H +1
1	1.00E-03	-3.00	2.50E-03	Ca+2
2	1.00E-03	-3.00	1.00E-03	Mg+2
4	1.00E-03	-3.00	5.00E-03	K +1
5	1.00E-05	-5.00	2.00E-03	Na+1
6	1.00E-05	-5.00	2.00E-05	Fe+3
7	1.00E-09	-9.00	0.00E+00	Fe+2
8	1.00E-05	-5.00	1.00E-05	Mn+2
9	1.00E-06	-6.00	1.00E-06	Cu+2
11	1.00E-06	-6.00	1.00E-06	Cd+2
12	1.00E-06	-6.00	5.00E-06	Zn+2
13	1.00E-06	-6.00	1.00E-06	Ni+2
16	1.00E-07	-7.00	1.00E-06	Co+2
17	1.00E-09	-9.00	0.00E+00	Co+3
20	1.00E-07	-7.00	1.50E-06	Al+3
33	1.00E-09	-9.00	0.00E+00	Cu+1
34	1.00E-09	-9.00	0.00E+00	Mn+3
99	1.00E-09	-9.00	0.00E+00	E-
101	1.00E-08	-8.00	0.00E+00	CO3
102	1.00E-03	-3.00	3.00E-03	SO4
103	1.00E-03	-3.00	2.00E-03	Cl
107	1.00E-03	-3.00	1.00E-03	NH3
109	1.00E-03	-3.00	1.00E-03	PO4
112	1.00E-04	-4.00	3.50E-03	SiO4
148	1.00E-06	-6.00	5.00E-05	BOH4
152	1.00E-08	-8.00	3.00E-08	MoO4

157	1.00E-03	-3.00	6.00E-03	NO3
167	1.00E-05	-5.00	1.90E-05	DHBZ
119	1.00E-05	-5.00	3.10E-05	SAL
168	1.00E-05	-5.00	4.90E-06	HMPA
163	1.00E-05	-5.00	1.70E-05	ACPH
169	1.00E-05	-5.00	7.00E-05	HBA
170	1.00E-05	-5.00	4.20E-05	DEMA
116	1.00E-05	-5.00	1.30E-05	ACAC
132	1.00E-05	-5.00	8.00E-06	PHTH
171	1.00E-05	-5.00	2.40E-05	MALI
172	1.00E-05	-5.00	3.20E-05	SUCA
173	1.00E-05	-5.00	2.60E-05	DMBA
164	1.00E-05	-5.00	7.30E-05	BZA
165	1.00E-05	-5.00	1.20E-04	PHEN
174	1.00E-05	-5.00	9.20E-05	PROP
166	1.00E-05	-5.00	2.70E-05	HBQN
161	1.00E-06	-6.00	1.00E-04	CAFF
162	1.00E-06	-6.00	0.00E+00	BQA

OUTPUT

ID	C	LOGC	LOGK	SPECIES:	TYPE I - COMPONENTS
1	7.35E-04	-3.13	0.00	Ca+2	1
2	8.59E-04	-3.07	0.00	Mg+2	1
4	4.93E-03	-2.31	0.00	K +1	1
5	1.98E-03	-2.70	0.00	Na+1	1
6	8.90E-17	-16.05	0.00	Fe+3	1
7	3.47E-10	-9.46	0.00	Fe+2	1
8	8.33E-06	-5.08	0.00	Mn+2	1
9	2.27E-08	-7.64	0.00	Cu+2	1
11	6.73E-07	-6.17	0.00	Cd+2	1
12	2.91E-06	-5.54	0.00	Zn+2	1
13	7.51E-07	-6.12	0.00	Ni+2	1
16	7.89E-07	-6.10	0.00	Co+2	1
17	2.55E-31	-30.59	0.00	Co+3	1
20	1.82E-11	-10.74	0.00	Al+3	1
33	4.24E-12	-11.37	0.00	Cu+1	1

34	2.00E-25	-24.70	0.00	Mn+3	1
99	8.32E-07	-6.08	0.00	E-	1
101	5.13E-09	-8.29	0.00	CO3	1
102	2.65E-03	-2.58	0.00	SO4	1
103	1.95E-03	-2.71	0.00	Cl	1
107	1.70E-06	-5.77	0.00	NH3	1
109	2.47E-11	-10.61	0.00	PO4	1
112	6.20E-22	-21.21	0.00	SiO4	1
148	9.49E-08	-7.02	0.00	BOH4	1
152	2.99E-08	-7.52	0.00	MoO4	1
157	5.97E-03	-2.22	0.00	NO3	1
167	8.65E-15	-14.06	0.00	DHBZ	1
119	3.39E-12	-11.47	0.00	SAL	1
168	4.76E-06	-5.32	0.00	HMPA	1
163	5.63E-09	-8.25	0.00	ACPH	1
169	6.89E-05	-4.16	0.00	HBA	1
170	7.30E-06	-5.14	0.00	DEMA	1
116	5.25E-08	-7.28	0.00	ACAC	1
132	7.08E-06	-5.15	0.00	PHTH	1
171	1.86E-05	-4.73	0.00	MALI	1
172	2.81E-05	-4.55	0.00	SUCA	1
173	2.53E-05	-4.60	0.00	DMBA	1
164	7.24E-05	-4.14	0.00	BZA	1
165	5.00E-08	-7.30	0.00	PHEN	1
174	8.96E-05	-4.05	0.00	PROP	1
166	2.40E-05	-4.62	0.00	HBQN	1
161	4.33E-07	-6.36	0.00	CAFF	1
162	3.69E-06	-5.43	0.00	BQA	1

ID	C	LOGC	LOGK	SPECIES:	TYPE II - COMPLEXES		
90556	5.65E-14	-13.25	-1.18	Co+2	2	CAFF	1
H +1	-1						
50000	3.16E-10	-9.50	-5.26	Al+3	1	H +1	-1
50002	3.98E-08	-7.40	-9.66	Al+3	1	H +1	-2
50004	3.16E-07	-6.50	-15.26	Al+3	1	H +1	-3
50006	6.75E-17	-16.17	-7.69	Al+3	2	H +1	-2

```
50008    8.19E-16  -15.09    12.62     SiO4    1    H +1    1
50010    8.38E-13  -12.08    22.13     SiO4    1    H +1    2
50012    2.84E-06   -5.55    35.16     SiO4    1    H +1    3
50014    3.50E-03   -2.46    44.75     SiO4    1    H +1    4
50016    9.73E-19  -18.01    -0.60     NO3     3    Al+3    1
50018    2.91E-15  -14.54     5.28     SO4     1    Al+3    1
H +1    1
50020    1.46E-11  -10.84     2.48     SO4     1    Al+3    1
50022    1.12E-15  -14.95     0.94     SO4     2    Al+3    1
50024    1.30E-33  -32.89    -3.68     SO4     3    Al+3    2
50026    3.23E-21  -20.49     3.85     Ca+2    1    SiO4    1
50028    6.92E-18  -17.16    13.68     Ca+2    1    SiO4    1
H +1    1
50030    4.55E-20  -19.34     4.93     Mg+2    1    SiO4    1
50032    1.44E-17  -16.84    13.93     Mg+2    1    SiO4    1
H +1    1
50034    5.17E-22  -21.29    22.47     Fe+3    1    SiO4    1
H +1    1
60000    1.09E-10   -9.96     1.03     Na+1    1    CO3     1
60002    1.69E-08   -7.77     9.72     Na+1    1    CO3     1
H +1    1
60004    1.73E-11  -10.76     3.70     Cd+2    1    CO3     1
60006    6.73E-17  -16.17     6.58     Cd+2    1    CO3     2
60008    1.77E-09   -8.75    12.21     Cd+2    1    CO3     1
H +1    1
60010    4.74E-11  -10.32     4.09     Ni+2    1    CO3     1
60012    3.36E-09   -8.47    12.44     Ni+2    1    CO3     1
H +1    1
60014    1.98E-11  -10.70     3.69     Co+2    1    CO3     1
60016    2.22E-09   -8.65    12.24     Co+2    1    CO3     1
H +1    1
60018    1.71E-07   -6.77     1.98     Cd+2    1    SO4     1
60020    1.45E-07   -6.84     1.86     Ni+2    1    SO4     1
60022    1.52E-07   -6.82     1.86     Co+2    1    SO4     1
60024    4.21E-06   -5.38     0.40     Mg+2    1    Cl      1
60026    7.22E-08   -7.14     1.74     Cd+2    1    Cl      1
60028    4.45E-10   -9.35     2.24     Cd+2    1    Cl      2
```

60029	5.47E-13	-12.26	2.04	Cd+2	1	Cl	3
60030	4.22E-12	-11.37	-2.54	Ni+2	1	Cl	1
60032	3.07E-09	-8.51	0.30	Co+2	1	Cl	1
60034	6.71E-10	-9.17	2.72	Ni+2	1	NH3	1
60036	1.69E-13	-12.77	4.89	Ni+2	1	NH3	2
60038	1.32E-17	-16.88	6.55	Ni+2	1	NH3	3
60040	2.96E-22	-21.53	7.67	Ni+2	1	NH3	4
60042	2.36E-27	-26.63	8.34	Ni+2	1	NH3	5
60044	3.74E-33	-32.43	8.31	Ni+2	1	NH3	6
60046	1.62E-10	-9.79	2.08	Co+2	1	NH3	1
60048	7.24E-15	-14.14	3.50	Co+2	1	NH3	2
60050	1.05E-19	-18.98	4.43	Co+2	1	NH3	3
60052	7.80E-25	-24.11	5.07	Co+2	1	NH3	4
60054	1.53E-30	-29.82	5.13	Co+2	1	NH3	5
60056	4.73E-37	-36.33	4.39	Co+2	1	NH3	6
60058	4.69E-08	-7.33	15.95	Cd+2	1	PO4	1
H +1	1						
60060	3.56E-11	-10.45	19.33	Cd+2	1	PO4	1
H +1	2						
60062	8.29E-09	-8.08	15.15	Ni+2	1	PO4	1
H +1	1						
60064	4.06E-09	-8.39	21.34	Ni+2	1	PO4	1
H +1	2						
60066	1.05E-08	-7.98	15.23	Co+2	1	PO4	1
H +1	1						
60068	7.32E-09	-8.14	0.26	Cd+2	1	NO3	1
60070	1.66E-11	-10.78	-0.16	Cd+2	1	NO3	2
60072	6.48E-09	-8.19	0.16	Ni+2	1	NO3	1
60074	6.72E-14	-13.17	-2.60	Ni+2	1	NO3	2
60076	4.30E-09	-8.37	-0.04	Co+2	1	NO3	1
60078	1.12E-13	-12.95	-2.40	Co+2	1	NO3	2
60092	1.34E-10	-9.87	-10.20	Cd+2	1	H +1	-1
60094	2.28E-14	-13.64	-20.47	Cd+2	1	H +1	-2
60096	5.22E-28	-27.28	-47.11	Cd+2	1	H +1	-4
60098	7.70E-16	-15.11	-9.27	Cd+2	2	H +1	-1
60100	5.53E-32	-31.26	-32.57	Cd+2	4	H +1	-4
60102	2.49E-10	-9.60	-9.98	Ni+2	1	H +1	-1

60104	4.96E-13	-12.30	-19.18	Ni+2	1	H +1	-2
60106	2.37E-17	-16.62	-30.00	Ni+2	1	H +1	-3
60108	4.69E-17	-16.33	-10.58	Ni+2	2	H +1	-1
60110	1.01E-26	-26.00	-27.50	Ni+2	4	H +1	-4
60112	4.24E-10	-9.37	-9.77	Co+2	1	H +1	-1
60114	9.49E-13	-12.02	-18.92	Co+2	1	H +1	-2
60116	7.89E-19	-18.10	-31.50	Co+2	1	H +1	-3
60118	6.87E-27	-26.16	-46.06	Co+2	1	H +1	-4
60120	1.64E-17	-16.79	-11.08	Co+2	2	H +1	-1
60122	1.99E-29	-28.70	-30.29	Co+2	4	H +1	-4
66124	1.38E-10	-9.86	3.59	Cd+2	1	ACAC	1
60126	3.63E-15	-14.44	6.29	Cd+2	1	ACAC	2
60128	2.22E-08	-7.65	5.75	Ni+2	1	ACAC	1
60130	3.44E-11	-10.46	10.22	Ni+2	1	ACAC	2
60132	6.00E-09	-8.22	5.16	Co+2	1	ACAC	1
60134	3.30E-12	-11.48	9.18	Co+2	1	ACAC	2
60136	2.39E-12	-11.62	6.02	Cd+2	1	SAL	1
60138	7.06E-09	-8.15	15.99	Cd+2	1	SAL	1
H +1	1						
60140	6.70E-11	-10.17	7.42	Ni+2	1	SAL	1
60142	1.19E-12	-11.92	12.17	Ni+2	1	SAL	1
H +1	1						
60144	4.15E-11	-10.38	7.19	Co+2	1	SAL	1
60146	6.28E-13	-12.20	11.87	Co+2	1	SAL	1
H +1	1						
60148	1.01E-07	-7.00	0.46	K +1	1	PHTH	1
60152	7.56E-10	-9.12	2.20	Cd+2	1	PHTH	1
60154	6.29E-14	-13.20	3.27	Cd+2	1	PHTH	2
60156	3.88E-13	-12.41	5.41	Cd+2	1	PHTH	1
H +1	1						
60158	1.86E-16	-15.73	7.24	Cd+2	1	PHTH	2
H +1	1						
60160	1.57E-09	-8.80	2.47	Ni+2	1	PHTH	1
60162	1.34E-12	-11.87	5.90	Ni+2	1	PHTH	1
H +1	1						
60164	4.44E-10	-9.35	1.90	Co+2	1	PHTH	1

60166	5.34E-12	-11.27	6.48	Co+2	1	PHTH	1
H +1	1						
60168	1.04E-10	-9.98	4.39	Ni+2	1	ACPH	1
60170	5.08E-16	-15.29	7.33	Ni+2	1	ACPH	2
60172	1.58E-10	-9.80	4.55	Co+2	1	ACPH	1
60174	7.72E-16	-15.11	7.49	Co+2	1	ACPH	2
60176	1.90E-09	-8.72	1.59	BZA	1	Cd+2	1
60178	2.81E-13	-12.55	1.90	BZA	2	Cd+2	1
60180	6.70E-10	-9.17	1.09	BZA	1	Ni+2	1
60182	4.14E-10	-9.38	0.86	BZA	1	Co+2	1
60184	2.86E-10	-9.54	20.57	Fe+3	1	DHBZ	1
60186	2.11E-09	-8.68	35.50	Fe+3	1	DHBZ	2
60188	1.35E-14	-13.87	44.37	Fe+3	1	DHBZ	3
60190	2.27E-12	-11.64	8.59	Cd+2	1	DHBZ	1
60192	1.30E-11	-10.89	9.30	Ni+2	1	DHBZ	1
60194	3.39E-20	-19.47	14.78	Ni+2	1	DHBZ	2
60196	6.52E-12	-11.19	8.98	Co+2	1	DHBZ	1
60198	1.42E-19	-18.85	15.38	Co+2	1	DHBZ	2
60200	8.64E-11	-10.06	1.43	Cd+2	1	HMPA	1
60202	4.31E-15	-14.37	2.45	Cd+2	1	HMPA	2
60204	4.39E-20	-19.36	2.78	Cd+2	1	HMPA	3
60206	2.59E-10	-9.59	1.86	Ni+2	1	HMPA	1
60208	2.05E-14	-13.69	3.08	Ni+2	1	HMPA	2
60210	2.51E-19	-18.60	3.49	Ni+2	1	HMPA	3
60212	1.64E-10	-9.78	1.64	Co+2	1	HMPA	1
60214	9.40E-15	-14.03	2.72	Co+2	1	HMPA	2
60216	8.15E-20	-19.09	2.98	Co+2	1	HMPA	3
60218	3.95E-10	-9.40	0.93	Cd+2	1	HBA	1
60220	2.78E-10	-9.56	0.73	Ni+2	1	HBA	1
60222	1.98E-10	-9.70	0.56	Co+2	1	HBA	1
60224	1.81E-07	-6.74	0.70	K +1	1	DEMA	1
60226	4.09E-09	-8.39	2.92	Cd+2	1	DEMA	1
60228	3.09E-09	-8.51	2.75	Ni+2	1	DEMA	1
60230	2.46E-09	-8.61	2.63	Co+2	1	DEMA	1
60232	6.72E-09	-8.17	2.73	Cd+2	1	MALI	1
60234	2.56E-11	-10.59	6.81	Cd+2	1	MALI	1
H +1	1						

60236	4.84E-08	-7.32	3.54	Ni+2	1	MALI	1
60238	8.81E-11	-10.06	7.30	Ni+2	1	MALI	1
H +1	1						
60240	2.49E-08	-7.60	3.23	Co+2	1	MALI	1
60242	5.97E-11	-10.22	7.11	Co+2	1	MALI	1
H +1	1						
60243	2.52E-07	-6.60	0.26	K +1	1	SUCA	1
60244	3.29E-09	-8.48	2.24	SUCA	1	Cd+2	1
60245	1.53E-09	-8.82	1.86	SUCA	1	Ni+2	1
60246	4.41E-17	-16.36	0.82	SUCA	1	Ni+2	1
H +1	1						
60248	1.54E-09	-8.81	1.84	SUCA	1	Co+2	1
60250	1.10E-09	-8.96	1.81	Cd+2	1	DMBA	1
60252	1.90E-09	-8.72	2.00	Ni+2	1	DMBA	1
60254	1.20E-09	-8.92	1.78	Co+2	1	DMBA	1
60256	1.38E-09	-8.86	1.36	Cd+2	1	PROP	1
60258	6.96E-13	-12.16	2.11	Cd+2	1	PROP	2
60260	6.00E-10	-9.22	0.95	Ni+2	1	PROP	1
60262	1.74E-13	-12.76	1.46	Ni+2	1	PROP	2
60264	5.49E-10	-9.26	0.89	Co+2	1	PROP	1
70000	1.32E-04	-3.88	1.83	Ca+2	1	SO4	1
70002	1.06E-06	-5.97	-0.13	Ca+2	1	Cl	1
70004	9.98E-09	-8.00	5.74	Ca+2	1	PO4	1
70006	4.67E-07	-6.33	13.91	Ca+2	1	PO4	1
H +1	1						
70008	9.10E-08	-7.04	19.70	Mg+2	1	PO4	1
H +1	2						
70010	7.79E-11	-10.11	27.24	Ca+2	1	PO4	2
H +1	2						
70012	2.90E-12	-11.54	32.31	Ca+2	1	PO4	2
H +1	3						
70014	7.91E-13	-12.10	28.38	Ca+2	2	PO4	2
H +1	2						
70020	3.52E-10	-9.45	-12.82	Ca+2	1	H +1	-1
70022	1.76E-09	-8.75	2.67	Ca+2	1	CO3	1
70024	8.44E-08	-7.07	10.85	Ca+2	1	CO3	1
H +1	1						

70026	6.42E-10	-9.19	-0.29	Ca+2	1	NH3	1
70028	1.73E-16	-15.76	-1.09	Ca+2	1	NH3	2
70030	2.95E-23	-22.53	-2.09	Ca+2	1	NH3	3
70032	1.27E-05	-4.90	0.46	Ca+2	1	NO3	1
70034	4.55E-08	-7.34	0.24	Ca+2	1	NO3	2
70054	1.28E-04	-3.89	1.75	Mg+2	1	SO4	1
70056	1.57E-08	-7.80	5.87	Mg+2	1	PO4	1
70058	1.73E-06	-5.76	14.41	Mg+2	1	PO4	1
H +1	1						
70060	3.44E-07	-6.46	20.21	Mg+2	1	PO4	1
H +1	2						
70062	1.02E-11	-10.99	32.79	Mg+2	1	PO4	2
H +1	3						
70064	8.50E-11	-10.07	27.21	Mg+2	1	PO4	2
H +1	2						
70066	4.11E-12	-11.39	28.96	Mg+2	2	PO4	2
H +1	2						
70072	7.84E-09	-8.11	-11.54	Mg+2	1	H +1	-1
70074	1.89E-26	-25.72	-39.46	Mg+2	4	H +1	-4
70076	1.16E-08	-7.94	3.42	Mg+2	1	CO3	1
70078	3.50E-07	-6.46	11.40	Mg+2	1	CO3	1
H +1	1						
70080	9.24E-09	-8.03	0.80	Mg+2	1	NH3	1
70082	1.34E-15	-14.87	-0.27	Mg+2	1	NH3	2
70084	6.00E-22	-21.22	-0.85	Mg+2	1	NH3	3
70086	1.29E-28	-27.89	-1.75	Mg+2	1	NH3	4
70112	4.93E-11	-10.31	-14.50	K +1	1	H +1	-1
70114	4.76E-05	-4.32	0.56	K +1	1	SO4	1
70116	2.61E-07	-6.58	12.83	K +1	1	PO4	1
H +1	1						
70118	1.27E-06	-5.90	-0.88	K +1	1	Cl	1
70120	1.58E-05	-4.80	-0.27	K +1	1	NO3	1
70124	1.52E-05	-4.82	0.46	Na+1	1	SO4	1
70126	4.52E-07	-6.34	1.51	Na+1	1	SO4	2
70132	1.35E-07	-6.87	12.94	Na+1	1	PO4	1
H +1	1						
70134	1.93E-08	-7.72	2.01	Na+1	1	BOH4	1

```
70136   7.89E-11  -10.10  -13.90    Na+1   1    H +1  -1
70138   2.77E-06   -5.56   -0.63    Na+1   1    NO3    1
70140   4.95E-16  -15.31    3.32    Fe+3   1    SO4    1
70142   1.65E-17  -16.78    4.42    Fe+3   1    SO4    2
70144   2.29E-18  -17.64    1.12    Fe+3   1    Cl     1
70146   1.15E-20  -19.94    1.53    Fe+3   1    Cl     2
70148   1.70E-24  -23.77    0.41    Fe+3   1    Cl     3
70150   1.59E-12  -11.80   21.36    Fe+3   1    PO4    1
H +1    1
70152   8.17E-18  -17.09   22.57    Fe+3   1    PO4    1
Fe+2    0    H +1   2
70154   2.05E-21  -20.69   28.52    Fe+3   2    PO4    1
H +1    1
70168   4.14E-15  -14.38    8.69    Fe+3   1    BOH4   1
70170   5.19E-15  -14.28   15.81    Fe+3   1    BOH4   2
70172   4.60E-17  -16.34   20.78    Fe+3   1    BOH4   3
70174   2.73E-16  -15.56    8.01    Fe+3   1    MoO4   1
70176   9.75E-23  -22.01   16.61    Fe+3   1    MoO4   3
70178   1.05E-12  -11.98   -2.43    Fe+3   1    H +1  -1
70180   7.76E-10   -9.11   -6.06    Fe+3   1    H +1  -2
70200   3.80E-07   -6.42   -9.87    Fe+3   1    H +1  -3
70202   1.29E-12  -11.89  -21.84    Fe+3   1    H +1  -4
70204   9.98E-23  -22.00   -2.90    Fe+3   2    H +1  -2
70206   4.66E-29  -28.33   -6.18    Fe+3   3    H +1  -4
70208   2.32E-18  -17.63    0.64    Fe+3   1    NO3    1
70220   4.84E-11  -10.32    1.72    SO4    1    Fe+2   1
70222   4.84E-17  -16.32    2.22    SO4    1    Fe+2   1
H +1    1
70224   2.63E-13  -12.58   -9.62    Fe+2   1    H +1  -1
70226   6.61E-18  -17.18  -20.72    Fe+2   1    H +1  -2
70228   1.10E-22  -21.96  -32.00    Fe+2   1    H +1  -3
70230   2.40E-30  -29.62  -46.16    Fe+2   1    H +1  -4
70240   3.41E-12  -11.47   15.10    PO4    1    Fe+2   1
H +1    1
70242   2.15E-12  -11.67   21.40    PO4    1    Fe+2   1
H +1    2
```

70244	4.42E-16	-15.35	28.32	PO4	2	Fe+2	1
H +1	2						
70266	7.65E-08	-7.12	15.07	Mn+2	1	PO4	1
H +1	1						
70268	5.17E-08	-7.29	21.40	Mn+2	1	PO4	1
H +1	2						
70270	5.97E-12	-11.22	28.07	Mn+2	1	PO4	2
H +1	2						
70272	1.33E-06	-5.87	1.78	Mn+2	1	SO4	1
70274	5.02E-10	-9.30	-10.72	Mn+2	1	H +1	-1
70276	3.10E-15	-14.51	-22.43	Mn+2	1	H +1	-2
70278	1.66E-20	-19.78	-34.20	Mn+2	1	H +1	-3
70280	7.25E-28	-27.14	-48.06	Mn+2	1	H +1	-4
70282	7.27E-15	-14.14	-10.48	Mn+2	2	H +1	-1
70284	1.59E-15	-14.80	-24.14	Mn+2	2	H +1	-3
70286	6.04E-09	-8.22	11.65	Mn+2	1	CO3	1
H +1	1						
70294	1.03E-10	-9.99	0.86	Mn+2	1	NH3	1
70296	7.47E-16	-15.13	1.49	Mn+2	1	NH3	2
70298	2.32E-21	-20.64	1.75	Mn+2	1	NH3	3
70300	1.47E-27	-26.83	1.32	Mn+2	1	NH3	4
70302	4.54E-08	-7.34	-0.04	Mn+2	1	NO3	1
70304	5.16E-10	-9.29	0.24	Mn+2	1	NO3	2
70318	5.75E-10	-9.24	15.51	Cu+2	1	PO4	1
H +1	1						
70320	9.32E-12	-11.03	20.22	Cu+2	1	PO4	1
H +1	2						
70322	4.39E-17	-16.36	32.00	Cu+2	1	PO4	2
H +1	3						
70324	7.92E-19	-18.10	31.40	Cu+2	2	PO4	2
H +1	2						
70326	5.65E-14	-13.25	28.61	Cu+2	1	PO4	2
H +1	2						
70328	4.58E-09	-8.34	1.88	Cu+2	1	SO4	1
70330	3.06E-10	-9.51	3.28	Cu+2	1	SO4	2
70332	1.51E-13	-12.82	2.55	Cu+2	1	SO4	3
70334	4.21E-08	-7.38	7.29	Cu+2	1	BOH4	1

70336	1.08E-09	-8.97	12.72	Cu+2	1	BOH4	2
70338	5.49E-14	-13.26	15.45	Cu+2	1	BOH4	3
70340	1.09E-09	-8.96	-7.82	Cu+2	1	H +1	-1
70342	2.73E-10	-9.56	-14.92	Cu+2	1	H +1	-2
70344	1.89E-16	-15.72	-27.58	Cu+2	1	H +1	-3
70346	9.92E-22	-21.00	-39.36	Cu+2	1	H +1	-4
70348	4.94E-14	-13.31	-11.02	Cu+2	2	H +1	-2
70350	1.70E-19	-18.77	-21.84	Cu+2	3	H +1	-4
70352	5.57E-32	-31.25	-20.18	Cu+2	4	H +1	-3
70364	2.17E-10	-9.66	6.27	Cu+2	1	CO3	1
70366	1.34E-15	-14.87	9.35	Cu+2	1	CO3	2
70368	6.41E-11	-10.19	0.16	Cu+2	1	Cl	1
70370	4.45E-10	-9.35	4.06	Cu+2	1	NH3	1
70372	1.51E-12	-11.82	7.36	Cu+2	1	NH3	2
70374	1.41E-15	-14.85	10.10	Cu+2	1	NH3	3
70376	1.87E-19	-18.73	11.99	Cu+2	1	NH3	4
70378	8.77E-26	-25.06	11.43	Cu+2	1	NH3	5
70380	1.47E-10	-9.83	-2.92	Cu+2	1	NH3	1
H +1	-1						
70382	4.27E-20	-19.37	-0.92	Cu+2	1	NH3	3
H +1	-1						
70384	9.98E-23	-22.00	-15.82	Cu+2	1	NH3	2
H +1	-2						
70386	2.47E-10	-9.61	0.26	Cu+2	1	NO3	1
70388	9.30E-13	-12.03	0.06	Cu+2	1	NO3	2
70424	1.16E-08	-7.93	14.71	Zn+2	1	PO4	1
H +1	1						
70426	1.37E-09	-8.86	20.28	Zn+2	1	PO4	1
H +1	2						
71208	5.11E-14	-13.29	32.96	Zn+2	1	PO4	2
H +1	3						
71210	4.81E-16	-15.32	29.97	Zn+2	2	PO4	2
H +1	2						
71212	1.81E-12	-11.74	28.01	Zn+2	1	PO4	2
H +1	2						
71214	6.13E-07	-6.21	1.90	Zn+2	1	SO4	1
71216	3.56E-08	-7.45	3.24	Zn+2	1	SO4	2

71218	8.04E-11	-10.09	3.17	Zn+2	1	SO4	3
71220	3.15E-13	-12.50	3.34	Zn+2	1	SO4	4
71222	6.97E-09	-8.16	-9.12	Zn+2	1	H +1	-1
71224	1.83E-08	-7.74	-15.20	Zn+2	1	H +1	-2
71226	3.66E-15	-14.44	-28.40	Zn+2	1	H +1	-3
71228	3.18E-21	-20.50	-40.96	Zn+2	1	H +1	-4
71230	3.52E-14	-13.45	-8.88	Zn+2	2	H +1	-1
71242	2.47E-10	-9.61	4.22	Zn+2	1	CO3	1
71243	2.11E-09	-8.68	11.65	Zn+2	1	CO3	1
H +1	1						
71244	8.78E-09	-8.06	0.19	Zn+2	1	Cl	1
71246	5.29E-11	-10.28	0.68	Zn+2	1	Cl	2
71248	3.26E-13	-12.49	1.18	Zn+2	1	Cl	3
71250	1.33E-15	-14.88	1.50	Zn+2	1	Cl	4
71252	8.03E-10	-9.10	2.21	Zn+2	1	NH3	1
71254	2.67E-13	-12.57	4.50	Zn+2	1	NH3	2
71256	1.04E-16	-15.98	6.86	Zn+2	1	NH3	3
71258	1.90E-20	-19.72	8.89	Zn+2	1	NH3	4
71260	4.84E-10	-9.32	-4.51	Zn+2	1	NH3	1
H +1	-1						
71262	2.99E-14	-13.52	-2.95	Zn+2	1	NH3	2
H +1	-1						
71264	7.89E-19	-18.10	-1.76	Zn+2	1	NH3	3
H +1	-1						
71266	1.64E-13	-12.79	-14.48	Zn+2	1	NH3	1
H +1	-2						
71268	1.09E-18	-17.96	-13.89	Zn+2	1	NH3	2
H +1	-2						
71270	1.88E-19	-18.73	-26.92	Zn+2	1	NH3	1
H +1	-3						
71300	2.51E-08	-7.60	0.16	Zn+2	1	NO3	1
71302	1.97E-10	-9.70	0.28	Zn+2	1	NO3	2
77300	1.86E-13	-12.73	10.18	NH3	2	Cu+1	1
77400	2.78E-25	-24.56	2.72	SO4	1	Mn+3	1
77402	2.35E-18	-17.63	0.57	Mn+3	1	H +1	-1
78600	1.99E-05	-4.70	10.09	CO3	1	H +1	1
78602	1.07E-05	-4.97	16.32	CO3	1	H +1	2

78604	4.72E-08	-7.33	1.75	SO4	1	H +1	1
78606	4.62E-22	-21.34	-5.76	SO4	1	H +1	2
78610	7.45E-06	-5.13	11.98	PO4	1	H +1	1
78612	2.15E-05	-4.67	18.94	PO4	1	H +1	2
78614	7.12E-10	-9.15	20.96	PO4	1	H +1	3
78616	2.26E-11	-10.65	30.07	PO4	2	H +1	3
78618	2.85E-10	-9.54	37.67	PO4	2	H +1	4
78620	5.44E-14	-13.26	40.45	PO4	2	H +1	5
78634	4.17E-08	-7.38	-13.88	H +1	-1		
78636	4.98E-05	-4.30	9.22	BOH4	1	H +1	1
78638	2.36E-18	-17.63	9.94	BOH4	3	H +1	1
78640	5.16E-15	-14.29	19.78	BOH4	3	H +1	2
78642	1.70E-21	-20.77	20.32	BOH4	4	H +1	2
78644	1.02E-18	-17.99	29.60	BOH4	4	H +1	3
78646	2.13E-23	-22.67	38.44	BOH4	5	H +1	4
78648	5.98E-11	-10.22	3.80	MoO4	1	H +1	1
78650	1.40E-13	-12.85	7.67	MoO4	1	H +1	2
78652	3.21E-19	-18.49	8.53	MoO4	1	H +1	3
78654	2.95E-16	-15.53	-6.32	Cl	1	H +1	1
78656	9.36E-04	-3.03	9.24	NH3	1	H +1	1
78700	4.38E-05	-4.36	10.62	Cl	1	NH3	1
H +1	1						
78702	1.84E-05	-4.73	10.11	SO4	1	NH3	1
H +1	1						
78708	5.44E-11	-10.26	-1.54	NO3	1	H +1	1
78710	2.35E-10	-9.63	8.39	ACAC	1	Al+3	1
78712	7.78E-10	-9.11	16.19	ACAC	2	Al+3	1
78714	2.52E-11	-10.60	21.98	ACAC	3	Al+3	1
78716	1.45E-08	-7.84	14.37	SAL	1	Al+3	1
78718	7.25E-13	-12.14	3.75	PHTH	1	Al+3	1
78720	2.69E-09	-8.57	7.32	PHTH	1	Al+3	1
78722	3.16E-11	-10.50	-2.12	BZA	1	Al+3	1
H +1	-1						
90100	3.14E-08	-7.50	13.06	DHBZ	1	H +1	1
90102	1.89E-05	-4.72	22.34	DHBZ	1	H +1	2
90104	7.79E-12	-11.11	6.02	Mg+2	1	DHBZ	1
90106	2.65E-13	-12.58	4.62	Ca+2	1	DHBZ	1

90108	7.55E-12	-11.12	8.02	Mn+2	1	DHBZ	1
90110	3.78E-10	-9.42	16.22	Mn+2	1	DHBZ	1
H +1	1						
90112	1.58E-15	-14.80	8.72	DHBZ	1	Fe+2	1
90114	7.90E-14	-13.10	16.92	DHBZ	1	Fe+2	1
H +1	1						
90116	3.27E-08	-7.49	14.22	Cu+2	1	DHBZ	1
90118	4.17E-10	-9.38	10.22	Zn+2	1	DHBZ	1
90120	1.14E-08	-7.94	3.88	HMPA	1	H +1	1
90122	6.37E-08	-7.20	1.26	Ca+2	1	HMPA	1
90124	5.92E-08	-7.23	1.16	Mg+2	1	HMPA	1
90126	5.74E-10	-9.24	1.16	Mn+2	1	HMPA	1
90128	7.55E-14	-13.12	1.66	HMPA	1	Fe+2	1
90130	9.88E-11	-10.01	2.96	Cu+2	1	HMPA	1
90132	1.26E-09	-8.90	1.96	Zn+2	1	HMPA	1
90134	5.86E-19	-18.23	3.14	Fe+3	1	HMPA	1
90136	1.77E-13	-12.75	2.12	Fe+3	1	HMPA	1
H +1	-1						
90138	3.09E-05	-4.51	13.46	SAL	1	H +1	1
90140	7.42E-09	-8.13	16.34	SAL	1	H +1	2
90141	1.22E-09	-8.92	5.62	Mg+2	1	SAL	1
90142	1.31E-10	-9.88	4.72	Ca+2	1	SAL	1
90144	3.29E-08	-7.48	13.62	Ca+2	1	SAL	1
H +1	1						
90146	4.69E-11	-10.33	6.22	Mn+2	1	SAL	1
90148	9.79E-15	-14.01	6.92	SAL	1	Fe+2	1
90150	6.41E-09	-8.19	10.92	Cu+2	1	SAL	1
90152	1.64E-10	-9.79	7.22	Zn+2	1	SAL	1
90154	1.45E-11	-10.84	16.68	Fe+3	1	SAL	1
90156	7.59E-17	-16.12	17.90	Fe+3	1	SAL	1
H +1	1						
90158	1.03E-16	-15.99	10.02	Mg+2	1	SAL	2
90160	8.85E-19	-18.05	8.02	Ca+2	1	SAL	2
90162	1.59E-18	-17.80	10.22	Mn+2	1	SAL	2
90164	1.66E-21	-20.78	11.62	SAL	2	Fe+2	1
90166	2.24E-09	-8.65	30.34	Fe+3	1	SAL	2
90168	1.73E-12	-11.76	18.82	Cu+2	1	SAL	2

90170	1.39E-23	-22.86	5.62	Zn+2	1	SAL	2
90172	1.70E-05	-4.77	9.98	ACPH	1	H +1	1
90174	7.53E-11	-10.12	1.26	Ca+2	1	ACPH	1
90176	1.35E-11	-10.87	2.46	Mn+2	1	ACPH	1
90178	9.27E-10	-9.03	6.86	Cu+2	1	ACPH	1
90180	2.98E-11	-10.53	3.26	Zn+2	1	ACPH	1
90182	1.74E-14	-13.76	10.54	Fe+3	1	ACPH	1
90184	5.23E-07	-6.28	4.38	HBA	1	H +1	1
90186	3.41E-07	-6.47	0.76	Mg+2	1	HBA	1
90188	1.84E-07	-6.73	0.56	Ca+2	1	HBA	1
90190	2.85E-10	-9.54	2.26	Cu+2	1	HBA	1
90192	3.65E-09	-8.44	1.26	Zn+2	1	HBA	1
90194	3.34E-05	-4.48	7.16	DEMA	1	H +1	1
90196	1.27E-09	-8.90	9.24	DEMA	1	H +1	2
90198	5.25E-08	-7.28	0.56	Na+1	1	DEMA	1
90200	4.15E-07	-6.38	1.82	Mg+2	1	DEMA	1
90202	1.04E-07	-6.98	7.72	Mg+2	1	DEMA	1
H +1	1						
90204	3.55E-07	-6.45	1.82	Ca+2	1	DEMA	1
90206	1.41E-07	-6.85	7.92	Ca+2	1	DEMA	1
H +1	1						
90208	8.03E-09	-8.10	2.12	Mn+2	1	DEMA	1
90210	2.76E-08	-7.56	5.22	Cu+2	1	DEMA	1
90212	8.72E-12	-11.06	8.22	Cu+2	1	DEMA	1
H +1	1						
90214	1.11E-08	-7.95	2.72	Zn+2	1	DEMA	1
90216	1.40E-09	-8.85	8.32	Zn+2	1	DEMA	1
H +1	1						
90218	7.83E-13	-12.11	9.08	Fe+3	1	DEMA	1
90220	2.59E-18	-17.59	10.10	Fe+3	1	DEMA	1
H +1	1						
90222	1.26E-05	-4.90	8.88	ACAC	1	H +1	1
90224	1.30E-07	-6.89	3.46	Mg+2	1	ACAC	1
90226	2.80E-08	-7.55	2.86	Ca+2	1	ACAC	1
90228	3.99E-09	-8.40	3.96	Mn+2	1	ACAC	1
90230	1.32E-12	-11.88	4.86	ACAC	1	Fe+2	1
90232	1.37E-07	-6.86	8.06	Cu+2	1	ACAC	1

90234	1.11E-08	-7.96	4.86	Zn+2	1	ACAC	1
90236	6.46E-14	-13.19	10.14	Fe+3	1	ACAC	1
90238	3.24E-07	-6.49	5.16	PHTH	1	H +1	1
90240	7.77E-11	-10.11	8.04	PHTH	1	H +1	2
90242	4.05E-08	-7.39	0.46	Na+1	1	PHTH	1
90244	4.33E-07	-6.36	1.92	Ca+2	1	PHTH	1
90246	9.80E-09	-8.01	2.22	Mn+2	1	PHTH	1
90248	5.33E-10	-9.27	3.52	Cu+2	1	PHTH	1
90250	5.42E-09	-8.27	2.42	Zn+2	1	PHTH	1
90252	3.80E-14	-13.42	7.78	Fe+3	1	PHTH	1
90254	7.54E-14	-13.12	4.82	Cu+2	1	PHTH	2
90256	7.65E-13	-12.12	3.72	Zn+2	1	PHTH	2
90258	4.26E-07	-6.37	4.86	MALI	1	H +1	1
90260	3.23E-10	-9.49	8.24	MALI	1	H +1	2
90262	1.06E-07	-6.97	0.46	Na+1	1	MALI	1
90264	2.10E-07	-6.68	0.36	K +1	1	MALI	1
90266	1.67E-06	-5.78	2.02	Mg+2	1	MALI	1
90268	5.29E-09	-8.28	6.02	Mg+2	1	MALI	1
H +1	1						
90270	2.27E-06	-5.64	2.22	Ca+2	1	MALI	1
90272	5.69E-09	-8.24	6.12	Ca+2	1	MALI	1
H +1	1						
90274	6.45E-08	-7.19	2.62	Mn+2	1	MALI	1
90276	5.36E-12	-11.27	2.92	MALI	1	Fe+2	1
90278	2.22E-09	-8.65	3.72	Cu+2	1	MALI	1
90280	5.57E-07	-6.25	6.12	Cu+2	1	MALI	1
90282	3.57E-08	-7.45	2.82	Zn+2	1	MALI	1
90284	7.12E-11	-10.15	6.62	Zn+2	1	MALI	1
H +1	1						
90286	9.98E-14	-13.00	7.78	Fe+3	1	MALI	1
90288	2.04E-06	-5.69	5.36	SUCA	1	H +1	1
90290	7.75E-09	-8.11	9.44	SUCA	1	H +1	2
90292	6.40E-08	-7.19	0.06	Na+1	1	SUCA	1
90294	8.01E-07	-6.10	1.52	Mg+2	1	SUCA	1
90296	8.01E-09	-8.10	6.02	Mg+2	1	SUCA	1
H +1	1						
90298	6.85E-07	-6.16	1.52	Ca+2	1	SUCA	1

90300	6.85E-09	-8.16	6.02	Ca+2	1	SUCA	1
H +1	1						
90302	1.55E-08	-7.81	1.82	SUCA	1	Mn+2	1
90304	7.76E-14	-13.11	3.02	SUCA	1	Mn+2	1
H +1	1						
90306	5.12E-13	-12.29	1.72	SUCA	1	Fe+2	1
90308	4.23E-10	-9.37	2.82	SUCA	1	Cu+2	1
90310	8.56E-09	-8.07	2.02	SUCA	1	Zn+2	1
90312	6.80E-11	-10.17	6.42	SUCA	1	Zn+2	1
H +1	1						
90314	9.53E-14	-13.02	7.58	Fe+3	1	SUCA	1
90316	3.04E-08	-7.52	3.58	DMBA	1	H +1	1
90318	2.50E-07	-6.60	1.06	Mg+2	1	DMBA	1
90320	4.26E-07	-6.37	1.36	Ca+2	1	DMBA	1
90322	3.31E-10	-9.48	2.76	Cu+2	1	DMBA	1
90324	5.32E-09	-8.27	1.86	Zn+2	1	DMBA	1
90326	2.75E-07	-6.56	4.08	BZA	1	H +1	1
90328	1.13E-07	-6.95	0.26	BZA	1	Mg+2	1
90330	1.54E-07	-6.81	0.46	BZA	1	Ca+2	1
90332	5.51E-09	-8.26	0.96	BZA	1	Mn+2	1
90334	9.48E-11	-10.02	1.76	BZA	1	Cu+2	1
90336	2.42E-09	-8.62	1.06	BZA	1	Zn+2	1
90338	1.78E-15	-14.75	5.44	BZA	1	Fe+3	1
90340	1.20E-04	-3.92	9.88	PHEN	1	H +1	1
90342	3.08E-16	-15.51	7.84	Fe+3	1	PHEN	1
90344	1.71E-06	-5.77	4.78	PROP	1	H +1	1
90346	3.52E-07	-6.45	0.66	Mg+2	1	PROP	1
90348	3.79E-07	-6.42	0.76	Ca+2	1	PROP	1
90350	1.86E-10	-9.73	1.96	Cu+2	1	PROP	1
90352	2.99E-09	-8.52	1.06	Zn+2	1	PROP	1
90354	3.48E-17	-16.46	3.64	Fe+3	1	PROP	1
90356	3.64E-09	-8.44	2.68	HBQN	1	H +1	1
90358	1.19E-06	-5.92	1.76	Mg+2	1	HBQN	1
90360	4.05E-07	-6.39	1.36	Ca+2	1	HBQN	1
90362	4.59E-08	-7.34	2.36	Mn+2	1	HBQN	1
90364	4.98E-08	-7.30	4.96	Cu+2	1	HBQN	1
90366	1.27E-06	-5.90	4.26	Zn+2	1	HBQN	1

90368	5.90E-14	-13.23	7.44	Fe+3	1	HBQN	1
90370	4.32E-10	-9.36	2.94	Mg+2	1	HBQN	2
90372	1.17E-10	-9.93	2.44	Ca+2	1	HBQN	2
90374	2.10E-11	-10.68	3.64	Mn+2	1	HBQN	2
90376	1.03E-12	-11.99	13.30	Fe+3	1	HBQN	2
90378	5.73E-09	-8.24	8.64	Cu+2	1	HBQN	2
90380	9.22E-10	-9.04	5.74	Zn+2	1	HBQN	2
90500	9.49E-05	-4.02	8.84	CAFF	1	H +1	1
90502	8.86E-07	-6.05	13.31	CAFF	1	H +1	2
90504	5.46E-12	-11.26	4.56	CAFF	1	Fe+2	1
90506	7.54E-19	-18.12	7.16	CAFF	1	Fe+2	2
90508	2.33E-14	-13.63	-4.31	CAFF	1	Fe+2	1
H +1	-1						
90510	2.11E-16	-15.68	0.01	CAFF	2	Fe+2	1
H +1	-1						
90512	1.91E-22	-21.72	-6.17	CAFF	3	Fe+2	1
H +1	-2						
90514	2.50E-10	-9.60	-4.66	Mn+2	1	CAFF	1
H +1	-1						
90516	1.34E-14	-13.87	-15.43	Mn+2	1	CAFF	1
H +1	-2						
90518	2.06E-08	-7.69	6.32	Cu+2	1	CAFF	1
90520	1.67E-10	-9.78	10.73	Cu+2	1	CAFF	1
H +1	1						
90522	8.39E-08	-7.08	0.43	Cu+2	1	CAFF	1
H +1	-1						
90524	5.26E-12	-11.28	3.87	Cu+2	2	CAFF	1
H +1	-1						
90526	1.11E-14	-13.96	0.92	Cu+2	2	CAFF	3
H +1	-3						
90528	1.43E-15	-14.85	7.81	Cu+2	3	CAFF	2
H +1	-2						
90530	2.79E-11	-10.55	-4.52	Cd+2	1	CAFF	1
H +1	-1						
90532	9.16E-19	-18.04	-12.14	Cd+2	1	CAFF	2
H +1	-2						

90534 7.90E-26 -25.10 -19.34 Cd+2 1 CAFF 3
H +1 -3
90536 2.52E-09 -8.60 3.30 Zn+2 1 CAFF 1
90538 5.76E-09 -8.24 -2.84 Zn+2 1 CAFF 1
H +1 -1
90540 8.27E-13 -12.08 -0.32 Zn+2 1 CAFF 2
H +1 -1
90542 2.93E-14 -13.53 -8.27 Zn+2 1 CAFF 2
H +1 -2
90544 5.16E-18 -17.29 -5.66 Zn+2 1 CAFF 3
H +1 -2
90546 5.66E-10 -9.25 -3.26 Ni+2 1 CAFF 1
H +1 -1
90548 2.90E-13 -12.54 -13.05 Ni+2 1 CAFF 1
H +1 -2
90550 6.01E-14 -13.22 -1.11 Ni+2 2 CAFF 1
H +1 -1
90552 1.05E-20 -19.98 -1.88 Ni+2 3 CAFF 2
H +1 -2
90554 1.92E-10 -9.72 -3.75 Co+2 1 CAFF 1
H +1 -1

ID C LOGC LOGK SPECIES: TYPE III - FIXED SOLIDS

50 -1.50E-02 -1.82 6.50 H +1 1
80000 6.54E-06 -5.18 12.67 Fe+3 1 E- 1
Fe+2 -1
80002 -2.35E-18 -17.63 25.70 Mn+2 -1 Mn+3 1
E- 1
80004 4.42E-12 -11.35 2.35 Cu+2 1 Cu+1 -1
E- 1
80006 -2.55E-31 -30.59 30.57 Co+2 -1 Co+3 1
E- 1
80008 -3.69E-06 -5.43 17.73 CAFF -1 BQA 1
E- 2 H +1 1
80010 -3.11E-05 -4.51 21.29 CO3 1 H +1 2

ID	C	LOGC	LOGK	SPECIES:	TYPE IV -
PRECIPITATED SOLIDS					
80102	3.23E-04	-3.49	40.99	Ca+2 5	PO4 3
H +1 -1					
80608	6.54E-06	-5.18	-10.44	Fe+3 2	Fe+2 1
H +1 -8					
84022	1.13E-06	-5.95	-8.76	Al+3 1	H +1 -3

ID	C	LOGC	LOGK	SPECIES:	TYPE V -
DISSOLVED SOLIDS					
80100	2.57E-02	-1.59	4.12	Ca+2 1	SO4 1
80090	1.89E-06	-5.72	-0.31	Na+1 1	Cl 1
80104	2.53E-07	-6.60	44.26	Ca+2 4	PO4 3
H +1 1					
80106	1.44E-02	-1.84	18.40	Ca+2 1	PO4 1
H +1 1					
80110	5.98E-14	-13.22	-23.09	Ca+2 1	H +1 -2
80112	3.20E-04	-3.50	27.12	Ca+2 3	PO4 2
80114	7.23E-03	-2.14	18.10	Ca+2 1	PO4 1
H +1 1					
80116	3.86E-04	-3.41	8.01	Ca+2 1	CO3 1
80200	9.73E-08	-7.01	23.40	Mg+2 3	PO4 2
80202	1.40E-03	-2.85	17.32	Mg+2 1	PO4 1
H +1 1					
80204	9.21E-08	-7.04	-16.97	Mg+2 1	H +1 -2
80206	1.80E-04	-3.75	7.61	Mg+2 1	CO3 1
80208	6.83E-08	-7.17	4.19	Mg+2 1	CO3 1
80210	1.82E-07	-6.74	16.04	Ca+2 1	Mg+2 1
CO3 2					
80211	3.63E-18	-17.44	28.05	Ca+2 1	Mg+2 3
CO3 4					
80212	3.70E-06	-5.43	20.51	Mg+2 1	NH3 1
PO4 1	H +1 1				
80214	6.31E-07	-6.20	9.78	Mg+2 1	K +1 1
PO4 1					
80600	7.76E-01	-0.11	-3.56	Fe+3 1	H +1 -3
80602	4.60E-02	-1.34	25.32	Fe+3 1	PO4 1

```
80606   8.51E-09   -8.07   -18.51     Fe+3   2     Fe+2   1
H +1   -8
80096   4.05E-25  -24.39   -10.00     Co+2   1     CO3    1
80700   3.31E-10   -9.48   -13.02     Fe+2   1     H +1  -2
80702   1.02E-08   -7.99     9.76     CO3    1     Fe+2   1
80704   4.04E-16  -15.39    34.20     PO4    2     Fe+2   3
80701   8.80E-11  -10.06     1.98     SO4    1     Fe+2   1
80800   3.99E-08   -7.40   -15.32     Mn+2   1     H +1  -2
80802   2.82E-05   -4.55     8.82     Mn+2   1     CO3    1
80900   3.60E-04   -3.44    -8.80     Cu+2   1     H +1  -2
80904   5.70E-09   -8.24    35.90     Cu+2   3     PO4    2
80906   1.65E-07   -6.78     9.15     Cu+2   1     CO3    1
80908   9.63E-07   -6.02     4.56     Cu+2   2     CO3    1
H +1   -2
80910   1.95E-11  -10.71    15.80     Cu+2   3     CO3    2
H +1   -2
80912   1.18E-07   -6.93    14.76     Cu+2   1     BOH4   2
81200   4.73E-05   -4.32    33.50     Zn+2   3     PO4    2
81202   3.11E-04   -3.51    10.32     Zn+2   1     CO3    1
81204   7.30E-06   -5.14   -12.60     Zn+2   1     H +1  -2
83302   3.37E-08   -7.47     6.61     Cl     1     Cu+1   1
83304   5.33E-19  -18.27   -13.40     Cu+1   1     H +1  -1
84000   2.61E-23  -22.58     4.89     Ca+2   2     SiO4   1
84002   1.65E-21  -20.78     6.69     Ca+2   2     SiO4   1
84004   2.01E-02   -1.70    65.33     Ca+2   1     SiO4   2
Al+3   2
84006   2.01E-12  -11.70    15.64     Mg+2   2     SiO4   1
84008   3.09E-02   -1.51    33.14     Na+1   1     SiO4   1
Al+3   1
84010   1.22E-03   -2.91    31.34     K +1   1     SiO4   1
Al+3   1
84012   4.21E-16  -15.38    24.75     SiO4   1     Fe+2   2
84014   1.20E-01   -0.92    31.36     Zn+2   2     SiO4   1
84016   4.96E-12  -11.30    20.06     Mn+2   2     SiO4   1
84018   5.50E-02   -1.26   -10.02     Al+3   1     H +1  -3
84020   7.76E-01   -0.11    -8.87     Al+3   1     H +1  -3
80098   4.03E-20  -19.39    -4.98     Ni+2   1     CO3    1
```

84024	0.00E+00	-51.85	-22.64	SO4	3	Al+3	2
84026	3.03E-06	-5.52	-4.84	K +1	1	SO4	2
Al+3	3	H +1	-6				
84028	4.19E-04	-3.38	17.97	Al+3	1	PO4	1
84030	1.12E-03	-2.95	11.51	Cd+2	1	CO3	1
84032	6.50E-10	-9.19	-0.44	Cd+2	1	SO4	1
84034	3.72E-04	-3.43	36.30	Cd+2	3	PO4	2
84036	1.67E-03	-2.78	7.88	Ca+2	1	MoO4	1
84038	3.56E-11	-10.45	0.14	Mg+2	1	MoO4	1
84040	6.81E-10	-9.17	6.00	Cu+2	1	MoO4	1
84042	1.73E-10	-9.76	7.22	MoO4	1	Fe+2	1
84044	1.12E-09	-8.95	3.65	Mn+2	1	MoO4	1
84046	2.51E-09	-8.60	4.46	Zn+2	1	MoO4	1

PERCENTAGE DISTRIBUTION OF COMPONENTS

BZA

99.2	PERCENT BOUND IN SPECIES #	164	BZA	1

Ca+2

29.4	PERCENT BOUND IN SPECIES #	1	Ca+2	1
5.3	PERCENT BOUND IN SPECIES #	70000	Ca+2	1

SO4 1

64.5	PERCENT BOUND IN SPECIES #	80102	Ca+2	5

PO4 3 H +1 -1

Mg+2

85.9	PERCENT BOUND IN SPECIES #	2	Mg+2	1
12.8	PERCENT BOUND IN SPECIES #	70054	Mg+2	1

SO4 1

K +1

```
          98.7      PERCENT BOUND IN SPECIES #     4    K +1    1

Na+1

          99.1      PERCENT BOUND IN SPECIES #     5    Na+1    1

Fe+3

           2.8      PERCENT BOUND IN SPECIES #70200    Fe+3    1
H +1   -3

          97.1      PERCENT BOUND IN SPECIES #80608    Fe+3    2
Fe+2    1     H +1   -8

SUCA

          87.8      PERCENT BOUND IN SPECIES #  172    SUCA    1
           6.4      PERCENT BOUND IN SPECIES #90288    SUCA    1
H +1    1
           2.5      PERCENT BOUND IN SPECIES #90294    Mg+2    1
SUCA    1
           2.1      PERCENT BOUND IN SPECIES #90298    Ca+2    1
SUCA    1

Mn+2

          83.3      PERCENT BOUND IN SPECIES #     8    Mn+2    1
          13.3      PERCENT BOUND IN SPECIES #70272    Mn+2    1
SO4     1

Cu+2

           2.3      PERCENT BOUND IN SPECIES #     9    Cu+2    1
```

```
          4.2     PERCENT BOUND IN SPECIES #70334    Cu+2    1
BOH4    1
          3.3     PERCENT BOUND IN SPECIES #90116    Cu+2    1
DHBZ    1
          2.8     PERCENT BOUND IN SPECIES #90210    Cu+2    1
DEMA    1
         13.7     PERCENT BOUND IN SPECIES #90232    Cu+2    1
ACAC    1
         55.7     PERCENT BOUND IN SPECIES #90280    Cu+2    1
MALI    1
          5.0     PERCENT BOUND IN SPECIES #90364    Cu+2    1
HBQN    1
          2.1     PERCENT BOUND IN SPECIES #90518    Cu+2    1
CAFF    1
          8.4     PERCENT BOUND IN SPECIES #90522    Cu+2    1
CAFF    1    H +1   -1

Cd+2
         67.3     PERCENT BOUND IN SPECIES #   11    Cd+2    1
         17.1     PERCENT BOUND IN SPECIES #60018    Cd+2    1
SO4     1
          7.2     PERCENT BOUND IN SPECIES #60026    Cd+2    1
Cl      1
          4.7     PERCENT BOUND IN SPECIES #60058    Cd+2    1
PO4     1    H +1    1

Zn+2
         58.1     PERCENT BOUND IN SPECIES #   12    Zn+2    1
```

```
          12.3      PERCENT BOUND IN SPECIES #71214    Zn+2    1
SO4     1
          25.4      PERCENT BOUND IN SPECIES #90366    Zn+2    1
HBQN    1

Ni+2
          75.1      PERCENT BOUND IN SPECIES #   13    Ni+2    1
          14.5      PERCENT BOUND IN SPECIES #60020    Ni+2    1
SO4     1
           2.2      PERCENT BOUND IN SPECIES #60128    Ni+2    1
ACAC    1
           4.8      PERCENT BOUND IN SPECIES #60236    Ni+2    1
MALI    1

Co+2
          78.9      PERCENT BOUND IN SPECIES #   16    Co+2    1
          15.2      PERCENT BOUND IN SPECIES #60022    Co+2    1
SO4     1
           1.0      PERCENT BOUND IN SPECIES #60066    Co+2    1
PO4     1    H +1   1
           2.5      PERCENT BOUND IN SPECIES #60240    Co+2    1
MALI    1

PHEN
         100.0      PERCENT BOUND IN SPECIES #90340    PHEN    1
H +1    1

MALI
```

```
          77.4     PERCENT BOUND IN SPECIES #  171   MALI    1
           1.8     PERCENT BOUND IN SPECIES #90258   MALI    1
H +1    1

           7.0     PERCENT BOUND IN SPECIES #90266   Mg+2    1
MALI    1

           9.4     PERCENT BOUND IN SPECIES #90270   Ca+2    1
MALI    1

           2.3     PERCENT BOUND IN SPECIES #90280   Cu+2    1
MALI    1


HBQN
          89.0     PERCENT BOUND IN SPECIES #  166   HBQN    1
           4.4     PERCENT BOUND IN SPECIES #90358   Mg+2    1
HBQN    1

           1.5     PERCENT BOUND IN SPECIES #90360   Ca+2    1
HBQN    1

           4.7     PERCENT BOUND IN SPECIES #90366   Zn+2    1
HBQN    1


PROP
          97.3     PERCENT BOUND IN SPECIES #  174   PROP    1
           1.9     PERCENT BOUND IN SPECIES #90344   PROP    1
H +1    1


CAFF
          98.5     PERCENT BOUND IN SPECIES #90500   CAFF    1
H +1    1
```

```
SO4
          88.5      PERCENT BOUND IN SPECIES #  102    SO4     1
           4.4      PERCENT BOUND IN SPECIES #70000    Ca+2    1
SO4     1
           4.3      PERCENT BOUND IN SPECIES #70054    Mg+2    1
SO4     1
           1.6      PERCENT BOUND IN SPECIES #70114    K +1    1
SO4     1

Cl
          97.5      PERCENT BOUND IN SPECIES #  103    Cl      1
           2.2      PERCENT BOUND IN SPECIES #78700    Cl      1
NH3     1    H +1   1

NH3
          93.6      PERCENT BOUND IN SPECIES #78656    NH3     1
H +1    1
           4.4      PERCENT BOUND IN SPECIES #78700    Cl      1
NH3     1    H +1   1
           1.8      PERCENT BOUND IN SPECIES #78702    SO4     1
NH3     1    H +1   1

DMBA
          97.2      PERCENT BOUND IN SPECIES #  173    DMBA    1
           1.6      PERCENT BOUND IN SPECIES #90320    Ca+2    1
DMBA    1

SiO4
```

```
          99.9      PERCENT BOUND IN SPECIES #50014    SiO4    1
H +1    4

BOH4
          99.7      PERCENT BOUND IN SPECIES #78636    BOH4    1
H +1    1

MoO4
          99.8      PERCENT BOUND IN SPECIES #  152    MoO4    1

NO3
          99.5      PERCENT BOUND IN SPECIES #  157    NO3     1

DHBZ
          99.6      PERCENT BOUND IN SPECIES #90102    DHBZ    1
H +1    2

SAL
          99.8      PERCENT BOUND IN SPECIES #90138    SAL     1
H +1    1

HMPA
          97.2      PERCENT BOUND IN SPECIES #  168    HMPA    1
           1.3      PERCENT BOUND IN SPECIES #90122    Ca+2    1
HMPA    1
           1.2      PERCENT BOUND IN SPECIES #90124    Mg+2    1
HMPA    1
```

```
ACPH
        100.0     PERCENT BOUND IN SPECIES #90172   ACPH   1
H +1   1

HBA
         98.5     PERCENT BOUND IN SPECIES #  169   HBA    1

DEMA
         17.4     PERCENT BOUND IN SPECIES #  170   DEMA   1
         79.5     PERCENT BOUND IN SPECIES #90194   DEMA   1
H +1   1

ACAC
         97.0     PERCENT BOUND IN SPECIES #90222   ACAC   1
H +1   1
          1.0     PERCENT BOUND IN SPECIES #90224   Mg+2   1
ACAC   1
          1.1     PERCENT BOUND IN SPECIES #90232   Cu+2   1
ACAC   1

PHTH
         88.5     PERCENT BOUND IN SPECIES #  132   PHTH   1
          1.3     PERCENT BOUND IN SPECIES #60148   K +1   1
PHTH   1
          4.0     PERCENT BOUND IN SPECIES #90238   PHTH   1
H +1   1
          5.4     PERCENT BOUND IN SPECIES #90244   Ca+2   1
PHTH   1
```

```
Al+3
          2.7     PERCENT BOUND IN SPECIES #50002   Al+3   1
H +1  -2
         21.1     PERCENT BOUND IN SPECIES #50004   Al+3   1
H +1  -3
         75.0     PERCENT BOUND IN SPECIES #84022   Al+3   1
H +1  -3

BQA
        100.0     PERCENT BOUND IN SPECIES #  162   BQA    1

Mn+3
        100.0     PERCENT BOUND IN SPECIES #77402   Mn+3   1
H +1  -1

Cu+1
         95.8     PERCENT BOUND IN SPECIES #   33   Cu+1   1
          4.2     PERCENT BOUND IN SPECIES #77300   NH3    2
Cu+1   1

Co+3
        100.0     PERCENT BOUND IN SPECIES #   17   Co+3   1

E-
        100.0     PERCENT BOUND IN SPECIES #   99   E-     1

CO3
```

```
          1.1     PERCENT BOUND IN SPECIES #70078   Mg+2    1
CO3     1    H +1   1

         64.0     PERCENT BOUND IN SPECIES #78600   CO3     1
H +1    1

         34.4     PERCENT BOUND IN SPECIES #78602   CO3     1
H +1    2


PO4

          2.2     PERCENT BOUND IN SPECIES #78612   PO4     1
H +1    2

         96.8     PERCENT BOUND IN SPECIES #80102   Ca+2    5
PO4     3    H +1   -1


Fe+2

        100.0     PERCENT BOUND IN SPECIES #80608   Fe+3    2
Fe+2    1    H +1   -8


H +1

         92.5     PERCENT BOUND IN SPECIES #50014   SiO4    1
H +1    4

          6.2     PERCENT BOUND IN SPECIES #78656   NH3     1
H +1    1
```

APPENDIX E

USE OF SPECIFIED CAFFEIC ACID AND ELECTRON CONCENTRATIONS TO MODEL THE EFFECTS OF THE $Caff^{2-}$ / BQA^{-} COUPLE (See chapter 5.4.4).

INPUT

IONIC STRENGTH = 2.00E-02

ID	X	LOGX	T	COMPONENTS
50	3.16E-07	-6.50	0.00E+00	H +1
1	1.00E-03	-3.00	2.50E-03	Ca+2
2	1.00E-03	-3.00	1.00E-03	Mg+2
4	1.00E-03	-3.00	5.00E-03	K +1
5	1.00E-05	-5.00	2.00E-03	Na+1
6	1.00E-05	-5.00	2.00E-05	Fe+3
7	1.00E-09	-9.00	0.00E+00	Fe+2
8	1.00E-05	-5.00	1.00E-05	Mn+2
9	1.00E-06	-6.00	1.00E-06	Cu+2
11	1.00E-06	-6.00	1.00E-06	Cd+2
12	1.00E-06	-6.00	5.00E-06	Zn+2
13	1.00E-06	-6.00	1.00E-06	Ni+2
16	1.00E-07	-7.00	1.00E-06	Co+2
17	1.00E-09	-9.00	0.00E+00	Co+3
20	1.00E-07	-7.00	1.50E-06	Al+3
33	1.00E-09	-9.00	0.00E+00	Cu+1
34	1.00E-09	-9.00	0.00E+00	Mn+3
99	1.00E-09	-9.00	1.00E-05	E-
101	1.00E-08	-8.00	0.00E+00	CO3
102	1.00E-03	-3.00	3.00E-03	SO4
103	1.00E-03	-3.00	2.00E-03	Cl
107	1.00E-03	-3.00	1.00E-03	NH3
109	1.00E-03	-3.00	1.00E-03	PO4
112	1.00E-04	-4.00	3.50E-03	SiO4
148	1.00E-06	-6.00	5.00E-05	BOH4
152	1.00E-08	-8.00	3.00E-08	MoO4

157	1.00E-03	-3.00	6.00E-03	NO3
167	1.00E-05	-5.00	1.90E-05	DHBZ
119	1.00E-05	-5.00	3.10E-05	SAL
168	1.00E-05	-5.00	4.90E-06	HMPA
163	1.00E-05	-5.00	1.70E-05	ACPH
169	1.00E-05	-5.00	7.00E-05	HBA
170	1.00E-05	-5.00	4.20E-05	DEMA
116	1.00E-05	-5.00	1.30E-05	ACAC
132	1.00E-05	-5.00	8.00E-06	PHTH
171	1.00E-05	-5.00	2.40E-05	MALI
172	1.00E-05	-5.00	3.20E-05	SUCA
173	1.00E-05	-5.00	2.60E-05	DMBA
164	1.00E-05	-5.00	7.30E-05	BZA
165	1.00E-05	-5.00	1.20E-04	PHEN
174	1.00E-05	-5.00	9.20E-05	PROP
166	1.00E-05	-5.00	2.70E-05	HBQN
161	1.00E-06	-6.00	9.50E-05	CAFF

OUTPUT

ID	C	LOGC	LOGK	SPECIES:	TYPE I - COMPONENTS
161	4.28E-07	-6.37	0.00	CAFF	1
1	7.35E-04	-3.13	0.00	Ca+2	1
2	8.59E-04	-3.07	0.00	Mg+2	1
4	4.93E-03	-2.31	0.00	K +1	1
5	1.98E-03	-2.70	0.00	Na+1	1
6	5.56E-17	-16.25	0.00	Fe+3	1
7	8.89E-10	-9.05	0.00	Fe+2	1
8	8.33E-06	-5.08	0.00	Mn+2	1
9	2.28E-08	-7.64	0.00	Cu+2	1
11	6.73E-07	-6.17	0.00	Cd+2	1
12	2.91E-06	-5.54	0.00	Zn+2	1
13	7.51E-07	-6.12	0.00	Ni+2	1
16	7.89E-07	-6.10	0.00	Co+2	1
17	6.22E-32	-31.21	0.00	Co+3	1
20	1.82E-11	-10.74	0.00	Al+3	1
33	1.74E-11	-10.76	0.00	Cu+1	1

34	4.87E-26	-25.31	0.00	Mn+3	1
99	3.41E-06	-5.47	0.00	E-	1
101	5.13E-09	-8.29	0.00	CO3	1
102	2.65E-03	-2.58	0.00	SO4	1
103	1.95E-03	-2.71	0.00	Cl	1
107	1.70E-06	-5.77	0.00	NH3	1
109	2.47E-11	-10.61	0.00	PO4	1
112	6.20E-22	-21.21	0.00	SiO4	1
148	9.49E-08	-7.02	0.00	BOH4	1
152	2.99E-08	-7.52	0.00	MoO4	1
157	5.97E-03	-2.22	0.00	NO3	1
167	8.65E-15	-14.06	0.00	DHBZ	1
119	3.39E-12	-11.47	0.00	SAL	1
168	4.76E-06	-5.32	0.00	HMPA	1
163	5.63E-09	-8.25	0.00	ACPH	1
169	6.89E-05	-4.16	0.00	HBA	1
170	7.30E-06	-5.14	0.00	DEMA	1
116	5.25E-08	-7.28	0.00	ACAC	1
132	7.08E-06	-5.15	0.00	PHTH	1
171	1.86E-05	-4.73	0.00	MALI	1
172	2.81E-05	-4.55	0.00	SUCA	1
173	2.53E-05	-4.60	0.00	DMBA	1
164	7.24E-05	-4.14	0.00	BZA	1
165	5.00E-08	-7.30	0.00	PHEN	1
174	8.96E-05	-4.05	0.00	PROP	1
166	2.40E-05	-4.62	0.00	HBQN	1

ID	C	LOGC	LOGK	SPECIES:	TYPE II - COMPLEXES	
90556	5.57E-14	-13.25	-1.18	Co+2	2	CAFF 1 H +1 -1
50000	3.16E-10	-9.50	-5.26	Al+3	1	H +1 -1
50002	3.98E-08	-7.40	-9.66	Al+3	1	H +1 -2
50004	3.16E-07	-6.50	-15.26	Al+3	1	H +1 -3
50006	6.75E-17	-16.17	-7.69	Al+3	2	H +1 -2
50008	8.19E-16	-15.09	12.62	SiO4	1	H +1 1
50010	8.38E-13	-12.08	22.13	SiO4	1	H +1 2

50012	2.84E-06	-5.55	35.16	SiO4	1	H +1	3
50014	3.50E-03	-2.46	44.75	SiO4	1	H +1	4
50016	9.73E-19	-18.01	-0.60	NO3	3	Al+3	1
50018	2.91E-15	-14.54	5.28	SO4	1	Al+3	1
H +1	1						
50020	1.46E-11	-10.84	2.48	SO4	1	Al+3	1
50022	1.12E-15	-14.95	0.94	SO4	2	Al+3	1
50024	1.30E-33	-32.89	-3.68	SO4	3	Al+3	2
50026	3.23E-21	-20.49	3.85	Ca+2	1	SiO4	1
50028	6.92E-18	-17.16	13.68	Ca+2	1	SiO4	1
H +1	1						
50030	4.55E-20	-19.34	4.93	Mg+2	1	SiO4	1
50032	1.44E-17	-16.84	13.93	Mg+2	1	SiO4	1
H +1	1						
50034	3.23E-22	-21.49	22.47	Fe+3	1	SiO4	1
H +1	1						
60000	1.09E-10	-9.96	1.03	Na+1	1	CO3	1
60002	1.69E-08	-7.77	9.72	Na+1	1	CO3	1
H +1	1						
60004	1.73E-11	-10.76	3.70	Cd+2	1	CO3	1
60006	6.73E-17	-16.17	6.58	Cd+2	1	CO3	2
60008	1.77E-09	-8.75	12.21	Cd+2	1	CO3	1
H +1	1						
60010	4.74E-11	-10.32	4.09	Ni+2	1	CO3	1
60012	3.36E-09	-8.47	12.44	Ni+2	1	CO3	1
H +1	1						
60014	1.98E-11	-10.70	3.69	Co+2	1	CO3	1
60016	2.22E-09	-8.65	12.24	Co+2	1	CO3	1
H +1	1						
60018	1.71E-07	-6.77	1.98	Cd+2	1	SO4	1
60020	1.45E-07	-6.84	1.86	Ni+2	1	SO4	1
60022	1.52E-07	-6.82	1.86	Co+2	1	SO4	1
60024	4.21E-06	-5.38	0.40	Mg+2	1	Cl	1
60026	7.22E-08	-7.14	1.74	Cd+2	1	Cl	1
60028	4.45E-10	-9.35	2.24	Cd+2	1	Cl	2
60029	5.47E-13	-12.26	2.04	Cd+2	1	Cl	3
60030	4.22E-12	-11.37	-2.54	Ni+2	1	Cl	1

60032	3.07E-09	-8.51	0.30	Co+2	1	Cl	1
60034	6.71E-10	-9.17	2.72	Ni+2	1	NH3	1
60036	1.69E-13	-12.77	4.89	Ni+2	1	NH3	2
60038	1.32E-17	-16.88	6.55	Ni+2	1	NH3	3
60040	2.96E-22	-21.53	7.67	Ni+2	1	NH3	4
60042	2.36E-27	-26.63	8.34	Ni+2	1	NH3	5
60044	3.74E-33	-32.43	8.31	Ni+2	1	NH3	6
60046	1.62E-10	-9.79	2.08	Co+2	1	NH3	1
60048	7.24E-15	-14.14	3.50	Co+2	1	NH3	2
60050	1.05E-19	-18.98	4.43	Co+2	1	NH3	3
60052	7.80E-25	-24.11	5.07	Co+2	1	NH3	4
60054	1.53E-30	-29.82	5.13	Co+2	1	NH3	5
60056	4.73E-37	-36.33	4.39	Co+2	1	NH3	6
60058	4.69E-08	-7.33	15.95	Cd+2	1	PO4	1
H +1	1						
60060	3.56E-11	-10.45	19.33	Cd+2	1	PO4	1
H +1	2						
60062	8.29E-09	-8.08	15.15	Ni+2	1	PO4	1
H +1	1						
60064	4.06E-09	-8.39	21.34	Ni+2	1	PO4	1
H +1	2						
60066	1.05E-08	-7.98	15.23	Co+2	1	PO4	1
H +1	1						
60068	7.32E-09	-8.14	0.26	Cd+2	1	NO3	1
60070	1.66E-11	-10.78	-0.16	Cd+2	1	NO3	2
60072	6.48E-09	-8.19	0.16	Ni+2	1	NO3	1
60074	6.72E-14	-13.17	-2.60	Ni+2	1	NO3	2
60076	4.30E-09	-8.37	-0.04	Co+2	1	NO3	1
60078	1.12E-13	-12.95	-2.40	Co+2	1	NO3	2
60092	1.34E-10	-9.87	-10.20	Cd+2	1	H +1	-1
60094	2.28E-14	-13.64	-20.47	Cd+2	1	H +1	-2
60096	5.22E-28	-27.28	-47.11	Cd+2	1	H +1	-4
60098	7.70E-16	-15.11	-9.27	Cd+2	2	H +1	-1
60100	5.53E-32	-31.26	-32.57	Cd+2	4	H +1	-4
60102	2.49E-10	-9.60	-9.98	Ni+2	1	H +1	-1

60104	4.96E-13	-12.30	-19.18	Ni+2	1	H +1	-2
60106	2.37E-17	-16.62	-30.00	Ni+2	1	H +1	-3
60108	4.69E-17	-16.33	-10.58	Ni+2	2	H +1	-1
60110	1.01E-26	-26.00	-27.50	Ni+2	4	H +1	-4
60112	4.24E-10	-9.37	-9.77	Co+2	1	H +1	-1
60114	9.49E-13	-12.02	-18.92	Co+2	1	H +1	-2
60116	7.89E-19	-18.10	-31.50	Co+2	1	H +1	-3
60118	6.87E-27	-26.16	-46.06	Co+2	1	H +1	-4
60120	1.64E-17	-16.79	-11.08	Co+2	2	H +1	-1
60122	1.99E-29	-28.70	-30.29	Co+2	4	H +1	-4
66124	1.38E-10	-9.86	3.59	Cd+2	1	ACAC	1
60126	3.63E-15	-14.44	6.29	Cd+2	1	ACAC	2
60128	2.22E-08	-7.65	5.75	Ni+2	1	ACAC	1
60130	3.44E-11	-10.46	10.22	Ni+2	1	ACAC	2
60132	6.00E-09	-8.22	5.16	Co+2	1	ACAC	1
60134	3.30E-12	-11.48	9.18	Co+2	1	ACAC	2
60136	2.39E-12	-11.62	6.02	Cd+2	1	SAL	1
60138	7.06E-09	-8.15	15.99	Cd+2	1	SAL	1
H +1	1						
60140	6.70E-11	-10.17	7.42	Ni+2	1	SAL	1
60142	1.19E-12	-11.92	12.17	Ni+2	1	SAL	1
H +1	1						
60144	4.15E-11	-10.38	7.19	Co+2	1	SAL	1
60146	6.28E-13	-12.20	11.87	Co+2	1	SAL	1
H +1	1						
60148	1.01E-07	-7.00	0.46	K +1	1	PHTH	1
60152	7.56E-10	-9.12	2.20	Cd+2	1	PHTH	1
60154	6.29E-14	-13.20	3.27	Cd+2	1	PHTH	2
60156	3.88E-13	-12.41	5.41	Cd+2	1	PHTH	1
H +1	1						
60158	1.86E-16	-15.73	7.24	Cd+2	1	PHTH	2
H +1	1						
60160	1.57E-09	-8.80	2.47	Ni+2	1	PHTH	1
60162	1.34E-12	-11.87	5.90	Ni+2	1	PHTH	1
H +1	1						
60164	4.44E-10	-9.35	1.90	Co+2	1	PHTH	1

60166	5.34E-12	-11.27	6.48	Co+2	1	PHTH	1
H +1	1						
60168	1.04E-10	-9.98	4.39	Ni+2	1	ACPH	1
60170	5.08E-16	-15.29	7.33	Ni+2	1	ACPH	2
60172	1.58E-10	-9.80	4.55	Co+2	1	ACPH	1
60174	7.72E-16	-15.11	7.49	Co+2	1	ACPH	2
60176	1.90E-09	-8.72	1.59	Cd+2	1	BZA	1
60178	2.81E-13	-12.55	1.90	Cd+2	1	BZA	2
60180	6.70E-10	-9.17	1.09	Ni+2	1	BZA	1
60182	4.14E-10	-9.38	0.86	Co+2	1	BZA	1
60184	1.79E-10	-9.75	20.57	Fe+3	1	DHBZ	1
60186	1.32E-09	-8.88	35.50	Fe+3	1	DHBZ	2
60188	8.44E-15	-14.07	44.37	Fe+3	1	DHBZ	3
60190	2.27E-12	-11.64	8.59	Cd+2	1	DHBZ	1
60192	1.30E-11	-10.89	9.30	Ni+2	1	DHBZ	1
60194	3.39E-20	-19.47	14.78	Ni+2	1	DHBZ	2
60196	6.52E-12	-11.19	8.98	Co+2	1	DHBZ	1
60198	1.42E-19	-18.85	15.38	Co+2	1	DHBZ	2
60200	8.64E-11	-10.06	1.43	Cd+2	1	HMPA	1
60202	4.31E-15	-14.37	2.45	Cd+2	1	HMPA	2
60204	4.39E-20	-19.36	2.78	Cd+2	1	HMPA	3
60206	2.59E-10	-9.59	1.86	Ni+2	1	HMPA	1
60208	2.05E-14	-13.69	3.08	Ni+2	1	HMPA	2
60210	2.51E-19	-18.60	3.49	Ni+2	1	HMPA	3
60212	1.64E-10	-9.78	1.64	Co+2	1	HMPA	1
60214	9.40E-15	-14.03	2.72	Co+2	1	HMPA	2
60216	8.15E-20	-19.09	2.98	Co+2	1	HMPA	3
60218	3.95E-10	-9.40	0.93	Cd+2	1	HBA	1
60220	2.78E-10	-9.56	0.73	Ni+2	1	HBA	1
60222	1.98E-10	-9.70	0.56	Co+2	1	HBA	1
60224	1.81E-07	-6.74	0.70	K +1	1	DEMA	1
60226	4.09E-09	-8.39	2.92	Cd+2	1	DEMA	1
60228	3.09E-09	-8.51	2.75	Ni+2	1	DEMA	1
60230	2.46E-09	-8.61	2.63	Co+2	1	DEMA	1
60232	6.72E-09	-8.17	2.73	MALI	1	Cd+2	1
60234	2.55E-11	-10.59	6.81	MALI	1	Cd+2	1
H +1	1						

60236	4.84E-08	-7.32	3.54	MALI	1	Ni+2	1
60238	8.81E-11	-10.06	7.30	MALI	1	Ni+2	1
H +1	1						
60240	2.49E-08	-7.60	3.23	MALI	1	Co+2	1
60242	5.97E-11	-10.22	7.11	MALI	1	Co+2	1
H +1	1						
60243	2.52E-07	-6.60	0.26	K +1	1	SUCA	1
60244	3.29E-09	-8.48	2.24	Cd+2	1	SUCA	1
60245	1.53E-09	-8.82	1.86	Ni+2	1	SUCA	1
60246	4.41E-17	-16.36	0.82	Ni+2	1	SUCA	1
H +1	1						
60248	1.54E-09	-8.81	1.84	Co+2	1	SUCA	1
60250	1.10E-09	-8.96	1.81	DMBA	1	Cd+2	1
60252	1.90E-09	-8.72	2.00	DMBA	1	Ni+2	1
60254	1.20E-09	-8.92	1.78	DMBA	1	Co+2	1
60256	1.38E-09	-8.86	1.36	Cd+2	1	PROP	1
60258	6.96E-13	-12.16	2.11	Cd+2	1	PROP	2
60260	6.00E-10	-9.22	0.95	Ni+2	1	PROP	1
60262	1.74E-13	-12.76	1.46	Ni+2	1	PROP	2
60264	5.49E-10	-9.26	0.89	Co+2	1	PROP	1
70000	1.32E-04	-3.88	1.83	Ca+2	1	SO4	1
70002	1.06E-06	-5.97	-0.13	Ca+2	1	Cl	1
70004	9.98E-09	-8.00	5.74	Ca+2	1	PO4	1
70006	4.67E-07	-6.33	13.91	Ca+2	1	PO4	1
H +1	1						
70008	9.10E-08	-7.04	19.70	Mg+2	1	PO4	1
H +1	2						
70010	7.79E-11	-10.11	27.24	Ca+2	1	PO4	2
H +1	2						
70012	2.90E-12	-11.54	32.31	Ca+2	1	PO4	2
H +1	3						
70014	7.91E-13	-12.10	28.38	Ca+2	2	PO4	2
H +1	2						
70020	3.52E-10	-9.45	-12.82	Ca+2	1	H +1	-1
70022	1.76E-09	-8.75	2.67	Ca+2	1	CO3	1

70024	8.44E-08	-7.07	10.85	Ca+2	1	CO3	1
H +1	1						
70026	6.42E-10	-9.19	-0.29	Ca+2	1	NH3	1
70028	1.73E-16	-15.76	-1.09	Ca+2	1	NH3	2
70030	2.95E-23	-22.53	-2.09	Ca+2	1	NH3	3
70032	1.27E-05	-4.90	0.46	Ca+2	1	NO3	1
70034	4.55E-08	-7.34	0.24	Ca+2	1	NO3	2
70054	1.28E-04	-3.89	1.75	Mg+2	1	SO4	1
70056	1.57E-08	-7.80	5.87	Mg+2	1	PO4	1
70058	1.73E-06	-5.76	14.41	Mg+2	1	PO4	1
H +1	1						
70060	3.44E-07	-6.46	20.21	Mg+2	1	PO4	1
H +1	2						
70062	1.02E-11	-10.99	32.79	Mg+2	1	PO4	2
H +1	3						
70064	8.50E-11	-10.07	27.21	Mg+2	1	PO4	2
H +1	2						
70066	4.11E-12	-11.39	28.96	Mg+2	2	PO4	2
H +1	2						
70072	7.84E-09	-8.11	-11.54	Mg+2	1	H +1	-1
70074	1.89E-26	-25.72	-39.46	Mg+2	4	H +1	-4
70076	1.16E-08	-7.94	3.42	Mg+2	1	CO3	1
70078	3.50E-07	-6.46	11.40	Mg+2	1	CO3	1
H +1	1						
70080	9.24E-09	-8.03	0.80	Mg+2	1	NH3	1
70082	1.34E-15	-14.87	-0.27	Mg+2	1	NH3	2
70084	6.00E-22	-21.22	-0.85	Mg+2	1	NH3	3
70086	1.29E-28	-27.89	-1.75	Mg+2	1	NH3	4
70112	4.93E-11	-10.31	-14.50	K +1	1	H +1	-1
70114	4.76E-05	-4.32	0.56	K +1	1	SO4	1
70116	2.61E-07	-6.58	12.83	K +1	1	PO4	1
H +1	1						
70118	1.27E-06	-5.90	-0.88	K +1	1	Cl	1
70120	1.58E-05	-4.80	-0.27	K +1	1	NO3	1
70124	1.52E-05	-4.82	0.46	Na+1	1	SO4	1
70126	4.52E-07	-6.34	1.51	Na+1	1	SO4	2

```
70132   1.35E-07   -6.87   12.94    Na+1   1    PO4    1
H +1    1
70134   1.93E-08   -7.72    2.01    Na+1   1    BOH4   1
70136   7.89E-11  -10.10  -13.90    Na+1   1    H +1  -1
70138   2.77E-06   -5.56   -0.63    Na+1   1    NO3    1
70140   3.09E-16  -15.51    3.32    Fe+3   1    SO4    1
70142   1.03E-17  -16.99    4.42    Fe+3   1    SO4    2
70144   1.43E-18  -17.84    1.12    Fe+3   1    Cl     1
70146   7.17E-21  -20.14    1.53    Fe+3   1    Cl     2
70148   1.06E-24  -23.97    0.41    Fe+3   1    Cl     3
70150   9.96E-13  -12.00   21.36    Fe+3   1    PO4    1
H +1    1
70152   5.11E-18  -17.29   22.57    Fe+3   1    PO4    1
Fe+2    0    H +1    2
70154   8.00E-22  -21.10   28.52    Fe+3   2    PO4    1
H +1    1
70168   2.59E-15  -14.59    8.69    Fe+3   1    BOH4   1
70170   3.24E-15  -14.49   15.81    Fe+3   1    BOH4   2
70172   2.87E-17  -16.54   20.78    Fe+3   1    BOH4   3
70174   1.71E-16  -15.77    8.01    Fe+3   1    MoO4   1
70176   6.09E-23  -22.22   16.61    Fe+3   1    MoO4   3
70178   6.54E-13  -12.18   -2.43    Fe+3   1    H +1  -1
70180   4.85E-10   -9.31   -6.06    Fe+3   1    H +1  -2
70200   2.37E-07   -6.62   -9.87    Fe+3   1    H +1  -3
70202   8.04E-13  -12.09  -21.84    Fe+3   1    H +1  -4
70204   3.90E-23  -22.41   -2.90    Fe+3   2    H +1  -2
70206   1.14E-29  -28.94   -6.18    Fe+3   3    H +1  -4
70208   1.45E-18  -17.84    0.64    Fe+3   1    NO3    1
70220   1.24E-10   -9.91    1.72    SO4    1    Fe+2   1
70222   1.24E-16  -15.91    2.22    SO4    1    Fe+2   1
H +1    1
70224   6.74E-13  -12.17   -9.62    Fe+2   1    H +1  -1
70226   1.69E-17  -16.77  -20.72    Fe+2   1    H +1  -2
70228   2.81E-22  -21.55  -32.00    Fe+2   1    H +1  -3
70230   6.14E-30  -29.21  -46.16    Fe+2   1    H +1  -4
```

70240	8.74E-12	-11.06	15.10	PO4	1	Fe+2	1
H +1	1						
70242	5.51E-12	-11.26	21.40	PO4	1	Fe+2	1
H +1	2						
70244	1.13E-15	-14.95	28.32	PO4	2	Fe+2	1
H +1	2						
70266	7.65E-08	-7.12	15.07	Mn+2	1	PO4	1
H +1	1						
70268	5.17E-08	-7.29	21.40	Mn+2	1	PO4	1
H +1	2						
70270	5.97E-12	-11.22	28.07	Mn+2	1	PO4	2
H +1	2						
70272	1.33E-06	-5.87	1.78	Mn+2	1	SO4	1
70274	5.02E-10	-9.30	-10.72	Mn+2	1	H +1	-1
70276	3.10E-15	-14.51	-22.43	Mn+2	1	H +1	-2
70278	1.66E-20	-19.78	-34.20	Mn+2	1	H +1	-3
70280	7.25E-28	-27.14	-48.06	Mn+2	1	H +1	-4
70282	7.27E-15	-14.14	-10.48	Mn+2	2	H +1	-1
70284	1.59E-15	-14.80	-24.14	Mn+2	2	H +1	-3
70286	6.04E-09	-8.22	11.65	Mn+2	1	CO3	1
H +1	1						
70294	1.03E-10	-9.99	0.86	Mn+2	1	NH3	1
70296	7.47E-16	-15.13	1.49	Mn+2	1	NH3	2
70298	2.32E-21	-20.64	1.75	Mn+2	1	NH3	3
70300	1.47E-27	-26.83	1.32	Mn+2	1	NH3	4
70302	4.54E-08	-7.34	-0.04	Mn+2	1	NO3	1
70304	5.16E-10	-9.29	0.24	Mn+2	1	NO3	2
70318	5.75E-10	-9.24	15.51	Cu+2	1	PO4	1
H +1	1						
70320	9.33E-12	-11.03	20.22	Cu+2	1	PO4	1
H +1	2						
70322	4.39E-17	-16.36	32.00	Cu+2	1	PO4	2
H +1	3						
70324	7.94E-19	-18.10	31.40	Cu+2	2	PO4	2
H +1	2						

70326	5.65E-14	-13.25	28.61	Cu+2	1	PO4	2
H +1	2						
70328	4.59E-09	-8.34	1.88	Cu+2	1	SO4	1
70330	3.06E-10	-9.51	3.28	Cu+2	1	SO4	2
70332	1.51E-13	-12.82	2.55	Cu+2	1	SO4	3
70334	4.22E-08	-7.38	7.29	Cu+2	1	BOH4	1
70336	1.08E-09	-8.97	12.72	Cu+2	1	BOH4	2
70338	5.50E-14	-13.26	15.45	Cu+2	1	BOH4	3
70340	1.09E-09	-8.96	-7.82	Cu+2	1	H +1	-1
70342	2.74E-10	-9.56	-14.92	Cu+2	1	H +1	-2
70344	1.89E-16	-15.72	-27.58	Cu+2	1	H +1	-3
70346	9.93E-22	-21.00	-39.36	Cu+2	1	H +1	-4
70348	4.95E-14	-13.31	-11.02	Cu+2	2	H +1	-2
70350	1.71E-19	-18.77	-21.84	Cu+2	3	H +1	-4
70352	5.60E-32	-31.25	-20.18	Cu+2	4	H +1	-3
70364	2.17E-10	-9.66	6.27	Cu+2	1	CO3	1
70366	1.34E-15	-14.87	9.35	Cu+2	1	CO3	2
70368	6.42E-11	-10.19	0.16	Cu+2	1	Cl	1
70370	4.45E-10	-9.35	4.06	Cu+2	1	NH3	1
70372	1.51E-12	-11.82	7.36	Cu+2	1	NH3	2
70374	1.42E-15	-14.85	10.10	Cu+2	1	NH3	3
70376	1.87E-19	-18.73	11.99	Cu+2	1	NH3	4
70378	8.79E-26	-25.06	11.43	Cu+2	1	NH3	5
70380	1.47E-10	-9.83	-2.92	Cu+2	1	NH3	1
H +1	-1						
70382	4.28E-20	-19.37	-0.92	Cu+2	1	NH3	3
H +1	-1						
70384	1.00E-22	-22.00	-15.82	Cu+2	1	NH3	2
H +1	-2						
70386	2.47E-10	-9.61	0.26	Cu+2	1	NO3	1
70388	9.32E-13	-12.03	0.06	Cu+2	1	NO3	2
70424	1.16E-08	-7.93	14.71	Zn+2	1	PO4	1
H +1	1						
70426	1.37E-09	-8.86	20.28	Zn+2	1	PO4	1
H +1	2						

```
71208    5.11E-14  -13.29    32.96     Zn+2   1    PO4    2
H +1   3
71210    4.81E-16  -15.32    29.97     Zn+2   2    PO4    2
H +1   2
71212    1.81E-12  -11.74    28.01     Zn+2   1    PO4    2
H +1   2
71214    6.13E-07   -6.21     1.90     Zn+2   1    SO4    1
71216    3.56E-08   -7.45     3.24     Zn+2   1    SO4    2
71218    8.04E-11  -10.09     3.17     Zn+2   1    SO4    3
71220    3.15E-13  -12.50     3.34     Zn+2   1    SO4    4
71222    6.97E-09   -8.16    -9.12     Zn+2   1    H +1  -1
71224    1.83E-08   -7.74   -15.20     Zn+2   1    H +1  -2
71226    3.66E-15  -14.44   -28.40     Zn+2   1    H +1  -3
71228    3.18E-21  -20.50   -40.96     Zn+2   1    H +1  -4
71230    3.52E-14  -13.45    -8.88     Zn+2   2    H +1  -1
71242    2.47E-10   -9.61     4.22     Zn+2   1    CO3    1
71243    2.11E-09   -8.68    11.65     Zn+2   1    CO3    1
H +1   1
71244    8.78E-09   -8.06     0.19     Zn+2   1    Cl     1
71246    5.29E-11  -10.28     0.68     Zn+2   1    Cl     2
71248    3.26E-13  -12.49     1.18     Zn+2   1    Cl     3
71250    1.33E-15  -14.88     1.50     Zn+2   1    Cl     4
71252    8.03E-10   -9.10     2.21     Zn+2   1    NH3    1
71254    2.67E-13  -12.57     4.50     Zn+2   1    NH3    2
71256    1.04E-16  -15.98     6.86     Zn+2   1    NH3    3
71258    1.90E-20  -19.72     8.89     Zn+2   1    NH3    4
71260    4.84E-10   -9.32    -4.51     Zn+2   1    NH3    1
H +1  -1
71262    2.99E-14  -13.52    -2.95     Zn+2   1    NH3    2
H +1  -1
71264    7.89E-19  -18.10    -1.76     Zn+2   1    NH3    3
H +1  -1
71266    1.64E-13  -12.79   -14.48     Zn+2   1    NH3    1
H +1  -2
71268    1.09E-18  -17.96   -13.89     Zn+2   1    NH3    2
H +1  -2
```

71270	1.88E-19	-18.73	-26.92	Zn+2	1	NH3	1
H +1	-3						
71300	2.51E-08	-7.60	0.16	Zn+2	1	NO3	1
71302	1.97E-10	-9.70	0.28	Zn+2	1	NO3	2
77300	7.64E-13	-12.12	10.18	NH3	2	Cu+1	1
77400	6.79E-26	-25.17	2.72	SO4	1	Mn+3	1
77402	5.72E-19	-18.24	0.57	Mn+3	1	H +1	-1
78600	1.99E-05	-4.70	10.09	CO3	1	H +1	1
78602	1.07E-05	-4.97	16.32	CO3	1	H +1	2
78604	4.72E-08	-7.33	1.75	SO4	1	H +1	1
78606	4.62E-22	-21.34	-5.76	SO4	1	H +1	2
78610	7.45E-06	-5.13	11.98	PO4	1	H +1	1
78612	2.15E-05	-4.67	18.94	PO4	1	H +1	2
78614	7.12E-10	-9.15	20.96	PO4	1	H +1	3
78616	2.26E-11	-10.65	30.07	PO4	2	H +1	3
78618	2.85E-10	-9.54	37.67	PO4	2	H +1	4
78620	5.44E-14	-13.26	40.45	PO4	2	H +1	5
78634	4.17E-08	-7.38	-13.88	H +1	-1		
78636	4.98E-05	-4.30	9.22	BOH4	1	H +1	1
78638	2.36E-18	-17.63	9.94	BOH4	3	H +1	1
78640	5.16E-15	-14.29	19.78	BOH4	3	H +1	2
78642	1.70E-21	-20.77	20.32	BOH4	4	H +1	2
78644	1.02E-18	-17.99	29.60	BOH4	4	H +1	3
78646	2.13E-23	-22.67	38.44	BOH4	5	H +1	4
78648	5.98E-11	-10.22	3.80	MoO4	1	H +1	1
78650	1.40E-13	-12.85	7.67	MoO4	1	H +1	2
78652	3.21E-19	-18.49	8.53	MoO4	1	H +1	3
78654	2.95E-16	-15.53	-6.32	Cl	1	H +1	1
78656	9.36E-04	-3.03	9.24	NH3	1	H +1	1
78700	4.38E-05	-4.36	10.62	Cl	1	NH3	1
H +1	1						
78702	1.84E-05	-4.73	10.11	SO4	1	NH3	1
H +1	1						
78708	5.44E-11	-10.26	-1.54	NO3	1	H +1	1

78710	2.35E-10	-9.63	8.39	ACAC	1	Al+3	1
78712	7.78E-10	-9.11	16.19	ACAC	2	Al+3	1
78714	2.52E-11	-10.60	21.98	ACAC	3	Al+3	1
78716	1.45E-08	-7.84	14.37	SAL	1	Al+3	1
78718	7.25E-13	-12.14	3.75	PHTH	1	Al+3	1
78720	2.69E-09	-8.57	7.32	PHTH	1	Al+3	1
78722	3.16E-11	-10.50	-2.12	BZA	1	Al+3	1
H +1	-1						
90100	3.14E-08	-7.50	13.06	DHBZ	1	H +1	1
90102	1.89E-05	-4.72	22.34	DHBZ	1	H +1	2
90104	7.79E-12	-11.11	6.02	Mg+2	1	DHBZ	1
90106	2.65E-13	-12.58	4.62	Ca+2	1	DHBZ	1
90108	7.55E-12	-11.12	8.02	Mn+2	1	DHBZ	1
90110	3.78E-10	-9.42	16.22	Mn+2	1	DHBZ	1
H +1	1						
90112	4.04E-15	-14.39	8.72	DHBZ	1	Fe+2	1
90114	2.02E-13	-12.69	16.92	DHBZ	1	Fe+2	1
H +1	1						
90116	3.27E-08	-7.49	14.22	Cu+2	1	DHBZ	1
90118	4.17E-10	-9.38	10.22	Zn+2	1	DHBZ	1
90120	1.14E-08	-7.94	3.88	HMPA	1	H +1	1
90122	6.37E-08	-7.20	1.26	Ca+2	1	HMPA	1
90124	5.92E-08	-7.23	1.16	Mg+2	1	HMPA	1
90126	5.74E-10	-9.24	1.16	Mn+2	1	HMPA	1
90128	1.94E-13	-12.71	1.66	HMPA	1	Fe+2	1
90130	9.89E-11	-10.00	2.96	Cu+2	1	HMPA	1
90132	1.26E-09	-8.90	1.96	Zn+2	1	HMPA	1
90134	3.66E-19	-18.44	3.14	Fe+3	1	HMPA	1
90136	1.11E-13	-12.96	2.12	Fe+3	1	HMPA	1
H +1	-1						
90138	3.09E-05	-4.51	13.46	SAL	1	H +1	1
90140	7.42E-09	-8.13	16.34	SAL	1	H +1	2
90141	1.22E-09	-8.92	5.62	Mg+2	1	SAL	1
90142	1.31E-10	-9.88	4.72	Ca+2	1	SAL	1
90144	3.29E-08	-7.48	13.62	Ca+2	1	SAL	1
H +1	1						
90146	4.69E-11	-10.33	6.22	Mn+2	1	SAL	1

90148	2.51E-14	-13.60	6.92	SAL	1	Fe+2	1
90150	6.42E-09	-8.19	10.92	Cu+2	1	SAL	1
90152	1.64E-10	-9.79	7.22	Zn+2	1	SAL	1
90154	9.04E-12	-11.04	16.68	Fe+3	1	SAL	1
90156	4.74E-17	-16.32	17.90	Fe+3	1	SAL	1
H +1	1						
90158	1.03E-16	-15.99	10.02	Mg+2	1	SAL	2
90160	8.85E-19	-18.05	8.02	Ca+2	1	SAL	2
90162	1.59E-18	-17.80	10.22	Mn+2	1	SAL	2
90164	4.26E-21	-20.37	11.62	SAL	2	Fe+2	1
90166	1.40E-09	-8.85	30.34	Fe+3	1	SAL	2
90168	1.73E-12	-11.76	18.82	Cu+2	1	SAL	2
90170	1.39E-23	-22.86	5.62	Zn+2	1	SAL	2
90172	1.70E-05	-4.77	9.98	ACPH	1	H +1	1
90174	7.53E-11	-10.12	1.26	Ca+2	1	ACPH	1
90176	1.35E-11	-10.87	2.46	Mn+2	1	ACPH	1
90178	9.28E-10	-9.03	6.86	Cu+2	1	ACPH	1
90180	2.98E-11	-10.53	3.26	Zn+2	1	ACPH	1
90182	1.09E-14	-13.96	10.54	Fe+3	1	ACPH	1
90184	5.23E-07	-6.28	4.38	HBA	1	H +1	1
90186	3.41E-07	-6.47	0.76	Mg+2	1	HBA	1
90188	1.84E-07	-6.73	0.56	Ca+2	1	HBA	1
90190	2.86E-10	-9.54	2.26	Cu+2	1	HBA	1
90192	3.65E-09	-8.44	1.26	Zn+2	1	HBA	1
90194	3.34E-05	-4.48	7.16	DEMA	1	H +1	1
90196	1.27E-09	-8.90	9.24	DEMA	1	H +1	2
90198	5.25E-08	-7.28	0.56	Na+1	1	DEMA	1
90200	4.15E-07	-6.38	1.82	Mg+2	1	DEMA	1
90202	1.04E-07	-6.98	7.72	Mg+2	1	DEMA	1
H +1	1						
90204	3.55E-07	-6.45	1.82	Ca+2	1	DEMA	1
90206	1.41E-07	-6.85	7.92	Ca+2	1	DEMA	1
H +1	1						
90208	8.03E-09	-8.10	2.12	Mn+2	1	DEMA	1
90210	2.76E-08	-7.56	5.22	Cu+2	1	DEMA	1
90212	8.73E-12	-11.06	8.22	Cu+2	1	DEMA	1
H +1	1						

90214	1.11E-08	-7.95	2.72	Zn+2	1	DEMA	1
90216	1.40E-09	-8.85	8.32	Zn+2	1	DEMA	1
H +1	1						
90218	4.89E-13	-12.31	9.08	Fe+3	1	DEMA	1
90220	1.62E-18	-17.79	10.10	Fe+3	1	DEMA	1
H +1	1						
90222	1.26E-05	-4.90	8.88	ACAC	1	H +1	1
90224	1.30E-07	-6.89	3.46	Mg+2	1	ACAC	1
90226	2.80E-08	-7.55	2.86	Ca+2	1	ACAC	1
90228	3.99E-09	-8.40	3.96	Mn+2	1	ACAC	1
90230	3.38E-12	-11.47	4.86	ACAC	1	Fe+2	1
90232	1.37E-07	-6.86	8.06	Cu+2	1	ACAC	1
90234	1.11E-08	-7.96	4.86	Zn+2	1	ACAC	1
90236	4.04E-14	-13.39	10.14	Fe+3	1	ACAC	1
90238	3.24E-07	-6.49	5.16	PHTH	1	H +1	1
90240	7.77E-11	-10.11	8.04	PHTH	1	H +1	2
90242	4.05E-08	-7.39	0.46	Na+1	1	PHTH	1
90244	4.33E-07	-6.36	1.92	Ca+2	1	PHTH	1
90246	9.80E-09	-8.01	2.22	Mn+2	1	PHTH	1
90248	5.34E-10	-9.27	3.52	Cu+2	1	PHTH	1
90250	5.42E-09	-8.27	2.42	Zn+2	1	PHTH	1
90252	2.38E-14	-13.62	7.78	Fe+3	1	PHTH	1
90254	7.55E-14	-13.12	4.82	Cu+2	1	PHTH	2
90256	7.65E-13	-12.12	3.72	Zn+2	1	PHTH	2
90258	4.26E-07	-6.37	4.86	MALI	1	H +1	1
90260	3.23E-10	-9.49	8.24	MALI	1	H +1	2
90262	1.06E-07	-6.97	0.46	Na+1	1	MALI	1
90264	2.10E-07	-6.68	0.36	K +1	1	MALI	1
90266	1.67E-06	-5.78	2.02	Mg+2	1	MALI	1
90268	5.29E-09	-8.28	6.02	Mg+2	1	MALI	1
H +1	1						
90270	2.27E-06	-5.64	2.22	Ca+2	1	MALI	1
90272	5.69E-09	-8.24	6.12	Ca+2	1	MALI	1
H +1	1						
90274	6.45E-08	-7.19	2.62	MALI	1	Mn+2	1
90276	1.37E-11	-10.86	2.92	MALI	1	Fe+2	1
90278	2.22E-09	-8.65	3.72	MALI	1	Cu+2	1

90280	5.58E-07	-6.25	6.12	MALI	1	Cu+2	1
90282	3.57E-08	-7.45	2.82	MALI	1	Zn+2	1
90284	7.12E-11	-10.15	6.62	MALI	1	Zn+2	1
H +1	1						
90286	6.23E-14	-13.21	7.78	Fe+3	1	MALI	1
90288	2.04E-06	-5.69	5.36	SUCA	1	H +1	1
90290	7.75E-09	-8.11	9.44	SUCA	1	H +1	2
90292	6.40E-08	-7.19	0.06	Na+1	1	SUCA	1
90294	8.01E-07	-6.10	1.52	Mg+2	1	SUCA	1
90296	8.01E-09	-8.10	6.02	Mg+2	1	SUCA	1
H +1	1						
90298	6.85E-07	-6.16	1.52	Ca+2	1	SUCA	1
90300	6.85E-09	-8.16	6.02	Ca+2	1	SUCA	1
H +1	1						
90302	1.55E-08	-7.81	1.82	Mn+2	1	SUCA	1
90304	7.76E-14	-13.11	3.02	Mn+2	1	SUCA	1
H +1	1						
90306	1.31E-12	-11.88	1.72	SUCA	1	Fe+2	1
90308	4.23E-10	-9.37	2.82	Cu+2	1	SUCA	1
90310	8.56E-09	-8.07	2.02	Zn+2	1	SUCA	1
90312	6.80E-11	-10.17	6.42	Zn+2	1	SUCA	1
H +1	1						
90314	5.95E-14	-13.23	7.58	Fe+3	1	SUCA	1
90316	3.04E-08	-7.52	3.58	DMBA	1	H +1	1
90318	2.50E-07	-6.60	1.06	DMBA	1	Mg+2	1
90320	4.26E-07	-6.37	1.36	DMBA	1	Ca+2	1
90322	3.31E-10	-9.48	2.76	DMBA	1	Cu+2	1
90324	5.32E-09	-8.27	1.86	DMBA	1	Zn+2	1
90326	2.75E-07	-6.56	4.08	BZA	1	H +1	1
90328	1.13E-07	-6.95	0.26	Mg+2	1	BZA	1
90330	1.54E-07	-6.81	0.46	Ca+2	1	BZA	1
90332	5.51E-09	-8.26	0.96	Mn+2	1	BZA	1
90334	9.49E-11	-10.02	1.76	Cu+2	1	BZA	1
90336	2.42E-09	-8.62	1.06	Zn+2	1	BZA	1
90338	1.11E-15	-14.95	5.44	Fe+3	1	BZA	1
90340	1.20E-04	-3.92	9.88	PHEN	1	H +1	1
90342	1.93E-16	-15.72	7.84	Fe+3	1	PHEN	1

90344	1.71E-06	-5.77	4.78	PROP	1	H +1	1
90346	3.52E-07	-6.45	0.66	Mg+2	1	PROP	1
90348	3.79E-07	-6.42	0.76	Ca+2	1	PROP	1
90350	1.86E-10	-9.73	1.96	Cu+2	1	PROP	1
90352	2.99E-09	-8.52	1.06	Zn+2	1	PROP	1
90354	2.18E-17	-16.66	3.64	Fe+3	1	PROP	1
90356	3.64E-09	-8.44	2.68	HBQN	1	H +1	1
90358	1.19E-06	-5.92	1.76	Mg+2	1	HBQN	1
90360	4.05E-07	-6.39	1.36	Ca+2	1	HBQN	1
90362	4.59E-08	-7.34	2.36	Mn+2	1	HBQN	1
90364	4.99E-08	-7.30	4.96	Cu+2	1	HBQN	1
90366	1.27E-06	-5.90	4.26	Zn+2	1	HBQN	1
90368	3.68E-14	-13.43	7.44	Fe+3	1	HBQN	1
90370	4.32E-10	-9.36	2.94	Mg+2	1	HBQN	2
90372	1.17E-10	-9.93	2.44	Ca+2	1	HBQN	2
90374	2.10E-11	-10.68	3.64	Mn+2	1	HBQN	2
90376	6.41E-13	-12.19	13.30	Fe+3	1	HBQN	2
90378	5.74E-09	-8.24	8.64	Cu+2	1	HBQN	2
90380	9.22E-10	-9.04	5.74	Zn+2	1	HBQN	2
90500	9.36E-05	-4.03	8.84	CAFF	1	H +1	1
90502	8.74E-07	-6.06	13.31	CAFF	1	H +1	2
90504	1.38E-11	-10.86	4.56	CAFF	1	Fe+2	1
90506	4.88E-18	-17.31	7.16	CAFF	1	Fe+2	2
90508	5.89E-14	-13.23	-4.31	CAFF	1	Fe+2	1
H +1	-1						
90510	5.26E-16	-15.28	0.01	CAFF	2	Fe+2	1
H +1	-1						
90512	4.68E-22	-21.33	-6.17	CAFF	3	Fe+2	1
H +1	-2						
90514	2.47E-10	-9.61	-4.66	Mn+2	1	CAFF	1
H +1	-1						
90516	1.32E-14	-13.88	-15.43	Mn+2	1	CAFF	1
H +1	-2						
90518	2.04E-08	-7.69	6.32	Cu+2	1	CAFF	1
90520	1.65E-10	-9.78	10.73	Cu+2	1	CAFF	1
H +1	1						

90522 8.29E-08 -7.08 0.43 Cu+2 1 CAFF 1
H +1 -1
90524 5.20E-12 -11.28 3.87 Cu+2 2 CAFF 1
H +1 -1
90526 1.06E-14 -13.97 0.92 Cu+2 2 CAFF 3
H +1 -3
90528 1.40E-15 -14.86 7.81 Cu+2 3 CAFF 2
H +1 -2
90530 2.75E-11 -10.56 -4.52 Cd+2 1 CAFF 1
H +1 -1
90532 8.91E-19 -18.05 -12.14 Cd+2 1 CAFF 2
H +1 -2
90534 7.58E-26 -25.12 -19.34 Cd+2 1 CAFF 3
H +1 -3
90536 2.48E-09 -8.61 3.30 Zn+2 1 CAFF 1
90538 5.68E-09 -8.25 -2.84 Zn+2 1 CAFF 1
H +1 -1
90540 8.04E-13 -12.09 -0.32 Zn+2 1 CAFF 2
H +1 -1
90542 2.85E-14 -13.55 -8.27 Zn+2 1 CAFF 2
H +1 -2
90544 4.96E-18 -17.30 -5.66 Zn+2 1 CAFF 3
H +1 -2
90546 5.58E-10 -9.25 -3.26 Ni+2 1 CAFF 1
H +1 -1
90548 2.86E-13 -12.54 -13.05 Ni+2 1 CAFF 1
H +1 -2
90550 5.93E-14 -13.23 -1.11 Ni+2 2 CAFF 1
H +1 -1
90552 1.02E-20 -19.99 -1.88 Ni+2 3 CAFF 2
H +1 -2
90554 1.90E-10 -9.72 -3.75 Co+2 1 CAFF 1
H +1 -1

ID C LOGC LOGK SPECIES: TYPE III - FIXED SOLIDS

50 -1.51E-02 -1.82 6.50 H +1 1

80000	6.59E-06	-5.18	12.67	Fe+3	1	E-	1	Fe+2	-1
80002	-5.72E-19	-18.24	25.70	Mn+2	-1	E-	1	Mn+3	1
80004	1.82E-11	-10.74	2.35	Cu+2	1	E-	1	Cu+1	-1
80006	-6.22E-32	-31.21	30.57	Co+2	-1	E-	1	Co+3	1
80010	-3.11E-05	-4.51	21.29	CO3	1	H +1	2		

ID	C	LOGC	LOGK	SPECIES:		TYPE IV - PRECIPITATED SOLIDS			
80102	3.23E-04	-3.49	40.99	Ca+2	5	PO4	3	H +1	-1
80608	6.59E-06	-5.18	-10.44	Fe+3	2	Fe+2	1	H +1	-8
84022	1.13E-06	-5.95	-8.76	Al+3	1	H +1	-3		

ID	C	LOGC	LOGK	SPECIES:		TYPE V - DISSOLVED SOLIDS			
80100	2.57E-02	-1.59	4.12	Ca+2	1	SO4	1		
80090	1.89E-06	-5.72	-0.31	Na+1	1	Cl	1		
80104	2.53E-07	-6.60	44.26	Ca+2	4	PO4	3	H +1	1
80106	1.44E-02	-1.84	18.40	Ca+2	1	PO4	1	H +1	1
80110	5.98E-14	-13.22	-23.09	Ca+2	1	H +1	-2		
80112	3.20E-04	-3.50	27.12	Ca+2	3	PO4	2		
80114	7.23E-03	-2.14	18.10	Ca+2	1	PO4	1	H +1	1
80116	3.86E-04	-3.41	8.01	Ca+2	1	CO3	1		
80200	9.73E-08	-7.01	23.40	Mg+2	3	PO4	2		
80202	1.40E-03	-2.85	17.32	Mg+2	1	PO4	1	H +1	1
80204	9.21E-08	-7.04	-16.97	Mg+2	1	H +1	-2		
80206	1.80E-04	-3.75	7.61	Mg+2	1	CO3	1		
80208	6.83E-08	-7.17	4.19	Mg+2	1	CO3	1		

```
80210   1.82E-07   -6.74   16.04   Ca+2   1   Mg+2   1
CO3   2
80211   3.63E-18  -17.44   28.05   Ca+2   1   Mg+2   3
CO3   4
80212   3.70E-06   -5.43   20.51   Mg+2   1   NH3    1
PO4   1   H +1   1
80214   6.31E-07   -6.20    9.78   Mg+2   1   K +1   1
PO4   1
80600   4.85E-01   -0.31   -3.56   Fe+3   1   H +1  -3
80602   2.87E-02   -1.54   25.32   Fe+3   1   PO4    1
80606   8.51E-09   -8.07  -18.51   Fe+3   2   Fe+2   1
H +1  -8
80096   4.05E-25  -24.39  -10.00   Co+2   1   CO3    1
80700   8.49E-10   -9.07  -13.02   Fe+2   1   H +1  -2
80702   2.62E-08   -7.58    9.76   CO3    1   Fe+2   1
80704   6.79E-15  -14.17   34.20   PO4    2   Fe+2   3
80701   2.26E-10   -9.65    1.98   SO4    1   Fe+2   1
80800   3.99E-08   -7.40  -15.32   Mn+2   1   H +1  -2
80802   2.82E-05   -4.55    8.82   Mn+2   1   CO3    1
80900   3.61E-04   -3.44   -8.80   Cu+2   1   H +1  -2
80904   5.72E-09   -8.24   35.90   Cu+2   3   PO4    2
80906   1.65E-07   -6.78    9.15   Cu+2   1   CO3    1
80908   9.65E-07   -6.02    4.56   Cu+2   2   CO3    1
H +1  -2
80910   1.96E-11  -10.71   15.80   Cu+2   3   CO3    2
H +1  -2
80912   1.18E-07   -6.93   14.76   Cu+2   1   BOH4   2
81200   4.74E-05   -4.32   33.50   Zn+2   3   PO4    2
81202   3.11E-04   -3.51   10.32   Zn+2   1   CO3    1
81204   7.30E-06   -5.14  -12.60   Zn+2   1   H +1  -2
83302   1.38E-07   -6.86    6.61   Cl     1   Cu+1   1
83304   2.19E-18  -17.66  -13.40   Cu+1   1   H +1  -1
84000   2.61E-23  -22.58    4.89   Ca+2   2   SiO4   1
84002   1.65E-21  -20.78    6.69   Ca+2   2   SiO4   1
84004   2.01E-02   -1.70   65.33   Ca+2   1   SiO4   2
Al+3   2
84006   2.01E-12  -11.70   15.64   Mg+2   2   SiO4   1
```

```
84008   3.09E-02   -1.51   33.14    Na+1   1    SiO4   1
Al+3   1
84010   1.22E-03   -2.91   31.34    K +1   1    SiO4   1
Al+3   1
84012   2.76E-15  -14.56   24.75    SiO4   1    Fe+2   2
84014   1.20E-01   -0.92   31.36    Zn+2   2    SiO4   1
84016   4.96E-12  -11.30   20.06    Mn+2   2    SiO4   1
84018   5.50E-02   -1.26  -10.02    Al+3   1    H +1  -3
84020   7.76E-01   -0.11   -8.87    Al+3   1    H +1  -3
80098   4.03E-20  -19.39   -4.98    Ni+2   1    CO3    1
84024   0.00E+00  -51.85  -22.64    SO4    3    Al+3   2
84026   3.03E-06   -5.52   -4.84    K +1   1    SO4    2
Al+3   3    H +1   -6
84028   4.19E-04   -3.38   17.97    Al+3   1    PO4    1
84030   1.12E-03   -2.95   11.51    Cd+2   1    CO3    1
84032   6.50E-10   -9.19   -0.44    Cd+2   1    SO4    1
84034   3.72E-04   -3.43   36.30    Cd+2   3    PO4    2
84036   1.67E-03   -2.78    7.88    Ca+2   1    MoO4   1
84038   3.56E-11  -10.45    0.14    Mg+2   1    MoO4   1
84040   6.82E-10   -9.17    6.00    Cu+2   1    MoO4   1
84042   4.42E-10   -9.35    7.22    MoO4   1    Fe+2   1
84044   1.12E-09   -8.95    3.65    Mn+2   1    MoO4   1
84046   2.51E-09   -8.60    4.46    Zn+2   1    MoO4   1
```

PERCENTAGE DISTRIBUTION OF COMPONENTS

```
DMBA
        97.2     PERCENT BOUND IN SPECIES #  173   DMBA   1
         1.6     PERCENT BOUND IN SPECIES #90320   DMBA   1
Ca+2   1

Ca+2
        29.4     PERCENT BOUND IN SPECIES #    1   Ca+2   1
         5.3     PERCENT BOUND IN SPECIES #70000   Ca+2   1
SO4    1
        64.5     PERCENT BOUND IN SPECIES #80102   Ca+2   5
PO4    3    H +1   -1
```

```
Mg+2
          85.9     PERCENT BOUND IN SPECIES #    2   Mg+2    1
          12.8     PERCENT BOUND IN SPECIES #70054   Mg+2    1
SO4     1

K +1
          98.7     PERCENT BOUND IN SPECIES #    4   K +1    1

Na+1
          99.1     PERCENT BOUND IN SPECIES #    5   Na+1    1

Fe+3
           1.8     PERCENT BOUND IN SPECIES #70200   Fe+3    1
H +1   -3
          98.2     PERCENT BOUND IN SPECIES #80608   Fe+3    2
Fe+2    1    H +1   -8

MALI
          77.4     PERCENT BOUND IN SPECIES #  171   MALI    1
           1.8     PERCENT BOUND IN SPECIES #90258   MALI    1
H +1    1
           7.0     PERCENT BOUND IN SPECIES #90266   Mg+2    1
MALI    1
           9.4     PERCENT BOUND IN SPECIES #90270   Ca+2    1
MALI    1
           2.3     PERCENT BOUND IN SPECIES #90280   MALI    1
Cu+2    1

Mn+2
          83.3     PERCENT BOUND IN SPECIES #    8   Mn+2    1
          13.3     PERCENT BOUND IN SPECIES #70272   Mn+2    1
SO4     1

Cu+2
           2.3     PERCENT BOUND IN SPECIES #    9   Cu+2    1
           4.2     PERCENT BOUND IN SPECIES #70334   Cu+2    1
BOH4    1
```

```
          3.3     PERCENT BOUND IN SPECIES #90116    Cu+2    1
DHBZ    1
          2.8     PERCENT BOUND IN SPECIES #90210    Cu+2    1
DEMA    1
         13.7     PERCENT BOUND IN SPECIES #90232    Cu+2    1
ACAC    1
         55.8     PERCENT BOUND IN SPECIES #90280    MALI    1
Cu+2    1
          5.0     PERCENT BOUND IN SPECIES #90364    Cu+2    1
HBQN    1
          2.0     PERCENT BOUND IN SPECIES #90518    Cu+2    1
CAFF    1
          8.3     PERCENT BOUND IN SPECIES #90522    Cu+2    1
CAFF    1    H +1   -1

Cd+2
         67.3     PERCENT BOUND IN SPECIES #   11    Cd+2    1
         17.1     PERCENT BOUND IN SPECIES #60018    Cd+2    1
SO4     1
          7.2     PERCENT BOUND IN SPECIES #60026    Cd+2    1
Cl      1
          4.7     PERCENT BOUND IN SPECIES #60058    Cd+2    1
PO4     1    H +1    1

Zn+2
         58.1     PERCENT BOUND IN SPECIES #   12    Zn+2    1
         12.3     PERCENT BOUND IN SPECIES #71214    Zn+2    1
SO4     1
         25.4     PERCENT BOUND IN SPECIES #90366    Zn+2    1
HBQN    1

Ni+2
         75.1     PERCENT BOUND IN SPECIES #   13    Ni+2    1
         14.5     PERCENT BOUND IN SPECIES #60020    Ni+2    1
SO4     1
          2.2     PERCENT BOUND IN SPECIES #60128    Ni+2    1
ACAC    1
```

```
          4.8     PERCENT BOUND IN SPECIES #60236   MALI    1
Ni+2    1

Co+2
         78.9     PERCENT BOUND IN SPECIES #   16   Co+2    1
         15.2     PERCENT BOUND IN SPECIES #60022   Co+2    1
SO4     1
          1.0     PERCENT BOUND IN SPECIES #60066   Co+2    1
PO4     1    H +1   1
          2.5     PERCENT BOUND IN SPECIES #60240   MALI    1
Co+2    1

BZA
         99.2     PERCENT BOUND IN SPECIES #  164   BZA     1

PHTH
         88.5     PERCENT BOUND IN SPECIES #  132   PHTH    1
          1.3     PERCENT BOUND IN SPECIES #60148   K +1    1
PHTH    1
          4.0     PERCENT BOUND IN SPECIES #90238   PHTH    1
H +1    1
          5.4     PERCENT BOUND IN SPECIES #90244   Ca+2    1
PHTH    1

PROP
         97.3     PERCENT BOUND IN SPECIES #  174   PROP    1
          1.9     PERCENT BOUND IN SPECIES #90344   PROP    1
H +1    1

PHEN
        100.0     PERCENT BOUND IN SPECIES #90340   PHEN    1
H +1    1

HBQN
         89.0     PERCENT BOUND IN SPECIES #  166   HBQN    1
          4.4     PERCENT BOUND IN SPECIES #90358   Mg+2    1
HBQN    1
```

```
          1.5     PERCENT BOUND IN SPECIES #90360   Ca+2    1
HBQN    1
          4.7     PERCENT BOUND IN SPECIES #90366   Zn+2    1
HBQN    1

CAFF
         98.5     PERCENT BOUND IN SPECIES #90500   CAFF    1
H +1    1

SO4
         88.5     PERCENT BOUND IN SPECIES #  102   SO4     1
          4.4     PERCENT BOUND IN SPECIES #70000   Ca+2    1
SO4     1
          4.3     PERCENT BOUND IN SPECIES #70054   Mg+2    1
SO4     1
          1.6     PERCENT BOUND IN SPECIES #70114   K +1    1
SO4     1

Cl
         97.5     PERCENT BOUND IN SPECIES #  103   Cl      1
          2.2     PERCENT BOUND IN SPECIES #78700   Cl      1
NH3     1    H +1   1

NH3
         93.6     PERCENT BOUND IN SPECIES #78656   NH3     1
H +1    1
          4.4     PERCENT BOUND IN SPECIES #78700   Cl      1
NH3     1    H +1   1
          1.8     PERCENT BOUND IN SPECIES #78702   SO4     1
NH3     1    H +1   1

SUCA
         87.8     PERCENT BOUND IN SPECIES #  172   SUCA    1
          6.4     PERCENT BOUND IN SPECIES #90288   SUCA    1
H +1    1
          2.5     PERCENT BOUND IN SPECIES #90294   Mg+2    1
SUCA    1
```

```
          2.1     PERCENT BOUND IN SPECIES #90298    Ca+2    1
SUCA    1

SiO4
         99.9     PERCENT BOUND IN SPECIES #50014    SiO4    1
H +1    4

BOH4
         99.7     PERCENT BOUND IN SPECIES #78636    BOH4    1
H +1    1

MoO4
         99.8     PERCENT BOUND IN SPECIES #  152    MoO4    1

NO3
         99.5     PERCENT BOUND IN SPECIES #  157    NO3     1

DHBZ
         99.6     PERCENT BOUND IN SPECIES #90102    DHBZ    1
H +1    2

SAL
         99.8     PERCENT BOUND IN SPECIES #90138    SAL     1
H +1    1

HMPA
         97.2     PERCENT BOUND IN SPECIES #  168    HMPA    1
          1.3     PERCENT BOUND IN SPECIES #90122    Ca+2    1
HMPA    1
          1.2     PERCENT BOUND IN SPECIES #90124    Mg+2    1
HMPA    1

ACPH
        100.0     PERCENT BOUND IN SPECIES #90172    ACPH    1
H +1    1

HBA
```

```
          98.5     PERCENT BOUND IN SPECIES #  169   HBA     1

DEMA
          17.4     PERCENT BOUND IN SPECIES #  170   DEMA    1
          79.5     PERCENT BOUND IN SPECIES #90194   DEMA    1
H +1    1

ACAC
          97.0     PERCENT BOUND IN SPECIES #90222   ACAC    1
H +1    1
           1.0     PERCENT BOUND IN SPECIES #90224   Mg+2    1
ACAC    1
           1.1     PERCENT BOUND IN SPECIES #90232   Cu+2    1
ACAC    1

Al+3
           2.7     PERCENT BOUND IN SPECIES #50002   Al+3    1
H +1   -2
          21.1     PERCENT BOUND IN SPECIES #50004   Al+3    1
H +1   -3
          75.0     PERCENT BOUND IN SPECIES #84022   Al+3    1
H +1   -3

E-
         100.0     PERCENT BOUND IN SPECIES #   99   E-      1

Mn+3
         100.0     PERCENT BOUND IN SPECIES #77402   Mn+3    1
H +1   -1

Cu+1
          95.8     PERCENT BOUND IN SPECIES #   33   Cu+1    1
           4.2     PERCENT BOUND IN SPECIES #77300   NH3     2
Cu+1    1

Co+3
         100.0     PERCENT BOUND IN SPECIES #   17   Co+3    1
```

```
CO3
          1.1     PERCENT BOUND IN SPECIES #70078   Mg+2    1
CO3     1    H +1    1
         64.0     PERCENT BOUND IN SPECIES #78600   CO3     1
H +1    1
         34.4     PERCENT BOUND IN SPECIES #78602   CO3     1
H +1    2

PO4
          2.2     PERCENT BOUND IN SPECIES #78612   PO4     1
H +1    2
         96.8     PERCENT BOUND IN SPECIES #80102   Ca+2    5
PO4     3    H +1   -1

Fe+2
        100.0     PERCENT BOUND IN SPECIES #80608   Fe+3    2
Fe+2    1    H +1   -8

H +1
         92.6     PERCENT BOUND IN SPECIES #50014   SiO4    1
H +1    4
          6.2     PERCENT BOUND IN SPECIES #78656   NH3     1
H +1    1
```

APPENDIX F

THE EFFECT OF LIGAND 4 (1 x 10^{-4} mol.dm^{-3}) ON METAL ION SPECIATION IN A SOIL SOLUTION (See chapter 5.4.5).

INPUT

IONIC STRENGTH = 2.00E-02

ID	X	LOGX	T	COMPONENTS
50	3.16E-07	-6.50	0.00E+00	H +1
1	1.00E-03	-3.00	2.50E-03	Ca+2
2	1.00E-03	-3.00	1.00E-03	Mg+2
4	1.00E-03	-3.00	5.00E-03	K +1
5	1.00E-05	-5.00	2.00E-03	Na+1
6	1.00E-05	-5.00	2.00E-05	Fe+3
7	1.00E-09	-9.00	0.00E+00	Fe+2
8	1.00E-05	-5.00	1.00E-05	Mn+2
9	1.00E-06	-6.00	1.00E-06	Cu+2
11	1.00E-06	-6.00	1.00E-06	Cd+2
12	1.00E-06	-6.00	5.00E-06	Zn+2
13	1.00E-06	-6.00	1.00E-06	Ni+2
16	1.00E-07	-7.00	1.00E-06	Co+2
17	1.00E-09	-9.00	0.00E+00	Co+3
20	1.00E-07	-7.00	1.50E-06	Al+3
33	1.00E-09	-9.00	0.00E+00	Cu+1
34	1.00E-09	-9.00	0.00E+00	Mn+3
99	1.00E-09	-9.00	1.00E-05	E-
101	1.00E-08	-8.00	0.00E+00	CO3
102	1.00E-03	-3.00	3.00E-03	SO4
103	1.00E-03	-3.00	2.00E-03	Cl
107	1.00E-03	-3.00	1.00E-03	NH3
109	1.00E-03	-3.00	1.00E-03	PO4
112	1.00E-04	-4.00	3.50E-03	SiO4
148	1.00E-06	-6.00	5.00E-05	BOH4
152	1.00E-08	-8.00	3.00E-08	MoO4
157	1.00E-03	-3.00	6.00E-03	NO3

167	1.00E-05	-5.00	1.90E-05	DHBZ
119	1.00E-05	-5.00	3.10E-05	SAL
168	1.00E-05	-5.00	4.90E-06	HMPA
163	1.00E-05	-5.00	1.70E-05	ACPH
169	1.00E-05	-5.00	7.00E-05	HBA
170	1.00E-05	-5.00	4.20E-05	DEMA
116	1.00E-05	-5.00	1.30E-05	ACAC
132	1.00E-05	-5.00	8.00E-06	PHTH
171	1.00E-05	-5.00	2.40E-05	MALI
172	1.00E-05	-5.00	3.20E-05	SUCA
173	1.00E-05	-5.00	2.60E-05	DMBA
164	1.00E-05	-5.00	7.30E-05	BZA
165	1.00E-05	-5.00	1.20E-04	PHEN
174	1.00E-05	-5.00	9.20E-05	PROP
166	1.00E-05	-5.00	2.70E-05	HBQN
161	1.00E-06	-6.00	9.50E-05	CAFF
178	1.00E-06	-6.00	1.00E-04	LIG4

OUTPUT

ID	C	LOGC	LOGK	SPECIES:	TYPE I - COMPONENTS
178	7.72E-10	-9.11	0.00	LIG4	1
1	6.87E-04	-3.16	0.00	Ca+2	1
2	8.48E-04	-3.07	0.00	Mg+2	1
4	4.93E-03	-2.31	0.00	K +1	1
5	1.98E-03	-2.70	0.00	Na+1	1
6	5.54E-17	-16.26	0.00	Fe+3	1
7	8.96E-10	-9.05	0.00	Fe+2	1
8	5.07E-06	-5.30	0.00	Mn+2	1
9	1.46E-12	-11.84	0.00	Cu+2	1
11	4.45E-09	-8.35	0.00	Cd+2	1
12	3.08E-09	-8.51	0.00	Zn+2	1
13	9.84E-10	-9.01	0.00	Ni+2	1
16	3.21E-09	-8.49	0.00	Co+2	1
17	2.50E-34	-33.60	0.00	Co+3	1
20	2.79E-13	-12.55	0.00	Al+3	1
33	1.13E-15	-14.95	0.00	Cu+1	1

34	2.93E-26	-25.53	0.00	Mn+3	1
99	3.45E-06	-5.46	0.00	E-	1
101	5.12E-09	-8.29	0.00	CO3	1
102	2.67E-03	-2.57	0.00	SO4	1
103	1.95E-03	-2.71	0.00	Cl	1
107	1.70E-06	-5.77	0.00	NH3	1
109	2.76E-11	-10.56	0.00	PO4	1
112	6.20E-22	-21.21	0.00	SiO4	1
148	9.50E-08	-7.02	0.00	BOH4	1
152	2.99E-08	-7.52	0.00	MoO4	1
157	5.97E-03	-2.22	0.00	NO3	1
167	8.66E-15	-14.06	0.00	DHBZ	1
119	3.39E-12	-11.47	0.00	SAL	1
168	4.77E-06	-5.32	0.00	HMPA	1
163	5.63E-09	-8.25	0.00	ACPH	1
169	6.90E-05	-4.16	0.00	HBA	1
170	7.32E-06	-5.14	0.00	DEMA	1
116	5.33E-08	-7.27	0.00	ACAC	1
132	7.12E-06	-5.15	0.00	PHTH	1
171	1.93E-05	-4.72	0.00	MALI	1
172	2.82E-05	-4.55	0.00	SUCA	1
173	2.53E-05	-4.60	0.00	DMBA	1
164	7.25E-05	-4.14	0.00	BZA	1
165	5.00E-08	-7.30	0.00	PHEN	1
174	8.96E-05	-4.05	0.00	PROP	1
166	2.53E-05	-4.60	0.00	HBQN	1
161	4.28E-07	-6.37	0.00	CAFF	1

ID	C	LOGC	LOGK	SPECIES:	TYPE II - COMPLEXES		
90556	9.20E-19	-18.04	-1.18	Co+2	2	CAFF	1
H +1	-1						
50000	4.85E-12	-11.31	-5.26	Al+3	1	H +1	-1
50002	6.10E-10	-9.21	-9.66	Al+3	1	H +1	-2
50004	4.85E-09	-8.31	-15.26	Al+3	1	H +1	-3
50006	1.59E-20	-19.80	-7.69	Al+3	2	H +1	-2
50008	8.19E-16	-15.09	12.62	SiO4	1	H +1	1

```
50010    8.38E-13  -12.08    22.13     SiO4    1    H +1    2
50012    2.84E-06   -5.55    35.16     SiO4    1    H +1    3
50014    3.50E-03   -2.46    44.75     SiO4    1    H +1    4
50016    1.49E-20  -19.83    -0.60     Al+3    1    NO3     3
50018    4.48E-17  -16.35     5.28     Al+3    1    SO4     1
H +1    1
50020    2.25E-13  -12.65     2.48     Al+3    1    SO4     1
50022    1.73E-17  -16.76     0.94     Al+3    1    SO4     2
50024    3.09E-37  -36.51    -3.68     Al+3    2    SO4     3
50026    3.02E-21  -20.52     3.85     Ca+2    1    SiO4    1
50028    6.47E-18  -17.19    13.68     Ca+2    1    SiO4    1
H +1    1
50030    4.49E-20  -19.35     4.93     Mg+2    1    SiO4    1
50032    1.42E-17  -16.85    13.93     Mg+2    1    SiO4    1
H +1    1
50034    3.22E-22  -21.49    22.47     Fe+3    1    SiO4    1
H +1    1
60000    1.09E-10   -9.96     1.03     Na+1    1    CO3     1
60002    1.69E-08   -7.77     9.72     Na+1    1    CO3     1
H +1    1
60004    1.14E-13  -12.94     3.70     Cd+2    1    CO3     1
60006    4.45E-19  -18.35     6.58     Cd+2    1    CO3     2
60008    1.17E-11  -10.93    12.21     Cd+2    1    CO3     1
H +1    1
60010    6.21E-14  -13.21     4.09     Ni+2    1    CO3     1
60012    4.40E-12  -11.36    12.44     Ni+2    1    CO3     1
H +1    1
60014    8.05E-14  -13.09     3.69     Co+2    1    CO3     1
60016    9.03E-12  -11.04    12.24     Co+2    1    CO3     1
H +1    1
60018    1.13E-09   -8.95     1.98     Cd+2    1    SO4     1
60020    1.90E-10   -9.72     1.86     Ni+2    1    SO4     1
60022    6.19E-10   -9.21     1.86     Co+2    1    SO4     1
60024    4.15E-06   -5.38     0.40     Mg+2    1    Cl      1
60026    4.77E-10   -9.32     1.74     Cd+2    1    Cl      1
60028    2.94E-12  -11.53     2.24     Cd+2    1    Cl      2
60029    3.62E-15  -14.44     2.04     Cd+2    1    Cl      3
```

60030	5.54E-15	-14.26	-2.54	Ni+2	1	Cl	1
60032	1.25E-11	-10.90	0.30	Co+2	1	Cl	1
60034	8.80E-13	-12.06	2.72	Ni+2	1	NH3	1
60036	2.22E-16	-15.65	4.89	Ni+2	1	NH3	2
60038	1.73E-20	-19.76	6.55	Ni+2	1	NH3	3
60040	3.87E-25	-24.41	7.67	Ni+2	1	NH3	4
60042	3.09E-30	-29.51	8.34	Ni+2	1	NH3	5
60044	4.91E-36	-35.31	8.31	Ni+2	1	NH3	6
60046	6.56E-13	-12.18	2.08	Co+2	1	NH3	1
60048	2.94E-17	-16.53	3.50	Co+2	1	NH3	2
60050	4.26E-22	-21.37	4.43	Co+2	1	NH3	3
60052	3.17E-27	-26.50	5.07	Co+2	1	NH3	4
60054	6.20E-33	-32.21	5.13	Co+2	1	NH3	5
60056	0.00E+00	-38.72	4.39	Co+2	1	NH3	6
60058	3.47E-10	-9.46	15.95	Cd+2	1	PO4	1
H +1	1						
60060	2.63E-13	-12.58	19.33	Cd+2	1	PO4	1
H +1	2						
60062	1.22E-11	-10.92	15.15	Ni+2	1	PO4	1
H +1	1						
60064	5.95E-12	-11.23	21.34	Ni+2	1	PO4	1
H +1	2						
60066	4.76E-11	-10.32	15.23	Co+2	1	PO4	1
H +1	1						
60068	4.84E-11	-10.32	0.26	Cd+2	1	NO3	1
60070	1.10E-13	-12.96	-0.16	Cd+2	1	NO3	2
60072	8.50E-12	-11.07	0.16	Ni+2	1	NO3	1
60074	8.81E-17	-16.05	-2.60	Ni+2	1	NO3	2
60076	1.75E-11	-10.76	-0.04	Co+2	1	NO3	1
60078	4.55E-16	-15.34	-2.40	Co+2	1	NO3	2
60080	9.93E-07	-6.00	11.46	Cd+2	1	LIG4	1
60082	8.16E-07	-6.09	12.03	Ni+2	1	LIG4	1
60084	1.51E-13	-12.82	14.41	Ni+2	1	LIG4	2
60086	1.83E-07	-6.74	17.88	Ni+2	1	LIG4	1
H +1	1						
60088	9.43E-07	-6.03	11.58	Co+2	1	LIG4	1

60088	9.43E-07	-6.03	11.58	Co+2	1	LIG4	1
60090	5.30E-08	-7.28	16.83	Co+2	1	LIG4	1
H +1	1						
60092	8.88E-13	-12.05	-10.20	Cd+2	1	H +1	-1
60094	1.51E-16	-15.82	-20.47	Cd+2	1	H +1	-2
60096	3.45E-30	-29.46	-47.11	Cd+2	1	H +1	-4
60098	3.36E-20	-19.47	-9.27	Cd+2	2	H +1	-1
60100	0.00E+00	-39.98	-32.57	Cd+2	4	H +1	-4
60102	3.26E-13	-12.49	-9.98	Ni+2	1	H +1	-1
60104	6.50E-16	-15.19	-19.18	Ni+2	1	H +1	-2
60106	3.11E-20	-19.51	-30.00	Ni+2	1	H +1	-3
60108	8.05E-23	-22.09	-10.58	Ni+2	2	H +1	-1
60110	2.96E-38	-37.53	-27.50	Ni+2	4	H +1	-4
60112	1.72E-12	-11.76	-9.77	Co+2	1	H +1	-1
60114	3.85E-15	-14.41	-18.92	Co+2	1	H +1	-2
60116	3.20E-21	-20.49	-31.50	Co+2	1	H +1	-3
60118	2.79E-29	-28.55	-46.06	Co+2	1	H +1	-4
60120	2.70E-22	-21.57	-11.08	Co+2	2	H +1	-1
60122	5.41E-39	-38.27	-30.29	Co+2	4	H +1	-4
66124	9.23E-13	-12.03	3.59	Cd+2	1	ACAC	1
60126	2.47E-17	-16.61	6.29	Cd+2	1	ACAC	2
60128	2.95E-11	-10.53	5.75	Ni+2	1	ACAC	1
60130	4.64E-14	-13.33	10.22	Ni+2	1	ACAC	2
60132	2.47E-11	-10.61	5.16	Co+2	1	ACAC	1
60134	1.38E-14	-13.86	9.18	Co+2	1	ACAC	2
60136	1.58E-14	-13.80	6.02	Cd+2	1	SAL	1
60138	4.67E-11	-10.33	15.99	Cd+2	1	SAL	1
H +1	1						
60140	8.79E-14	-13.06	7.42	Ni+2	1	SAL	1
60142	1.56E-15	-14.81	12.17	Ni+2	1	SAL	1
H +1	1						
60144	1.69E-13	-12.77	7.19	Co+2	1	SAL	1
60146	2.55E-15	-14.59	11.87	Co+2	1	SAL	1
H +1	1						
60148	1.01E-07	-6.99	0.46	K +1	1	PHTH	1
60152	5.03E-12	-11.30	2.20	Cd+2	1	PHTH	1
60154	4.20E-16	-15.38	3.27	Cd+2	1	PHTH	2

60156	2.58E-15	-14.59	5.41	Cd+2	1	PHTH	1
H +1	1						
60158	1.24E-18	-17.91	7.24	Cd+2	1	PHTH	2
H +1	1						
60160	2.07E-12	-11.68	2.47	Ni+2	1	PHTH	1
60162	1.76E-15	-14.75	5.90	Ni+2	1	PHTH	1
H +1	1						
60164	1.81E-12	-11.74	1.90	Co+2	1	PHTH	1
60166	2.18E-14	-13.66	6.48	Co+2	1	PHTH	1
H +1	1						
60168	1.36E-13	-12.87	4.39	Ni+2	1	ACPH	1
60170	6.66E-19	-18.18	7.33	Ni+2	1	ACPH	2
60172	6.40E-13	-12.19	4.55	Co+2	1	ACPH	1
60174	3.14E-18	-17.50	7.49	Co+2	1	ACPH	2
60176	1.26E-11	-10.90	1.59	BZA	1	Cd+2	1
60178	1.86E-15	-14.73	1.90	BZA	2	Cd+2	1
60180	8.78E-13	-12.06	1.09	BZA	1	Ni+2	1
60182	1.68E-12	-11.77	0.86	BZA	1	Co+2	1
60184	1.79E-10	-9.75	20.57	Fe+3	1	DHBZ	1
60186	1.32E-09	-8.88	35.50	Fe+3	1	DHBZ	2
60188	8.46E-15	-14.07	44.37	Fe+3	1	DHBZ	3
60190	1.50E-14	-13.82	8.59	Cd+2	1	DHBZ	1
60192	1.70E-14	-13.77	9.30	Ni+2	1	DHBZ	1
60194	4.45E-23	-22.35	14.78	Ni+2	1	DHBZ	2
60196	2.65E-14	-13.58	8.98	Co+2	1	DHBZ	1
60198	5.78E-22	-21.24	15.38	Co+2	1	DHBZ	2
60200	5.72E-13	-12.24	1.43	Cd+2	1	HMPA	1
60202	2.86E-17	-16.54	2.45	Cd+2	1	HMPA	2
60204	2.91E-22	-21.54	2.78	Cd+2	1	HMPA	3
60206	3.40E-13	-12.47	1.86	Ni+2	1	HMPA	1
60208	2.69E-17	-16.57	3.08	Ni+2	1	HMPA	2
60210	3.30E-22	-21.48	3.49	Ni+2	1	HMPA	3
60212	6.68E-13	-12.18	1.64	Co+2	1	HMPA	1
60214	3.83E-17	-16.42	2.72	Co+2	1	HMPA	2
60216	3.32E-22	-21.48	2.98	Co+2	1	HMPA	3
60218	2.61E-12	-11.58	0.93	Cd+2	1	HBA	1
60220	3.65E-13	-12.44	0.73	Ni+2	1	HBA	1

60222	8.03E-13	-12.10	0.56	Co+2	1	HBA	1
60224	1.81E-07	-6.74	0.70	K +1	1	DEMA	1
60226	2.71E-11	-10.57	2.92	Cd+2	1	DEMA	1
60228	4.05E-12	-11.39	2.75	Ni+2	1	DEMA	1
60230	1.00E-11	-11.00	2.63	Co+2	1	DEMA	1
60232	4.61E-11	-10.34	2.73	Cd+2	1	MALI	1
60234	1.75E-13	-12.76	6.81	Cd+2	1	MALI	1
H +1	1						
60236	6.58E-11	-10.18	3.54	Ni+2	1	MALI	1
60238	1.20E-13	-12.92	7.30	Ni+2	1	MALI	1
H +1	1						
60240	1.05E-10	-9.98	3.23	Co+2	1	MALI	1
60242	2.52E-13	-12.60	7.11	Co+2	1	MALI	1
H +1	1						
60243	2.53E-07	-6.60	0.26	K +1	1	SUCA	1
60244	2.18E-11	-10.66	2.24	SUCA	1	Cd+2	1
60245	2.01E-12	-11.70	1.86	SUCA	1	Ni+2	1
60246	5.80E-20	-19.24	0.82	SUCA	1	Ni+2	1
H +1	1						
60248	6.25E-12	-11.20	1.84	SUCA	1	Co+2	1
60250	7.28E-12	-11.14	1.81	Cd+2	1	DMBA	1
60252	2.49E-12	-11.60	2.00	Ni+2	1	DMBA	1
60254	4.89E-12	-11.31	1.78	Co+2	1	DMBA	1
60256	9.14E-12	-11.04	1.36	Cd+2	1	PROP	1
60258	4.61E-15	-14.34	2.11	Cd+2	1	PROP	2
60260	7.86E-13	-12.10	0.95	Ni+2	1	PROP	1
60262	2.28E-16	-15.64	1.46	Ni+2	1	PROP	2
60264	2.23E-12	-11.65	0.89	Co+2	1	PROP	1
70000	1.24E-04	-3.91	1.83	Ca+2	1	SO4	1
70002	9.93E-07	-6.00	-0.13	Ca+2	1	Cl	1
70004	1.04E-08	-7.98	5.74	Ca+2	1	PO4	1
70006	4.88E-07	-6.31	13.91	Ca+2	1	PO4	1
H +1	1						
70008	9.52E-08	-7.02	19.70	Mg+2	1	PO4	1
H +1	2						

70010	9.12E-11	-10.04	27.24	Ca+2	1	PO4	2
H +1	2						
70012	3.39E-12	-11.47	32.31	Ca+2	1	PO4	2
H +1	3						
70014	8.66E-13	-12.06	28.38	Ca+2	2	PO4	2
H +1	2						
70020	3.29E-10	-9.48	-12.82	Ca+2	1	H +1	-1
70022	1.65E-09	-8.78	2.67	Ca+2	1	CO3	1
70024	7.89E-08	-7.10	10.85	Ca+2	1	CO3	1
H +1	1						
70026	6.00E-10	-9.22	-0.29	Ca+2	1	NH3	1
70028	1.62E-16	-15.79	-1.09	Ca+2	1	NH3	2
70030	2.76E-23	-22.56	-2.09	Ca+2	1	NH3	3
70032	1.18E-05	-4.93	0.46	Ca+2	1	NO3	1
70034	4.26E-08	-7.37	0.24	Ca+2	1	NO3	2
70054	1.27E-04	-3.90	1.75	Mg+2	1	SO4	1
70056	1.74E-08	-7.76	5.87	Mg+2	1	PO4	1
70058	1.91E-06	-5.72	14.41	Mg+2	1	PO4	1
H +1	1						
70060	3.80E-07	-6.42	20.21	Mg+2	1	PO4	1
H +1	2						
70062	1.26E-11	-10.90	32.79	Mg+2	1	PO4	2
H +1	3						
70064	1.05E-10	-9.98	27.21	Mg+2	1	PO4	2
H +1	2						
70066	5.01E-12	-11.30	28.96	Mg+2	2	PO4	2
H +1	2						
70072	7.73E-09	-8.11	-11.54	Mg+2	1	H +1	-1
70074	1.79E-26	-25.75	-39.46	Mg+2	4	H +1	-4
70076	1.14E-08	-7.94	3.42	Mg+2	1	CO3	1
70078	3.45E-07	-6.46	11.40	Mg+2	1	CO3	1
H +1	1						
70080	9.11E-09	-8.04	0.80	Mg+2	1	NH3	1
70082	1.32E-15	-14.88	-0.27	Mg+2	1	NH3	2
70084	5.92E-22	-21.23	-0.85	Mg+2	1	NH3	3
70086	1.27E-28	-27.90	-1.75	Mg+2	1	NH3	4

70112	4.93E-11	-10.31	-14.50	K +1	1	H +1	-1
70114	4.78E-05	-4.32	0.56	K +1	1	SO4	1
70116	2.92E-07	-6.54	12.83	K +1	1	PO4	1
H +1	1						
70118	1.27E-06	-5.90	-0.88	K +1	1	Cl	1
70120	1.58E-05	-4.80	-0.27	K +1	1	NO3	1
70124	1.52E-05	-4.82	0.46	Na+1	1	SO4	1
70126	4.56E-07	-6.34	1.51	Na+1	1	SO4	2
70132	1.51E-07	-6.82	12.94	Na+1	1	PO4	1
H +1	1						
70134	1.93E-08	-7.72	2.01	Na+1	1	BOH4	1
70136	7.89E-11	-10.10	-13.90	Na+1	1	H +1	-1
70138	2.77E-06	-5.56	-0.63	Na+1	1	NO3	1
70140	3.09E-16	-15.51	3.32	Fe+3	1	SO4	1
70142	1.04E-17	-16.98	4.42	Fe+3	1	SO4	2
70144	1.43E-18	-17.85	1.12	Fe+3	1	Cl	1
70146	7.15E-21	-20.15	1.53	Fe+3	1	Cl	2
70148	1.06E-24	-23.98	0.41	Fe+3	1	Cl	3
70150	1.11E-12	-11.95	21.36	Fe+3	1	PO4	1
H +1	1						
70152	5.70E-18	-17.24	22.57	Fe+3	1	PO4	1
H +1	2						
70154	8.89E-22	-21.05	28.52	Fe+3	2	PO4	1
H +1	1						
70168	2.58E-15	-14.59	8.69	Fe+3	1	BOH4	1
70170	3.23E-15	-14.49	15.81	Fe+3	1	BOH4	2
70172	2.87E-17	-16.54	20.78	Fe+3	1	BOH4	3
70174	1.70E-16	-15.77	8.01	Fe+3	1	MoO4	1
70176	6.07E-23	-22.22	16.61	Fe+3	1	MoO4	3
70178	6.51E-13	-12.19	-2.43	Fe+3	1	H +1	-1
70180	4.83E-10	-9.32	-6.06	Fe+3	1	H +1	-2
70200	2.37E-07	-6.63	-9.87	Fe+3	1	H +1	-3
70202	8.01E-13	-12.10	-21.84	Fe+3	1	H +1	-4
70204	3.87E-23	-22.41	-2.90	Fe+3	2	H +1	-2
70206	1.12E-29	-28.95	-6.18	Fe+3	3	H +1	-4
70208	1.44E-18	-17.84	0.64	Fe+3	1	NO3	1
70220	1.25E-10	-9.90	1.72	SO4	1	Fe+2	1

70222	1.25E-16	-15.90	2.22	SO4	1	Fe+2	1
H +1	1						
70224	6.80E-13	-12.17	-9.62	Fe+2	1	H +1	-1
70226	1.71E-17	-16.77	-20.72	Fe+2	1	H +1	-2
70228	2.83E-22	-21.55	-32.00	Fe+2	1	H +1	-3
70230	6.19E-30	-29.21	-46.16	Fe+2	1	H +1	-4
70240	9.86E-12	-11.01	15.10	Fe+2	1	PO4	1
H +1	1						
70242	6.22E-12	-11.21	21.40	Fe+2	1	PO4	1
H +1	2						
70244	1.43E-15	-14.84	28.32	Fe+2	1	PO4	2
H +1	2						
70266	5.21E-08	-7.28	15.07	Mn+2	1	PO4	1
H +1	1						
70268	3.52E-08	-7.45	21.40	Mn+2	1	PO4	1
H +1	2						
70270	4.55E-12	-11.34	28.07	Mn+2	1	PO4	2
H +1	2						
70272	8.15E-07	-6.09	1.78	Mn+2	1	SO4	1
70274	3.05E-10	-9.52	-10.72	Mn+2	1	H +1	-1
70276	1.88E-15	-14.73	-22.43	Mn+2	1	H +1	-2
70278	1.01E-20	-20.00	-34.20	Mn+2	1	H +1	-3
70280	4.41E-28	-27.36	-48.06	Mn+2	1	H +1	-4
70282	2.69E-15	-14.57	-10.48	Mn+2	2	H +1	-1
70284	5.89E-16	-15.23	-24.14	Mn+2	2	H +1	-3
70286	3.67E-09	-8.44	11.65	Mn+2	1	CO3	1
H +1	1						
70294	6.25E-11	-10.20	0.86	Mn+2	1	NH3	1
70296	4.54E-16	-15.34	1.49	Mn+2	1	NH3	2
70298	1.41E-21	-20.85	1.75	Mn+2	1	NH3	3
70300	8.91E-28	-27.05	1.32	Mn+2	1	NH3	4
70302	2.76E-08	-7.56	-0.04	Mn+2	1	NO3	1
70304	3.14E-10	-9.50	0.24	Mn+2	1	NO3	2
70318	4.12E-14	-13.38	15.51	Cu+2	1	PO4	1
H +1	1						

```
70320   6.68E-16  -15.17   20.22    Cu+2  1   PO4   1
H +1  2
70322   3.52E-21  -20.45   32.00    Cu+2  1   PO4   2
H +1  3
70324   4.07E-27  -26.39   31.40    Cu+2  2   PO4   2
H +1  2
70326   4.53E-18  -17.34   28.61    Cu+2  1   PO4   2
H +1  2
70328   2.95E-13  -12.53    1.88    Cu+2  1   SO4   1
70330   1.97E-14  -13.70    3.28    Cu+2  1   SO4   2
70332   9.79E-18  -17.01    2.55    Cu+2  1   SO4   3
70334   2.70E-12  -11.57    7.29    Cu+2  1   BOH4  1
70336   6.91E-14  -13.16   12.72    Cu+2  1   BOH4  2
70338   3.52E-18  -17.45   15.45    Cu+2  1   BOH4  3
70340   6.97E-14  -13.16   -7.82    Cu+2  1   H +1  -1
70342   1.75E-14  -13.76  -14.92    Cu+2  1   H +1  -2
70344   1.21E-20  -19.92  -27.58    Cu+2  1   H +1  -3
70346   6.35E-26  -25.20  -39.36    Cu+2  1   H +1  -4
70348   2.03E-22  -21.69  -11.02    Cu+2  2   H +1  -2
70350   4.47E-32  -31.35  -21.84    Cu+2  3   H +1  -4
70352   0.00E+00  -48.03  -20.18    Cu+2  4   H +1  -3
70364   1.39E-14  -13.86    6.27    Cu+2  1   CO3   1
70366   8.57E-20  -19.07    9.35    Cu+2  1   CO3   2
70368   4.11E-15  -14.39    0.16    Cu+2  1   Cl    1
70370   2.85E-14  -13.55    4.06    Cu+2  1   NH3   1
70372   9.68E-17  -16.01    7.36    Cu+2  1   NH3   2
70374   9.06E-20  -19.04   10.10    Cu+2  1   NH3   3
70376   1.20E-23  -22.92   11.99    Cu+2  1   NH3   4
70378   5.62E-30  -29.25   11.43    Cu+2  1   NH3   5
70380   9.43E-15  -14.03   -2.92    Cu+2  1   NH3   1
H +1  -1
70382   2.74E-24  -23.56   -0.92    Cu+2  1   NH3   3
H +1  -1
70384   6.40E-27  -26.19  -15.82    Cu+2  1   NH3   2
H +1  -2
70386   1.58E-14  -13.80    0.26    Cu+2  1   NO3   1
```

```
70388    5.96E-17  -16.22     0.06     Cu+2   1     NO3    2
70424    1.38E-11  -10.86    14.71     Zn+2   1     PO4    1
H +1   1
70426    1.62E-12  -11.79    20.28     Zn+2   1     PO4    1
H +1   2
71208    6.79E-17  -16.17    32.96     Zn+2   1     PO4    2
H +1   3
71210    6.77E-22  -21.17    29.97     Zn+2   2     PO4    2
H +1   2
71212    2.41E-15  -14.62    28.01     Zn+2   1     PO4    2
H +1   2
71214    6.53E-10   -9.19     1.90     Zn+2   1     SO4    1
71216    3.81E-11  -10.42     3.24     Zn+2   1     SO4    2
71218    8.63E-14  -13.06     3.17     Zn+2   1     SO4    3
71220    3.40E-16  -15.47     3.34     Zn+2   1     SO4    4
71222    7.39E-12  -11.13    -9.12     Zn+2   1     H +1  -1
71224    1.94E-11  -10.71   -15.20     Zn+2   1     H +1  -2
71226    3.88E-18  -17.41   -28.40     Zn+2   1     H +1  -3
71228    3.38E-24  -23.47   -40.96     Zn+2   1     H +1  -4
71230    3.95E-20  -19.40    -8.88     Zn+2   2     H +1  -1
71242    2.62E-13  -12.58     4.22     Zn+2   1     CO3    1
71243    2.23E-12  -11.65    11.65     Zn+2   1     CO3    1
H +1   1
71244    9.31E-12  -11.03     0.19     Zn+2   1     Cl     1
71246    5.61E-14  -13.25     0.68     Zn+2   1     Cl     2
71248    3.46E-16  -15.46     1.18     Zn+2   1     Cl     3
71250    1.41E-18  -17.85     1.50     Zn+2   1     Cl     4
71252    8.51E-13  -12.07     2.21     Zn+2   1     NH3    1
71254    2.83E-16  -15.55     4.50     Zn+2   1     NH3    2
71256    1.10E-19  -18.96     6.86     Zn+2   1     NH3    3
71258    2.01E-23  -22.70     8.89     Zn+2   1     NH3    4
71260    5.13E-13  -12.29    -4.51     Zn+2   1     NH3    1
H +1  -1
71262    3.17E-17  -16.50    -2.95     Zn+2   1     NH3    2
H +1  -1
```

```
71264   8.36E-22  -21.08   -1.76    Zn+2   1    NH3    3
H +1  -1
71266   1.74E-16  -15.76  -14.48    Zn+2   1    NH3    1
H +1  -2
71268   1.15E-21  -20.94  -13.89    Zn+2   1    NH3    2
H +1  -2
71270   1.99E-22  -21.70  -26.92    Zn+2   1    NH3    1
H +1  -3
71300   2.66E-11  -10.58    0.16    Zn+2   1    NO3    1
71302   2.09E-13  -12.68    0.28    Zn+2   1    NO3    2
77300   4.95E-17  -16.31   10.18    NH3    2    Cu+1   1
77400   4.10E-26  -25.39    2.72    SO4    1    Mn+3   1
77402   3.44E-19  -18.46    0.57    Mn+3   1    H +1  -1
78600   1.99E-05   -4.70   10.09    CO3    1    H +1   1
78602   1.07E-05   -4.97   16.32    CO3    1    H +1   2
78604   4.74E-08   -7.32    1.75    SO4    1    H +1   1
78606   4.64E-22  -21.33   -5.76    SO4    1    H +1   2
78610   8.35E-06   -5.08   11.98    PO4    1    H +1   1
78612   2.41E-05   -4.62   18.94    PO4    1    H +1   2
78614   7.98E-10   -9.10   20.96    PO4    1    H +1   3
78616   2.84E-11  -10.55   30.07    PO4    2    H +1   3
78618   3.57E-10   -9.45   37.67    PO4    2    H +1   4
78620   6.81E-14  -13.17   40.45    PO4    2    H +1   5
78634   4.17E-08   -7.38  -13.88    H +1  -1
78636   4.99E-05   -4.30    9.22    BOH4   1    H +1   1
78638   2.36E-18  -17.63    9.94    BOH4   3    H +1   1
78640   5.17E-15  -14.29   19.78    BOH4   3    H +1   2
78642   1.70E-21  -20.77   20.32    BOH4   4    H +1   2
78644   1.03E-18  -17.99   29.60    BOH4   4    H +1   3
78646   2.14E-23  -22.67   38.44    BOH4   5    H +1   4
78648   5.98E-11  -10.22    3.80    MoO4   1    H +1   1
78650   1.40E-13  -12.85    7.67    MoO4   1    H +1   2
78652   3.21E-19  -18.49    8.53    MoO4   1    H +1   3
78654   2.95E-16  -15.53   -6.32    Cl     1    H +1   1
78656   9.36E-04   -3.03    9.24    NH3    1    H +1   1
```

78700	4.38E-05	-4.36	10.62	Cl	1	NH3	1
H +1	1						
78702	1.85E-05	-4.73	10.11	SO4	1	NH3	1
H +1	1						
78708	5.45E-11	-10.26	-1.54	NO3	1	H +1	1
78710	3.65E-12	-11.44	8.39	Al+3	1	ACAC	1
78712	1.23E-11	-10.91	16.19	Al+3	1	ACAC	2
78714	4.04E-13	-12.39	21.98	Al+3	1	ACAC	3
78716	2.22E-10	-9.65	14.37	Al+3	1	SAL	1
78718	1.12E-14	-13.95	3.75	Al+3	1	PHTH	1
78720	4.15E-11	-10.38	7.32	Al+3	1	PHTH	1
78722	4.85E-13	-12.31	-2.12	BZA	1	Al+3	1
H +1	-1						
90100	3.15E-08	-7.50	13.06	DHBZ	1	H +1	1
90102	1.90E-05	-4.72	22.34	DHBZ	1	H +1	2
90104	7.70E-12	-11.11	6.02	Mg+2	1	DHBZ	1
90106	2.48E-13	-12.61	4.62	Ca+2	1	DHBZ	1
90108	4.60E-12	-11.34	8.02	Mn+2	1	DHBZ	1
90110	2.31E-10	-9.64	16.22	Mn+2	1	DHBZ	1
H +1	1						
90112	4.08E-15	-14.39	8.72	DHBZ	1	Fe+2	1
90114	2.04E-13	-12.69	16.92	DHBZ	1	Fe+2	1
H +1	1						
90116	2.10E-12	-11.68	14.22	Cu+2	1	DHBZ	1
90118	4.43E-13	-12.35	10.22	Zn+2	1	DHBZ	1
90120	1.14E-08	-7.94	3.88	HMPA	1	H +1	1
90122	5.96E-08	-7.22	1.26	Ca+2	1	HMPA	1
90124	5.85E-08	-7.23	1.16	Mg+2	1	HMPA	1
90126	3.50E-10	-9.46	1.16	Mn+2	1	HMPA	1
90128	1.95E-13	-12.71	1.66	HMPA	1	Fe+2	1
90130	6.34E-15	-14.20	2.96	Cu+2	1	HMPA	1
90132	1.34E-12	-11.87	1.96	Zn+2	1	HMPA	1
90134	3.65E-19	-18.44	3.14	Fe+3	1	HMPA	1
90136	1.10E-13	-12.96	2.12	Fe+3	1	HMPA	1
H +1	-1						
90138	3.10E-05	-4.51	13.46	SAL	1	H +1	1
90140	7.43E-09	-8.13	16.34	SAL	1	H +1	2

90141	1.20E-09	-8.92	5.62	Mg+2	1	SAL	1
90142	1.22E-10	-9.91	4.72	Ca+2	1	SAL	1
90144	3.07E-08	-7.51	13.62	Ca+2	1	SAL	1
H +1	1						
90146	2.86E-11	-10.54	6.22	Mn+2	1	SAL	1
90148	2.53E-14	-13.60	6.92	SAL	1	Fe+2	1
90150	4.11E-13	-12.39	10.92	Cu+2	1	SAL	1
90152	1.74E-13	-12.76	7.22	Zn+2	1	SAL	1
90154	9.01E-12	-11.05	16.68	Fe+3	1	SAL	1
90156	4.73E-17	-16.33	17.90	Fe+3	1	SAL	1
H +1	1						
90158	1.02E-16	-15.99	10.02	Mg+2	1	SAL	2
90160	8.29E-19	-18.08	8.02	Ca+2	1	SAL	2
90162	9.69E-19	-18.01	10.22	Mn+2	1	SAL	2
90164	4.30E-21	-20.37	11.62	SAL	2	Fe+2	1
90166	1.40E-09	-8.85	30.34	Fe+3	1	SAL	2
90168	1.11E-16	-15.96	18.82	Cu+2	1	SAL	2
90170	1.48E-26	-25.83	5.62	Zn+2	1	SAL	2
90172	1.70E-05	-4.77	9.98	ACPH	1	H +1	1
90174	7.03E-11	-10.15	1.26	Ca+2	1	ACPH	1
90176	8.23E-12	-11.08	2.46	Mn+2	1	ACPH	1
90178	5.94E-14	-13.23	6.86	Cu+2	1	ACPH	1
90180	3.15E-14	-13.50	3.26	Zn+2	1	ACPH	1
90182	1.08E-14	-13.97	10.54	Fe+3	1	ACPH	1
90184	5.23E-07	-6.28	4.38	HBA	1	H +1	1
90186	3.37E-07	-6.47	0.76	Mg+2	1	HBA	1
90188	1.72E-07	-6.76	0.56	Ca+2	1	HBA	1
90190	1.83E-14	-13.74	2.26	Cu+2	1	HBA	1
90192	3.87E-12	-11.41	1.26	Zn+2	1	HBA	1
90194	3.35E-05	-4.48	7.16	DEMA	1	H +1	1
90196	1.27E-09	-8.90	9.24	DEMA	1	H +1	2
90198	5.27E-08	-7.28	0.56	Na+1	1	DEMA	1
90200	4.10E-07	-6.39	1.82	Mg+2	1	DEMA	1
90202	1.03E-07	-6.99	7.72	Mg+2	1	DEMA	1
H +1	1						
90204	3.32E-07	-6.48	1.82	Ca+2	1	DEMA	1

90206	1.32E-07	-6.88	7.92	Ca+2	1	DEMA	1
H +1	1						
90208	4.89E-09	-8.31	2.12	Mn+2	1	DEMA	1
90210	1.77E-12	-11.75	5.22	Cu+2	1	DEMA	1
90212	5.60E-16	-15.25	8.22	Cu+2	1	DEMA	1
H +1	1						
90214	1.18E-11	-10.93	2.72	Zn+2	1	DEMA	1
90216	1.49E-12	-11.83	8.32	Zn+2	1	DEMA	1
H +1	1						
90218	4.88E-13	-12.31	9.08	Fe+3	1	DEMA	1
90220	1.62E-18	-17.79	10.10	Fe+3	1	DEMA	1
H +1	1						
90222	1.28E-05	-4.89	8.88	ACAC	1	H +1	1
90224	1.30E-07	-6.88	3.46	Mg+2	1	ACAC	1
90226	2.65E-08	-7.58	2.86	Ca+2	1	ACAC	1
90228	2.46E-09	-8.61	3.96	Mn+2	1	ACAC	1
90230	3.46E-12	-11.46	4.86	ACAC	1	Fe+2	1
90232	8.91E-12	-11.05	8.06	Cu+2	1	ACAC	1
90234	1.19E-11	-10.92	4.86	Zn+2	1	ACAC	1
90236	4.08E-14	-13.39	10.14	Fe+3	1	ACAC	1
90238	3.26E-07	-6.49	5.16	PHTH	1	H +1	1
90240	7.81E-11	-10.11	8.04	PHTH	1	H +1	2
90242	4.07E-08	-7.39	0.46	Na+1	1	PHTH	1
90244	4.07E-07	-6.39	1.92	Ca+2	1	PHTH	1
90246	5.99E-09	-8.22	2.22	Mn+2	1	PHTH	1
90248	3.44E-14	-13.46	3.52	Cu+2	1	PHTH	1
90250	5.77E-12	-11.24	2.42	Zn+2	1	PHTH	1
90252	2.38E-14	-13.62	7.78	Fe+3	1	PHTH	1
90254	4.88E-18	-17.31	4.82	Cu+2	1	PHTH	2
90256	8.20E-16	-15.09	3.72	Zn+2	1	PHTH	2
90258	4.42E-07	-6.35	4.86	MALI	1	H +1	1
90260	3.35E-10	-9.47	8.24	MALI	1	H +1	2
90262	1.10E-07	-6.96	0.46	Na+1	1	MALI	1
90264	2.18E-07	-6.66	0.36	K +1	1	MALI	1
90266	1.71E-06	-5.77	2.02	Mg+2	1	MALI	1
90268	5.41E-09	-8.27	6.02	Mg+2	1	MALI	1
H +1	1						

90270	2.20E-06	-5.66	2.22	Ca+2	1	MALI	1
90272	5.52E-09	-8.26	6.12	Ca+2	1	MALI	1
H +1	1						
90274	4.07E-08	-7.39	2.62	Mn+2	1	MALI	1
90276	1.44E-11	-10.84	2.92	MALI	1	Fe+2	1
90278	1.47E-13	-12.83	3.72	Cu+2	1	MALI	1
90280	3.70E-11	-10.43	6.12	Cu+2	1	MALI	1
90282	3.92E-11	-10.41	2.82	Zn+2	1	MALI	1
90284	7.83E-14	-13.11	6.62	Zn+2	1	MALI	1
H +1	1						
90286	6.44E-14	-13.19	7.78	Fe+3	1	MALI	1
90288	2.04E-06	-5.69	5.36	SUCA	1	H +1	1
90290	7.77E-09	-8.11	9.44	SUCA	1	H +1	2
90292	6.41E-08	-7.19	0.06	Na+1	1	SUCA	1
90294	7.92E-07	-6.10	1.52	Mg+2	1	SUCA	1
90296	7.92E-09	-8.10	6.02	Mg+2	1	SUCA	1
H +1	1						
90298	6.41E-07	-6.19	1.52	Ca+2	1	SUCA	1
90300	6.41E-09	-8.19	6.02	Ca+2	1	SUCA	1
H +1	1						
90302	9.44E-09	-8.02	1.82	SUCA	1	Mn+2	1
90304	4.73E-14	-13.32	3.02	SUCA	1	Mn+2	1
H +1	1						
90306	1.33E-12	-11.88	1.72	SUCA	1	Fe+2	1
90308	2.71E-14	-13.57	2.82	SUCA	1	Cu+2	1
90310	9.10E-12	-11.04	2.02	SUCA	1	Zn+2	1
90312	7.22E-14	-13.14	6.42	SUCA	1	Zn+2	1
H +1	1						
90314	5.94E-14	-13.23	7.58	Fe+3	1	SUCA	1
90316	3.05E-08	-7.52	3.58	DMBA	1	H +1	1
90318	2.47E-07	-6.61	1.06	Mg+2	1	DMBA	1
90320	3.99E-07	-6.40	1.36	Ca+2	1	DMBA	1
90322	2.12E-14	-13.67	2.76	Cu+2	1	DMBA	1
90324	5.65E-12	-11.25	1.86	Zn+2	1	DMBA	1
90326	2.76E-07	-6.56	4.08	BZA	1	H +1	1
90328	1.12E-07	-6.95	0.26	BZA	1	Mg+2	1
90330	1.44E-07	-6.84	0.46	BZA	1	Ca+2	1

90332	3.35E-09	-8.47	0.96	BZA	1	Mn+2	1
90334	6.08E-15	-14.22	1.76	BZA	1	Cu+2	1
90336	2.56E-12	-11.59	1.06	BZA	1	Zn+2	1
90338	1.11E-15	-14.96	5.44	BZA	1	Fe+3	1
90340	1.20E-04	-3.92	9.88	PHEN	1	H +1	1
90342	1.92E-16	-15.72	7.84	Fe+3	1	PHEN	1
90344	1.71E-06	-5.77	4.78	PROP	1	H +1	1
90346	3.47E-07	-6.46	0.66	Mg+2	1	PROP	1
90348	3.54E-07	-6.45	0.76	Ca+2	1	PROP	1
90350	1.19E-14	-13.92	1.96	Cu+2	1	PROP	1
90352	3.17E-12	-11.50	1.06	Zn+2	1	PROP	1
90354	2.17E-17	-16.66	3.64	Fe+3	1	PROP	1
90356	3.83E-09	-8.42	2.68	HBQN	1	H +1	1
90358	1.24E-06	-5.91	1.76	Mg+2	1	HBQN	1
90360	3.99E-07	-6.40	1.36	Ca+2	1	HBQN	1
90362	2.94E-08	-7.53	2.36	Mn+2	1	HBQN	1
90364	3.37E-12	-11.47	4.96	Cu+2	1	HBQN	1
90366	1.42E-09	-8.85	4.26	Zn+2	1	HBQN	1
90368	3.87E-14	-13.41	7.44	Fe+3	1	HBQN	1
90370	4.74E-10	-9.32	2.94	Mg+2	1	HBQN	2
90372	1.21E-10	-9.92	2.44	Ca+2	1	HBQN	2
90374	1.42E-11	-10.85	3.64	Mn+2	1	HBQN	2
90376	7.10E-13	-12.15	13.30	Fe+3	1	HBQN	2
90378	4.08E-13	-12.39	8.64	Cu+2	1	HBQN	2
90380	1.09E-12	-11.96	5.74	Zn+2	1	HBQN	2
90382	7.55E-06	-5.12	10.49	LIG4	1	H +1	1
90384	1.65E-06	-5.78	16.33	LIG4	1	H +1	2
90386	1.62E-10	-9.79	18.82	LIG4	1	H +1	3
90388	1.86E-15	-14.73	20.38	LIG4	1	H +1	4
90390	4.63E-05	-4.33	7.94	Ca+2	1	LIG4	1
90392	1.72E-05	-4.76	14.01	Ca+2	1	LIG4	1
H +1	1						
90394	5.33E-06	-5.27	6.91	Mg+2	1	LIG4	1
90396	7.36E-06	-5.13	13.55	Mg+2	1	LIG4	1
H +1	1						
90398	1.87E-07	-6.73	18.64	Fe+3	1	LIG4	1

```
90400    1.38E-12  -11.86    -0.20     LIG4   1     Fe+2   1
H +1  -1
90402    3.24E-08   -7.49    10.67     LIG4   1     Fe+2   1
90404    9.50E-15  -14.02    13.25     LIG4   2     Fe+2   1
90406    9.51E-18  -17.02    16.75     LIG4   2     Fe+2   1
H +1   1
90408    2.08E-11  -10.68    29.59     LIG4   2     Fe+2   1
H +1   2
90410    3.19E-06   -5.50     8.91     Mn+2   1     LIG4   1
90412    7.14E-07   -6.15    14.76     Mn+2   1     LIG4   1
H +1   1
90414    2.35E-10   -9.63     4.82     Cu+2   1     LIG4   1
H +1  -1
90416    9.81E-07   -6.01    14.94     Cu+2   1     LIG4   1
90418    1.83E-08   -7.74    19.71     Cu+2   1     LIG4   1
H +1   1
90420    6.26E-10   -9.20     1.92     Zn+2   1     LIG4   1
H +1  -1
90422    4.87E-06   -5.31    12.31     Zn+2   1     LIG4   1
90424    1.28E-07   -6.89    17.23     Zn+2   1     LIG4   1
H +1   1
90426    1.49E-06   -5.83    15.84     Al+3   1     LIG4   1
90428    3.42E-10   -9.47    18.70     Al+3   1     LIG4   1
H +1   1
90500    9.37E-05   -4.03     8.84     CAFF   1     H +1   1
90502    8.75E-07   -6.06    13.31     CAFF   1     H +1   2
90504    1.39E-11  -10.86     4.56     CAFF   1     Fe+2   1
90506    4.97E-18  -17.30     7.16     CAFF   1     Fe+2   2
90508    5.94E-14  -13.23    -4.31     CAFF   1     Fe+2   1
H +1  -1
90510    5.31E-16  -15.27     0.01     CAFF   2     Fe+2   1
H +1  -1
90512    4.74E-22  -21.32    -6.17     CAFF   3     Fe+2   1
H +1  -2
90514    1.50E-10   -9.82    -4.66     Mn+2   1     CAFF   1
H +1  -1
```

```
90516    8.06E-15  -14.09  -15.43     Mn+2   1     CAFF   1
H +1   -2
90518    1.30E-12  -11.88    6.32     Cu+2   1     CAFF   1
90520    1.06E-14  -13.97   10.73     Cu+2   1     CAFF   1
H +1    1
90522    5.31E-12  -11.27    0.43     Cu+2   1     CAFF   1
H +1   -1
90524    2.13E-20  -19.67    3.87     Cu+2   2     CAFF   1
H +1   -1
90526    4.37E-23  -22.36    0.92     Cu+2   2     CAFF   3
H +1   -3
90528    3.66E-28  -27.44    7.81     Cu+2   3     CAFF   2
H +1   -2
90530    1.82E-13  -12.74   -4.52     Cd+2   1     CAFF   1
H +1   -1
90532    5.90E-21  -20.23  -12.14     Cd+2   1     CAFF   2
H +1   -2
90534    5.03E-28  -27.30  -19.34     Cd+2   1     CAFF   3
H +1   -3
90536    2.63E-12  -11.58    3.30     Zn+2   1     CAFF   1
90538    6.03E-12  -11.22   -2.84     Zn+2   1     CAFF   1
H +1   -1
90540    8.54E-16  -15.07   -0.32     Zn+2   1     CAFF   2
H +1   -1
90542    3.03E-17  -16.52   -8.27     Zn+2   1     CAFF   2
H +1   -2
90544    5.27E-21  -20.28   -5.66     Zn+2   1     CAFF   3
H +1   -2
90546    7.33E-13  -12.14   -3.26     Ni+2   1     CAFF   1
H +1   -1
90548    3.76E-16  -15.43  -13.05     Ni+2   1     CAFF   1
H +1   -2
90550    1.02E-19  -18.99   -1.11     Ni+2   2     CAFF   1
H +1   -1
90552    2.31E-29  -28.64   -1.88     Ni+2   3     CAFF   2
H +1   -2
```

90554 7.72E-13 -12.11 -3.75 Co+2 1 CAFF 1
H +1 -1

ID C LOGC LOGK SPECIES: TYPE III - FIXED SOLIDS

50 -1.51E-02 -1.82 6.50 H +1 1
80000 6.55E-06 -5.18 12.67 Fe+3 1 Fe+2 -1
E- 1
80002 -3.44E-19 -18.46 25.70 Mn+2 -1 Mn+3 1
E- 1
80004 1.18E-15 -14.93 2.35 Cu+2 1 Cu+1 -1
E- 1
80006 1.62E-23 -22.79 30.57 Co+2 -1 Co+3 1
E- 1
80010 -3.11E-05 -4.51 21.29 CO3 1 H +1 2

ID C LOGC LOGK SPECIES: TYPE IV - PRECIPITATED SOLIDS

80102 3.21E-04 -3.49 40.99 Ca+2 5 PO4 3
H +1 -1
80608 6.51E-06 -5.19 -10.44 Fe+3 2 Fe+2 1
H +1 -8

ID C LOGC LOGK SPECIES: TYPE V - DISSOLVED SOLIDS

80098 5.29E-23 -22.28 -4.98 Ni+2 1 CO3 1
80100 2.42E-02 -1.62 4.12 Ca+2 1 SO4 1
80090 1.89E-06 -5.72 -0.31 Na+1 1 Cl 1
80104 2.71E-07 -6.57 44.26 Ca+2 4 PO4 3
H +1 1
80106 1.51E-02 -1.82 18.40 Ca+2 1 PO4 1
H +1 1
80110 5.58E-14 -13.25 -23.09 Ca+2 1 H +1 -2
80112 3.27E-04 -3.49 27.12 Ca+2 3 PO4 2
80114 7.56E-03 -2.12 18.10 Ca+2 1 PO4 1
H +1 1
80116 3.61E-04 -3.44 8.01 Ca+2 1 CO3 1

80200	1.17E-07	-6.93	23.40	Mg+2	3	PO4	2
80202	1.55E-03	-2.81	17.32	Mg+2	1	PO4	1
H +1	1						
80204	9.09E-08	-7.04	-16.97	Mg+2	1	H +1	-2
80206	1.77E-04	-3.75	7.61	Mg+2	1	CO3	1
80208	6.74E-08	-7.17	4.19	Mg+2	1	CO3	1
80210	1.68E-07	-6.77	16.04	Ca+2	1	Mg+2	1
CO3	2						
80211	3.25E-18	-17.49	28.05	Ca+2	1	Mg+2	3
CO3	4						
80212	4.09E-06	-5.39	20.51	Mg+2	1	NH3	1
PO4	1	H +1	1				
80214	6.97E-07	-6.16	9.78	Mg+2	1	K +1	1
PO4	1						
80600	4.83E-01	-0.32	-3.56	Fe+3	1	H +1	-3
80602	3.20E-02	-1.49	25.32	Fe+3	1	PO4	1
80606	8.51E-09	-8.07	-18.51	Fe+3	2	Fe+2	1
H +1	-8						
80096	1.64E-27	-26.78	-10.00	Co+2	1	CO3	1
80700	8.56E-10	-9.07	-13.02	Fe+2	1	H +1	-2
80702	2.64E-08	-7.58	9.76	Fe+2	1	CO3	1
80704	8.71E-15	-14.06	34.20	Fe+2	3	PO4	2
80701	2.28E-10	-9.64	1.98	SO4	1	Fe+2	1
80800	2.43E-08	-7.62	-15.32	Mn+2	1	H +1	-2
80802	1.72E-05	-4.77	8.82	Mn+2	1	CO3	1
80900	2.31E-08	-7.64	-8.80	Cu+2	1	H +1	-2
80904	1.88E-21	-20.73	35.90	Cu+2	3	PO4	2
80906	1.06E-11	-10.98	9.15	Cu+2	1	CO3	1
80908	3.95E-15	-14.40	4.56	Cu+2	2	CO3	1
H +1	-2						
80910	5.13E-24	-23.29	15.80	Cu+2	3	CO3	2
H +1	-2						
80912	7.57E-12	-11.12	14.76	Cu+2	1	BOH4	2
81200	7.07E-14	-13.15	33.50	Zn+2	3	PO4	2
81202	3.30E-07	-6.48	10.32	Zn+2	1	CO3	1
81204	7.74E-09	-8.11	-12.60	Zn+2	1	H +1	-2
83302	8.95E-12	-11.05	6.61	Cl	1	Cu+1	1

83304	1.42E-22	-21.85	-13.40	Cu+1	1	H +1	-1
84000	2.28E-23	-22.64	4.89	Ca+2	2	SiO4	1
84002	1.44E-21	-20.84	6.69	Ca+2	2	SiO4	1
84004	4.42E-06	-5.35	65.33	Ca+2	1	Al+3	2
SiO4	2						
84006	1.95E-12	-11.71	15.64	Mg+2	2	SiO4	1
84008	4.74E-04	-3.32	33.14	Na+1	1	Al+3	1
SiO4	1						
84010	1.87E-05	-4.73	31.34	K +1	1	Al+3	1
SiO4	1						
84012	2.81E-15	-14.55	24.75	SiO4	1	Fe+2	2
84014	1.35E-07	-6.87	31.36	Zn+2	2	SiO4	1
84016	1.83E-12	-11.74	20.06	Mn+2	2	SiO4	1
84018	8.43E-04	-3.07	-10.02	Al+3	1	H +1	-3
84020	1.19E-02	-1.92	-8.87	Al+3	1	H +1	-3
84022	1.53E-02	-1.81	-8.76	Al+3	1	H +1	-3
84024	0.00E+00	-55.47	-22.64	Al+3	2	SO4	3
84026	1.10E-11	-10.96	-4.84	K +1	1	Al+3	3
SO4	2	H +1	-6				
84028	7.20E-06	-5.14	17.97	Al+3	1	PO4	1
84030	7.39E-06	-5.13	11.51	Cd+2	1	CO3	1
84032	4.31E-12	-11.37	-0.44	Cd+2	1	SO4	1
84034	1.35E-10	-9.87	36.30	Cd+2	3	PO4	2
84036	1.56E-03	-2.81	7.88	Ca+2	1	MoO4	1
84038	3.51E-11	-10.46	0.14	Mg+2	1	MoO4	1
84040	4.36E-14	-13.36	6.00	Cu+2	1	MoO4	1
84042	4.45E-10	-9.35	7.22	MoO4	1	Fe+2	1
84044	6.78E-10	-9.17	3.65	Mn+2	1	MoO4	1
84046	2.66E-12	-11.57	4.46	Zn+2	1	MoO4	1

PERCENTAGE DISTRIBUTION OF COMPONENTS

BZA

99.3 PERCENT BOUND IN SPECIES # 164 BZA 1

Ca+2

27.5 PERCENT BOUND IN SPECIES # 1 Ca+2 1

```
          5.0     PERCENT BOUND IN SPECIES #70000    Ca+2    1
SO4     1
          1.9     PERCENT BOUND IN SPECIES #90390    Ca+2    1
LIG4    1
         64.3     PERCENT BOUND IN SPECIES #80102    Ca+2    5
PO4     3    H +1   -1

Mg+2
         84.8     PERCENT BOUND IN SPECIES #     2    Mg+2    1
         12.7     PERCENT BOUND IN SPECIES #70054    Mg+2    1
SO4     1

K +1
         98.7     PERCENT BOUND IN SPECIES #     4    K +1    1

Na+1
         99.1     PERCENT BOUND IN SPECIES #     5    Na+1    1

Fe+3
          1.8     PERCENT BOUND IN SPECIES #70200    Fe+3    1
H +1   -3
          1.4     PERCENT BOUND IN SPECIES #90398    Fe+3    1
LIG4    1
         96.8     PERCENT BOUND IN SPECIES #80608    Fe+3    2
Fe+2    1    H +1   -8

SUCA
         88.0     PERCENT BOUND IN SPECIES #   172    SUCA    1
          6.4     PERCENT BOUND IN SPECIES #90288    SUCA    1
H +1    1
          2.5     PERCENT BOUND IN SPECIES #90294    Mg+2    1
SUCA    1
          2.0     PERCENT BOUND IN SPECIES #90298    Ca+2    1
SUCA    1

Mn+2
         50.7     PERCENT BOUND IN SPECIES #     8    Mn+2    1
```

```
          8.1     PERCENT BOUND IN SPECIES #70272    Mn+2    1
SO4     1
         31.9     PERCENT BOUND IN SPECIES #90410    Mn+2    1
LIG4    1
          7.1     PERCENT BOUND IN SPECIES #90412    Mn+2    1
LIG4    1    H +1    1

Cu+2
         98.1     PERCENT BOUND IN SPECIES #90416    Cu+2    1
LIG4    1
          1.8     PERCENT BOUND IN SPECIES #90418    Cu+2    1
LIG4    1    H +1    1

Cd+2
         99.3     PERCENT BOUND IN SPECIES #60080    Cd+2    1
LIG4    1

Zn+2
         97.3     PERCENT BOUND IN SPECIES #90422    Zn+2    1
LIG4    1
          2.6     PERCENT BOUND IN SPECIES #90424    Zn+2    1
LIG4    1    H +1    1

Ni+2
         81.6     PERCENT BOUND IN SPECIES #60082    Ni+2    1
LIG4    1
         18.3     PERCENT BOUND IN SPECIES #60086    Ni+2    1
LIG4    1    H +1    1

Co+2
         94.3     PERCENT BOUND IN SPECIES #60088    Co+2    1
LIG4    1
          5.3     PERCENT BOUND IN SPECIES #60090    Co+2    1
LIG4    1    H +1    1

PHEN
```

```
        100.0     PERCENT BOUND IN SPECIES #90340   PHEN    1
H +1    1

Al+3
         99.6     PERCENT BOUND IN SPECIES #90426   Al+3    1
LIG4    1

HBQN
         93.8     PERCENT BOUND IN SPECIES #  166   HBQN    1
          4.6     PERCENT BOUND IN SPECIES #90358   Mg+2    1
HBQN    1
          1.5     PERCENT BOUND IN SPECIES #90360   Ca+2    1
HBQN    1

PROP
         97.4     PERCENT BOUND IN SPECIES #  174   PROP    1
          1.9     PERCENT BOUND IN SPECIES #90344   PROP    1
H +1    1

CAFF
         98.6     PERCENT BOUND IN SPECIES #90500   CAFF    1
H +1    1

LIG4
          7.6     PERCENT BOUND IN SPECIES #90382   LIG4    1
H +1    1
          1.7     PERCENT BOUND IN SPECIES #90384   LIG4    1
H +1    2
         46.3     PERCENT BOUND IN SPECIES #90390   Ca+2    1
LIG4    1
         17.2     PERCENT BOUND IN SPECIES #90392   Ca+2    1
LIG4    1    H +1    1
          5.3     PERCENT BOUND IN SPECIES #90394   Mg+2    1
LIG4    1
          7.4     PERCENT BOUND IN SPECIES #90396   Mg+2    1
LIG4    1    H +1    1
```

```
            3.2     PERCENT BOUND IN SPECIES #90410    Mn+2    1
LIG4    1
            4.9     PERCENT BOUND IN SPECIES #90422    Zn+2    1
LIG4    1
            1.5     PERCENT BOUND IN SPECIES #90426    Al+3    1
LIG4    1

SO4
           88.9     PERCENT BOUND IN SPECIES #  102    SO4     1
            4.1     PERCENT BOUND IN SPECIES #70000    Ca+2    1
SO4     1
            4.2     PERCENT BOUND IN SPECIES #70054    Mg+2    1
SO4     1
            1.6     PERCENT BOUND IN SPECIES #70114    K +1    1
SO4     1

Cl
           97.5     PERCENT BOUND IN SPECIES #  103    Cl      1
            2.2     PERCENT BOUND IN SPECIES #78700    Cl      1
NH3     1    H +1    1

NH3
           93.6     PERCENT BOUND IN SPECIES #78656    NH3     1
H +1    1
            4.4     PERCENT BOUND IN SPECIES #78700    Cl      1
NH3     1    H +1    1
            1.9     PERCENT BOUND IN SPECIES #78702    SO4     1
NH3     1    H +1    1

DMBA
           97.4     PERCENT BOUND IN SPECIES #  173    DMBA    1
            1.5     PERCENT BOUND IN SPECIES #90320    Ca+2    1
DMBA    1

SiO4
           99.9     PERCENT BOUND IN SPECIES #50014    SiO4    1
H +1    4
```

```
BOH4
          99.8      PERCENT BOUND IN SPECIES #78636    BOH4    1
H +1    1

MoO4
          99.8      PERCENT BOUND IN SPECIES #  152    MoO4    1

NO3
          99.5      PERCENT BOUND IN SPECIES #  157    NO3     1

DHBZ
          99.8      PERCENT BOUND IN SPECIES #90102    DHBZ    1
H +1    2

SAL
          99.9      PERCENT BOUND IN SPECIES #90138    SAL     1
H +1    1

HMPA
          97.3      PERCENT BOUND IN SPECIES #  168    HMPA    1
           1.2      PERCENT BOUND IN SPECIES #90122    Ca+2    1
HMPA    1
           1.2      PERCENT BOUND IN SPECIES #90124    Mg+2    1
HMPA    1

ACPH
         100.0      PERCENT BOUND IN SPECIES #90172    ACPH    1
H +1    1

HBA
          98.5      PERCENT BOUND IN SPECIES #  169    HBA     1

DEMA
          17.4      PERCENT BOUND IN SPECIES #  170    DEMA    1
          79.7      PERCENT BOUND IN SPECIES #90194    DEMA    1
H +1    1
```

```
ACAC
          98.4      PERCENT BOUND IN SPECIES #90222   ACAC   1
H +1   1
           1.0      PERCENT BOUND IN SPECIES #90224   Mg+2   1
ACAC   1

PHTH
          89.0      PERCENT BOUND IN SPECIES #  132   PHTH   1
           1.3      PERCENT BOUND IN SPECIES #60148   K +1   1
PHTH   1
           4.1      PERCENT BOUND IN SPECIES #90238   PHTH   1
H +1   1
           5.1      PERCENT BOUND IN SPECIES #90244   Ca+2   1
PHTH   1

MALI
          80.3      PERCENT BOUND IN SPECIES #  171   MALI   1
           1.8      PERCENT BOUND IN SPECIES #90258   MALI   1
H +1   1
           7.1      PERCENT BOUND IN SPECIES #90266   Mg+2   1
MALI   1
           9.2      PERCENT BOUND IN SPECIES #90270   Ca+2   1
MALI   1

Fe+2
          99.5      PERCENT BOUND IN SPECIES #80608   Fe+3   2
Fe+2   1    H +1   -8

Co+3
         100.0      PERCENT BOUND IN SPECIES #   17   Co+3   1

Mn+3
         100.0      PERCENT BOUND IN SPECIES #77402   Mn+3   1
H +1  -1

Cu+1
```

```
          95.8     PERCENT BOUND IN SPECIES #   33   Cu+1    1
           4.2     PERCENT BOUND IN SPECIES #77300   NH3     2
Cu+1    1

E-
         100.0     PERCENT BOUND IN SPECIES #   99   E-      1

CO3
           1.1     PERCENT BOUND IN SPECIES #70078   Mg+2    1
CO3     1    H +1    1
          64.1     PERCENT BOUND IN SPECIES #78600   CO3     1
H +1    1
          34.4     PERCENT BOUND IN SPECIES #78602   CO3     1
H +1    2

PO4
           2.4     PERCENT BOUND IN SPECIES #78612   PO4     1
H +1    2
          96.4     PERCENT BOUND IN SPECIES #80102   Ca+2    5
PO4     3    H +1   -1

H +1
          92.3     PERCENT BOUND IN SPECIES #50014   SiO4    1
H +1    4
           6.2     PERCENT BOUND IN SPECIES #78656   NH3     1
H +1    1
```