THE MANUFACTURE OF MONOSODIUM PHOSPHATE FROM WET PROCESS ACID BY AMINE EXTRACTION

BY

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SYNOPSIS

Monosodium phosphate (NaH_2PO_4) may be prepared from a mixture of phosphoric acid and sodium chloride on the principle that an amine in organic solution can extract the elements of hydrochloric acid (HCl). This is possible because amines are more selective for hydrochloric than for phosphoric acid.

If wet process phosphoric acid is used, the impurities must be separated in some way from the final product. The work described here involves a study of the distribution of phosphoric acid itself, and the impurities trivalent iron and sulphate, between aqueous solutions and kerosene solutions of the commercial amine Amberlite LA-1.

In a countercurrent extraction process, approximately twenty theoretical stages would be needed to reduce the iron concentration to the food grade level. Sulphate is held in the organic phase. Monosodium phosphate can be recovered by stripping the organic phase with a sodium chloride solution.

An attempt was made to explain the extraction of phosphoric and sulphuric acids from a mixture. It was found that amine extraction followed a pattern similar to that of gas adsorption, and a modified BET equation gave a fair but not highly accurate fit of the distribution data.

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INTRODUCTION

Orthophosphoric acid of a high degree of purity is an important commercial chemical. From it are derived the ortho- and polyphosphate salts which are used in detergents, water treatment, metal surface finishing, cattle feeds and also in such products as baking powder, soft drinks and toothpaste. For the majority of purposes it is the salts, rather than the acid, which are required, sodium being the most usual cation employed.

Pure phosphoric acid is commonly prepared by reducing phosphate rock in an electric furnace, burning the elemental phosphorus evolved and dissolving the resulting phosphorus pentoxide in water. To a lesser extent, orthophosphate salts are prepared from wet process phosphoric acid, by progressive neutralisation and precipitation of impurities.

The purpose of this study is to examine a novel method of preparing the salt sodium dihydrogen orthophosphate, using wet process phosphoric acid and sodium chloride. Phosphoric acid is extracted by a solution of a high molecular weight secondary amine, which is then stripped with sodium chloride. The process works because the amine is more selective for hydrochloric than for phosphoric acid, and so, in the stripping step, an exchange of chloride and dihydrogen phosphate ions takes place, resulting in an aqueous solution of sodium dihydrogen phosphate.

Because the amine solution has different selectivities for phosphoric acid and the various impurities present, separation can be achieved with a suitably designed counter-current operation.

CHAPTER 1

BACKGROUND TO PHOSPHATE TECHNOLOGY

1.1 DIFFERENT APPROACHES TO THE PROBLEM OF PURIFICATION

The raw material of the phosphate industry is phosphate rock, a mineral which contains considerable amounts of various impurities. Most of the rock which is mined goes into the production of fertilisers, and so a high degree of purification is not necessary, but for many applications, and especially food purposes, extreme purity is required.

The most common method of manufacturing a pure phosphoric acid is to burn elemental phosphorus obtained by reducing phosphate rock with coke in an electric furnace (1). The product obtained by dissolving in water the phosphorus pentoxide thus formed, is known as thermal grade acid. In a properly operating plant, it is very pure, but the process is expensive. Electric furnaces are heavy consumers of electricity, and conditions in the plant are highly corrosive, with the attendant risk of contamination of the product with traces of the plant construction materials.

For fertiliser applications, the usual way of preparing phosphoric acid is to treat phosphate rock with sulphuric acid, and then filter off the calcium sulphate precipitated (2). This is known as the wet process and, throughout this dissertation, the term will be used to refer only to phosphoric acid produced with sulphuric acid in this way. The resulting acid may be purified to some extent by evaporation followed by further precipitation and filtration. A typical composition for a South African evaporated acid (3) is given in Table 1.1. In the case of some acids, aluminium is also present as an impurity.

TABLE 1.1

COMPOSITION OF A TYPICAL SOUTH AFRICAN WET PROCESS PHOSPHORIC ACID AFTER EVAPORATION

Component	Weight %
P	22,5
Mg	1,1
Fe	0,26
Ca	0,003
Mn	0,021
Cu	0,004
Ni	0,0012
F	0,24
SO_3	1,9

Wet process acid is much cheaper than the thermal grade, and can be used to make pure phosphate salts by a process of progressive neutralisation and precipitation (4). As the pH is increased, impurities come out of solution, each impurity having a pH at which its solubility is a minimum. Final purification is achieved by crystallising the phosphate from solution. In spite of the relative cheapness of wet process phosphoric acid, this method of purification has not been generally preferred to the use of thermal grade acid.

The other strong mineral acids may also be used to attack phosphate rock. The use of nitric acid has been described (5,6), but the more important acid is hydrochloric.

When this acid is used, the resulting solution contains calcium chloride, which is highly soluble, unlike calcium sulphate, and so a further separation step is required. The Israeli Mining Industries Institute for Research and Development (hereafter referred to as I.M.I.) has developed a process based on extraction with butanol (7,8,9,10,11) which went into full scale production in the early 1960's. The product is more concentrated than unevaporated wet process acid (80% phosphoric acid by weight) and is also much purer (12). For instance, iron is only 0,03% (cf. the value in Table 1.1).

However, the use of hydrochloric acid is feasible only in localities where the acid is readily available, such as Israel with its chloride-rich Dead Sea. In South Africa, sulphuric acid is cheap and plentiful, and so this study is confined to processes based on this acid.

1.2 METHODS OF PURIFYING WET PROCESS PHOSPHORIC ACID

1.2.1 Processes Based on Organic Solvents

The methods described in this section refer to the purification of H_3PO_4 solutions produced by the sulphuric acid wet process. The manufacture of pure phosphate salts is considered separately in Section 1.5. Of course, if pure H_3PO_4 is available these salts may be obtained by neutralisation with NaOH or Na_2CO_3.

The use of polar solvents for H_3PO_4 was proposed by C.H. Milligan in the 1930's (13), who suggested that the gypsum produced in the wet process need not be filtered off, but that H_3PO_4 be separated from the slurry by solvent extraction. However, the presence of the gypsum causes three serious difficulties (14). In the case of solvents such as butanol, which are partly miscible with water, the aqueous acid concentration should be above the plait point[1] of the ternary diagram H_3PO_4-H_2O-solvent, and this may be difficult to arrange. Also, it is possible to have H_2SO_4 extracted in preference to H_3PO_4, with the gypsum redissolving and calcium phosphate precipitating, and finally, solvent recovery from the gypsum cake is difficult. Hence it is better to accept the necessity of filtering the acid from the gypsum cake prior to further purification operations.

Another idea involves the addition of a completely miscible solvent, such as methanol, to the filtered acid (15), which causes precipitation of a portion of the impurities. This is an inefficient method, however, and the levels of some impurities, such as H_2SO_4, are not reduced at all.

Many different solvents and organic solutions have been proposed for extracting H_3PO_4, and while the general flow layouts are all similar, the details of the processes may differ significantly. In fact, because of the very wide selections of extractants available, in the form of either single components or mixtures, and the infinite range of possible parameters, it is very difficult to find one process design which can be shown to be more suitable for a particular application than any other.

1.2.2 Organic Phases Suitable for Phosphoric Acid Extraction

The main classes of organic extractants comprise alcohols, both straight chain and cyclic, ketones, ethers, alkyl phosphates, amines and amides. A diluent may be used, particularly with the latter three classes. Typical diluents are benzene and kerosene.

One patent (16), which describes a method for separating H_3PO_4 from the impurities titanium and vanadium, gives a useful list of various extractants and diluents.

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[1] The plait point is the point on the triangular phase diagram at which the tie-lines become infinitely short, and the two phases become one.

Amines are mentioned generally in several references (17,18,19,20). In particular, the use of tri-n-octylamine (21) and tricaprylylamine (22) has been described.

1.2.3 Schemes for Impurity Removal in Liquid Extraction

If a solvent exhibits a different selectivity for H_3PO_4 and a particular impurity, separation can be achieved by using a number of countercurrent extraction stages. If the impurity prefers the aqueous phase, it will be separated in the extraction process. If it prefers the organic phase, there are two ways of removing it. One is to extract it from the aqueous phase until that phase is virtually pure with respect to the impurity, and then to extract H_3PO_4 (10). This results in an organic phase not contaminated with any of the impurity.

The other way is to extract both H_3PO_4 and the preferentially selected impurity, and then to use a stagewise stripping operation resulting in a pure aqueous solution of the acid and an organic phase containing the impurity.

In some proposed schemes, pre-treatment of the phosphate rock is used, or some complexing agent may be added to change selectivities (21). The large-scale addition of salts such as $CaCl_2$ also aids extraction and impurity removal, and is described here in Section 1.2.5.

In general, anionic impurities prefer the organic phase, while cationic impurities prefer the aqueous phase, although there exceptions. Many cations, especially those of the transition elements, are complexed in orthophosphate solution, this complexing being very strong in the case of some, such as iron III (23). All the impurities, and the H_3PO_4, interfere with other, and so the overall extraction picture is likely to be complex.

There follow a few examples of liquid extraction purification processes which have been proposed:

1) Phosphate rock is calcined and treated with H_3PO_4 itself to remove impurities such as iron. It is then treated with H_2SO_4, and the slurry contacted with a C_3 to C_8 alcohol (24).
2) An organic phase consisting of an alkyl or aryl phosphate dissolved in kerosene is used. First, sulphate and fluoride are pre-extracted, and then the H_3PO_4. The acid may be recovered with a water strip, or Na_2CO_3 may be used to give sodium phosphate salts (25).
3) The stripping process in 2 can be done with a 40% NaH_2PO_4 solution. This seems to have advantages for keeping certain impurities in the organic phase (26).
4) A long chain amine or amine salt may be used, first to extract impurities, and then H_3PO_4. A C_{10} alcohol is used as a solubiliser for the organic phase, and stripping is by water (22).
5) This is another amine proposal similar to 4. Precipitaion of Fe^{3+} and Al^{3+} may be prevented by the addition of a sequestering agent, such as a polycarboxylic acid (17).
6) Addition of a small amount of H_2SO_4 (0,1 - 5%) may enhance H_3PO_4 extraction by boosting the hydrogen ion level. Extraction with dipropyl ether and water stripping are suggested (27).
7) In an amine extraction process, stagewise stripping with a solution containing a polyphosphate holds Fe^{3+} in the organic phase. The resulting strip solution may contain as little as 2 ppm iron (21).

1.2.4 The Use of Ion Exchange Resins

Cation exchange resins may be used to prepare H_3PO_4, but the method is not to attempt the removal of cationic impurities by ion exchange, since many of these are too strongly complexed with phosphate to participate. However, phosphate rock may be dissolved in H_3PO_4 itself at a high temperature and then, on cooling, crystals of pure $Ca(H_2PO_4)_2.H_2O$ form which are separated, redissolved and treated with a cation resin in the hydrogen form to replace the calcium and thus give H_3PO_4 (28). A variation of this process uses nitric acid to dissolve phosphate rock after which, it is claimed, $CaHPO_4$ can be precipitated by the addition of ammonia. The precipitate is then treated with H_3PO_4 to form $Ca(H_2PO_4)_2.H_2O$, and so on (29).

The dissolution of some phosphates themselves by cation exchange resins has been described (30). Such a process is more of a curiosity than a real alternative, and the resulting acid still contains some impurities.

Phosphate may be adsorbed on to a strong base anion exchanger from non-acid solutions, and thus separated from impurities (31). However, since acidity seriously impairs the process, it cannot be used on H_3PO_4 solutions, and so is not the answer to this purification problem.

A serious disadvantage, which all these ion exchange processes share, is the necessity for regeneration of the resin, which would contribute greatly to the cost.

1.2.5 Chloride Addition to Wet Process Acid

Where H_3PO_4 is produced by the sulphuric acid wet process, it is possible to add chloride in the form of $CaCl_2$ and HCl, thus enabling the I.M.I. process to be carried out (14,32). This process was mentioned in Section 1.1 and is described more fully in Section 1.3. It depends greatly on the effect of $CaCl_2$, which aids extraction of H_3PO_4 and the retention of impurities in the aqueous phase.

The I.M.I process, as used in Israel, employs HCl to dissolve the phosphate rock, and so the proportions of $CaCl_2$ and H_3PO_4 in the resulting liquor are more or less fixed. On the other hand, if the chloride is added only after preparation of

H_3PO_4 by the wet process, these proportions may be varied so as to give the best possible extraction and purification characteristics.

If a source of HCl is available, this can be used to dissolve some phosphate rock and thus produce the $CaCl_2$ required. Also, the process needs a certain amount of free HCl, and this may be kept in closed cycle.

If HCl is not readily available, the $CaCl_2$ must also be kept in closed cycle, by treating the effluent brine to precipitate impurities and concentrating it by evaporation.

The process can easily achieve a product acid of detergent or food grade purity (33).

1.3 THE I.M.I. BUTANOL-BASED PROCESS

The I.M.I. process (7,8,9,10,11) has achieved great industrial success, and is also a good model for other processes. Consequently, it requires further discussion.

A simplified plant layout is given in Fig. 1.1. After the phosphate rock has been dissolved in HCl, the solution is passed through a thickener to remove suspended matter, and then flows to the extraction section of the plant, where it is contacted countercurrently with butanol. The loaded butanol passes first to the purification and then to the washing section. Water is fed into the washing section, and this removes most of the acid. A portion of the washings is evaporated to produce the product acid. Some HCl and butanol come off in the process, and these streams are recycled back to the points where they are required. The rest of the washings is passed on to the purification section, where it reduces the concentration of some of the impurities in the loaded butanol from the extraction section. The aqueous effluent from the purification section is added to the acid feed.

The washed organic phase is used to strip the last traces of H_3PO_4 from the depleted acid feed in the stripping section.

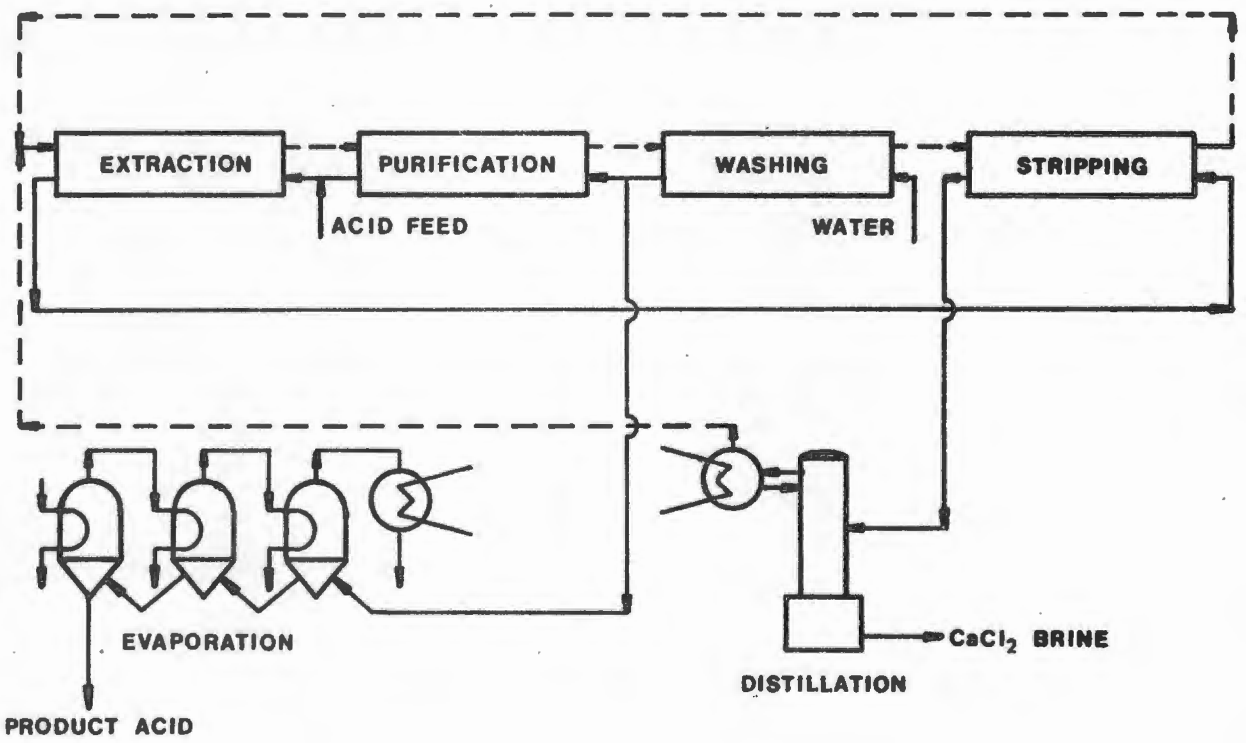

FIG. 1.1

The I.M.I. phosphoric acid process.
——— Aqueous streams. ----- Organic streams.

The spent $CaCl_2$ brine is distilled to recover butanol, which has appreciable solubility in water. There is no essential difference in the operation of the extraction and stripping sections.

Mixer-settlers are used throughout, and I.M.I. has developed its own design (9,34) which has proved to be very effective.

An interesting aspect of the process is the effect which $CaCl_2$ has on the extraction of H_3PO_4 and the retention of impurities. At high aqueous acid concentrations, the presence of $CaCl_2$ suppresses the extraction of acid, whereas at low acid concentrations, the opposite effect occurs. Some figures for the distribution coefficient $K_{H_3PO_4(solv/aq)}$ for the system H_3PO_4-$CaCl_2$-H_2O-(iso-amyl alcohol) have been published (14). This alcohol behaves in a similar way to butanol.

Cationic impurities tend to stay in the aqueous phase in the form of chlorides, and the overall result is that virtually complete separation of H_3PO_4 from the $CaCl_2$ brine can be effected, with a large degree of purification. This is in contrast to some processes which extract only part of the acid, and rely on the remainder to carry the impurities (10).

1.4 PURIFICATION BY TEMPERATURE CYCLING

Since the extraction of H_3PO_4 is exothermic, recovery from the organic phase can be effected by a rise in temperature. The process has been studied at I.M.I. (35), where n-butyl ether was selected as a suitable solvent. It has the advantage of producing a concentrated product in a simple manner, but purification is not complete.

1.5 PRODUCTION OF PURE ORTHOPHOSPHATE SALTS

1.5.1 A New Approach

Most of the very pure phosphoric acid produced is converted to salts, usually of sodium and sometimes of potassium, which are then used as they are, or after conversion to polyphosphates, mainly in the detergent and food industries.

As mentioned in Section 1.1, the traditional method of making pure phosphate salts is to neutralise thermal grade acid, with progressive neutralisation of wet process acid also finding application. However, certain integrated processes have been proposed as more satisfactory production methods. These processes are aimed at producing the phosphate salt required in a specific and direct manner, using the cheapest starting materials available.

A good example is a process (36) patented by I.M.I. whereby NaCl or KCl is used as the source of the alkali metal. The salt is mixed with an equimolar amount of $H_3PO_4$and heated in the presence of n-octane. This solvent extracts HCl to give the dihydrogen salt. It is not possible to replace further hydrogens as n-octane is not basic enough to perform this operation. The method does not bring about much purification, and so only pure acid should be used. The great advantage is the substitution of alkali chlorides for the more expensive hydroxides or carbonates which are normally used.

1.5.2 The Use of Amines

Robert Kunin of the Rohm and Haas Co. Ltd., has suggested a process (37) based on a remarkable property of certain amines, namely their ability to form salts of different acids with widely differing readiness. For instance, the amine chloride is far more stable than the amine phosphate, and in an acidic aqueous/organic system with both phosphate and chloride present, the former ion prefers the aqueous phase while the latter prefers the organic, and so a separation is achieved. The selectivity may be higher than 100 (see Chapter 3). If an amine loaded with phosphate is contacted with a solution of NaCl, an exhange of Cl^- and $H_2PO_4^-$ ions takes place, resulting in an aqueous solution of NaH_2PO_4 and an organic phase containing HCl, which can be removed by treatment with a lime slurry, thus converting the amine back to its free base form, ready for re-use.

The idea is simple and effective, and forms the basis of this thesis.

1.6 THE DEVELOPMENT OF AMINE EXTRACTION PROCESSES

The process described by Kunin involves anion exchange, and amines used in this way are often known as liquid anion exchangers. They must be virtually insoluble in water, and consequently, only high molecular weight amines are used. The commonest varieties are aliphatic secondary and tertiary amines; their action is very similar to that of the weakly basic ion exchange resins which have the same functional groups. The amine is generally dissolved in a solvent, in order to reduce the viscosity and the slight water solubility.

In 1948, Smith and Page reported the ability of long chain aliphatic amines to complex organic and inorganic acids (38). A number of interesting applications was suggested, for example, the purification of penicillin.

The first large-scale amine extraction process was for the recovery of uranium from dilute leach liquors. This was described in 1958 (39). In acid sulphate solution, some of the uranium is present in the form of the complexes $[UO_2(SO_4)_2]^{2-}$ and $[UO_2(SO_4)_3]^{4-}$, and these are extracted in preference to all other anions. The process was also studied in South Africa in the early 1960's, (40) and has subsequently been implemented in this country.

Other metals such as vanadium and tungsten may also be extracted by amine processes (41). In fact, there is a vast scope for the use of amines and similar compounds in hydrometallurgy.

Apart from H_3PO_4, other acids may also be purified by amine extraction (42). A process for the recovery of HF from dilute solutions has been described (43), and its implementation has made the production of this chemical considerably cheaper.

CHAPTER 2

A PROPOSED EXTRACTION PROCESS FOR MONOSODIUM PHOSPHATE

2.1 AMINES AS LIQUID ANION EXCHANGERS

In his paper entitled 'Ion Exchange in Chemical Synthesis' (37), Robert Kunin describes several applications for anion exchangers both solid and liquid. These are:

Alkali bicarbonates from carbon dioxide and alkali chlorides;

Alkali bisulphites from sulphur dioxide and alkali chlorides;

Alkali dihydrogen phosphates from phosphoric acid and alkali chlorides;

Alkali salts of organic acids using alkali chlorides.

In the case of di- and tribasic acids, the replacement of the second hydrogen atom is also discussed, although this is much more difficult to accomplish.

The conversion of an acid HA to its sodium salt may be represented as follows:

$$R_2NH + HA + NaCl \rightleftharpoons R_2NH_2Cl + NaA \qquad \text{-----}\ 2.1$$

If the amine is more selective for Cl^- than for A^-, the equilibium favours the forward reaction, as desired. For most anions, this is indeed the case.

Another method of achieving the same result is first to load the amine with HA and then to strip with NaCl, whereupon exchange of A^- and Cl^- ions takes place:

$$\left.\begin{array}{l} R_2NH + HA \rightleftharpoons R_2NH_2A \\ R_2NH_2A + NaCl \rightleftharpoons R_2NH_2Cl + NaA \end{array}\right\} \qquad \text{-----}\ 2.2$$

This process really is anion exchange, as opposed to equation 1.1, which looks more like liquid extraction. It may appear that both 1.1 and 1.2 are so essentially similar that no important difference exists; however, when it comes to certain practical situations, the difference is very important indeed.

Equations 2.1 and 2.2 are more specific examples of the general organic solvent process for the formation of salts:

$$MX_{aq} + HY_{org} \rightleftharpoons MY_{aq} + HX_{org} \quad \text{-----} \quad 2.3$$

where M represents the cation and X, Y are the two anions. Such processes, using various organic phases, have been described, including their application to NaH_2PO_4 manufacture (44,45). Amine solutions form just one group in a whole range of possible organic extractants, and their use introduces no unique departure from the general principle. However, because of the spectacular selectivities which many amines exhibit, their use is eminently suitable.

It should be remembered that the amine mechanism depends on the protonation of the basic amino group, and subsequent attachment of an anion. Consequently, acids which have a high dissociation constant are more readily extracted, and this selectivity decreases with increasing basicity of the amine, since a strong base is effective for neutralising both strong and weak acids. This limits one to the use of weak bases, such as secondary and tertiary aliphatic amines, and tends to exclude such strong bases as quaternary ammonium salts.

The necessity to use weak bases does have the disadvantage that it becomes difficult to neutralise the second hydrogen atom of di- and tribasic acids, although this difficulty may sometimes be overcome by staging.

2.2 KUNIN'S PREPARATION OF NaH_2PO_4

The amine which Kunin used in his synthesis was Amberlite LA-1, which is not one chemically pure substance, but rather a group of secondary aliphatic amines of molecular weight 351 - 393 (46). A 30% H_3PO_4 solution was used, and this was mixed with LA-1 on an equimolar basis. Presumably, no diluent was used with the LA-1. Extraction of 99% of the H_3PO_4 is claimed, to form the $H_2PO_4^-$ salt of the amine, which was then stripped with saturated NaCl solution at various amine to NaCl molar ratios. At a ratio of 1 to 1,33, 100% conversion of NaCl to NaH_2PO_4 was obtained. Na_2HPO_4 was also produced, but not to such a great extent. For instance, at an amine to NaCl ratio of 1 to 1, 16% of the NaH_2PO_4 was converted to Na_2HPO_4.

Kunin also used a dirty wet process H_3PO_4, in conjunction with a 40% solution of LA-1 in kerosene. This time, the NaCl solution was added to the acid before extraction. On shaking with LA-1, a precipitate occurred in the aqueous phase, caused by impurities coming out of solution under the influence of increasing pH. This precipitate was filtered off and the aqueous filtrate contacted with more LA-1, separated, evaporated and fused to the glassy phosphate which was analysed and found to be substantially free of impurities. The conclusion was that LA-1 could be used to produce pure NaH_2PO_4 from wet process H_3PO_4.

2.3 SOME PRACTICAL CONSIDERATIONS

The above preparation from wet process H_3PO_4 looks reasonable, but on closer inspection, serious difficulties emerge. Firstly, the formation of a precipitate during a liquid extraction operation would be most awkward from an engineering point of view. One of the big advantages of an extraction process for NaH_2PO_4 would be the avoidance of the necessity to filter precipitates. In tests done in the early stages of the present study it was found that precipitates, far from settling entirely to the bottom, form a thick scum at the aqueous/organic interface, and prevent complete phase separation. Such a situation, while not a great hindrance in a laboratory test, would be quite unacceptable industrially, as it results both in very difficult process operation and serious loss of organic phase.

Another consideration is the extent to which cations are precipitated. Although Kunin indicates complete precipitation, he does not mention cations such as Mg^{2+}, which may tend to be only partly precipitated. In the absence of very rigorous pH control, cations are also likely to be left in solution.

In view of the above, Kunin's method, without modifications, was ruled out as a plausible solution to the problem. It should be noted that when he used wet process H_3PO_4, he added the NaCl before the amine extraction step, whereas with pure H_3PO_4, he used amine extraction of the acid and subsequent stripping with NaCl. This is an indication that the extraction-stripping method did not work for wet process H_3PO_4.

2.4 FINDING A VIABLE PROCESS

2.4.1 Preliminary Steps

Before starting on any experimental work involving the determination of extraction isotherms and distribution coefficients, it was necessary to decide upon a process flow sheet which would be industrially feasible and free of the problems mentioned above. For the sake of simplicity, LA-1 was to be used throughout, with kerosene as the diluent. Because amine salts sometimes come out of organic solution to form a third phase, it was found necessary to add a more polar compound than kerosene as a solubiliser, and for this purpose n-decanol was used.

This alcohol had been used in the previously mentioned study of uranium extraction (40), and proved quite satisfactory.

2.4.2 Extraction of Phosphoric Acid with LA-1

Preliminary tests were done using H_3PO_4 solutions of various concentrations, containing no impurities, and various organic phase mixtures, initially without decanol. Kerosene solutions containing 10% by volume of LA-1 were used, this concentration being equivalent to about 0,22 M (46).

When shaken with very dilute H_3PO_4 solutions, 0,5 M or less, a white emulsion formed, from which a certain amount of clear amine solution eventually settled out on the top, but which otherwise remained stable, even after several weeks. The reason for this is the limited solubility of the amine phosphate salts in the kerosene, from which they may be precipitated into the aqueous phase. At higher aqueous H_3PO_4 concentrations, this effect does not occur. The amine phosphate takes up extra H_3PO_4 molecules as follows:

$$R_2NH_2H_2PO_4 + H_3PO_4 \rightleftharpoons R_2NH_2H_2PO_4.H_3PO_4 \quad \text{-----} \; 2.4$$

This seems to stabilise the salts, keeping them in solution. In the absence of decanol, an aqueous H_3PO_4 concentration of about 5 M is needed to prevent cloudiness forming in the aqueous phase. Of course, the aqueous concentrations referred to are those at equilibrium, not the initial concentration before contacting the two phases.

With H_2SO_4 and HCl, no precipitation of the salts occurs under any circumstances.

As the aqueous H_3PO_4 concentration is increased still further, the amine/H_3PO_4 complexes again become insoluble, and form a third phase consisting of a dark brown viscous layer at the aqueous/organic interface. This does not present such a serious problem as the salt precipitation at low H_3PO_4 concentration, but it must be avoided for ease of organic phase handling. Third phase formation is common in amine/acid extraction systems, and has been described for the case of Amberlite LA-2/hexane/H_2SO_4 (47).

The addition of decanol inhibits both precipitation of amine salts and third phase formation. It was found that a relatively large amount of decanol is required, compared to that necessary for uranium extraction, the amount eventually decided upon being twice the volume of LA-1 used. This makes it possible to work down to an aqueous H_3PO_4 concentration of 1-2 M, and 3rd phase starts forming at 14 M. These figures are fairly independent of the actual LA-1 concentration.

Another effect of decanol is to increase the organic H_3PO_4 concentration in equilibrium with any given aqueous H_3PO_4 concentration.

The amine/H_3PO_4 complexes in the organic phase are always hydrated, and so, for material balance, it is necessary to know how much water is extracted along with the acid. Fig. 2.1 shows the extraction curves for H_3PO_4 and water with 5% LA-1, 10% decanol (by volume) in kerosene. The acid curve was obtained by titration using a pH meter, and the water curve by a material balance method involving weighing. (See Section 3.9 and Appendix B.)

2.4.3 The Effect of Cationic and Anionic Impurities

In considering possible process flow sheets, it is important to know how the various impurities distribute themselves between the aqueous and organic phases. Anionic impurities prefer the organic phase, being extracted in preference to phosphate. The main anionic impurities are sulphate, fluorosilicate and arsenate.

The cationic impurities cause more trouble than the anionic. Many cations are complexed in phosphate solution (23), and this causes them to be co-extracted with phosphate to varying extents. The most troublesome cation is Fe^{3+}, which is the most strongly complexed, so that any process which deals effectively with it must also deal more than adequately with the other cations, such as Mg^{2+}, Ca^{2+}, Cu^{2+} and Al^{3+} when it is present.

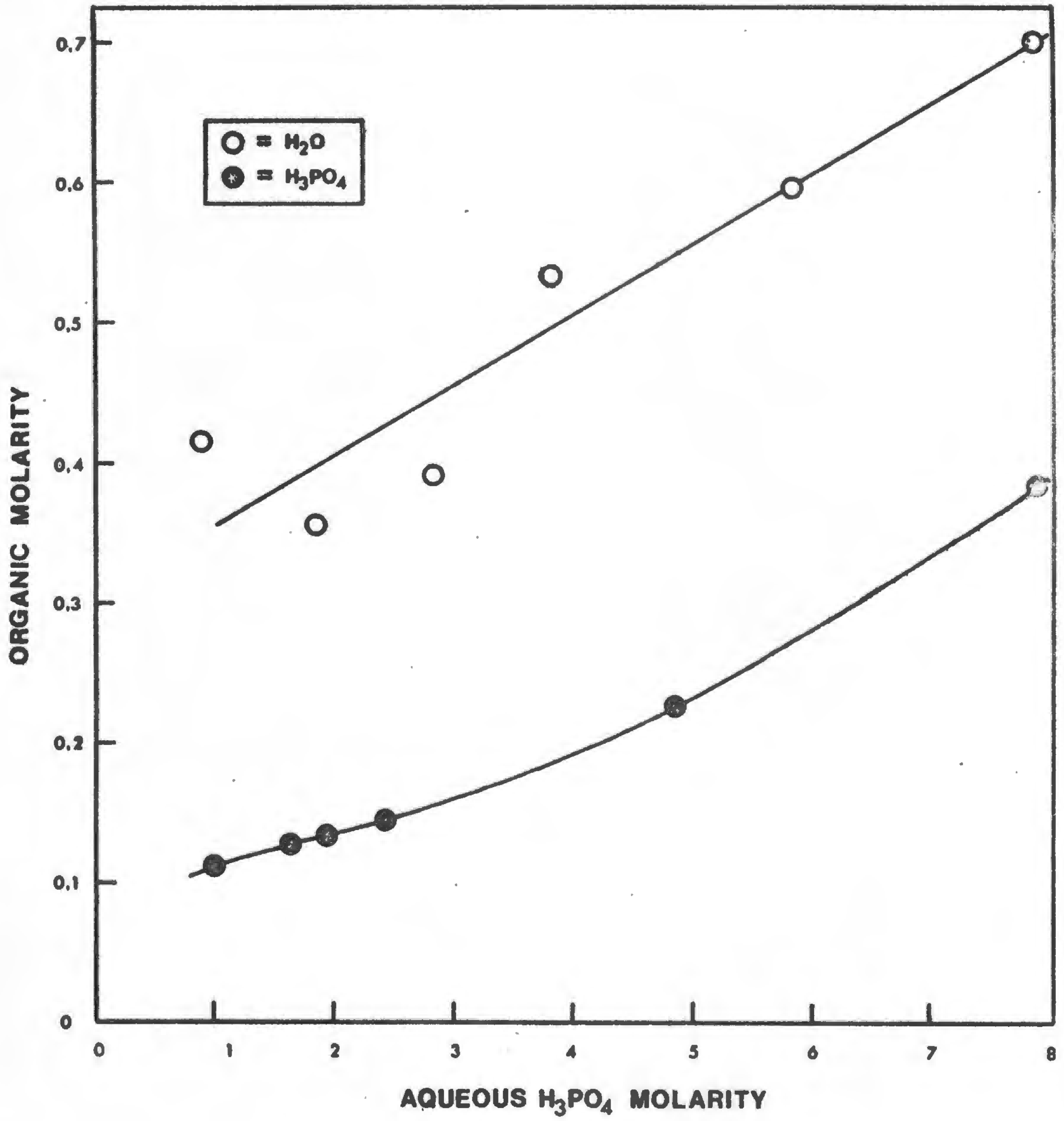

FIG. 2.1

H_3PO_4 and H_2O extraction curves for 5% LA-1, 10% decanol in kerosene. (Volume %.)

In acid systems not containing chloride, Fe^{3+} favours the aqueous phase, this preference increasing with increasing aqueous H_3PO_4 concentration.

When chloride is present, Fe^{3+} may be extracted into the organic phase as the complex $FeCl_4^-$ (9,48). This suggests that it may be removed by extracting from a wet process H_3PO_4/NaCl mixture, leaving an NaH_2PO_4 solution free of both Fe^{3+} and anionic impurities, but still containing other cations such as Mg^{2+}. Unfortunately, this method of Fe^{3+} removal does not work under all conditions but only, in the process under consideration, at very low acid concentrations. Fig. 2.2 shows the amount of Fe^{3+} remaining in the aqueous phase after contact with a 10% LA-1 solution (without decanol). The 1 to 1 molar ratio mixture of H_3PO_4 and NaCl was at a concentration of 0,22 M, and various ratios of LA-1 to H_3PO_4/NaCl were used. At a 2 to 1 ratio, 92% of the Fe^{3+} was removed, and this in only one contact step.

The difficulty with low product concentration is that evaporation becomes very costly. At higher concentrations, it becomes more difficult to remove Fe^{3+}. For instance, if NaH_2PO_4 is added to make the solution up to 1 M, the amount of Fe^{3+} removed at an LA-1 to H_3PO_4/NaCl ratio of 2 to 1 is only 50%, and at 5 M, virtually no Fe^{3+} is removed at all.

On regenerating the LA-1 solutions used in the test with lime, it was found that a great deal of crudding took place. This was caused by the presence of Fe^{3+} in the LA-1 solution, and constitutes perhaps the most serious disadvantage of extracting Fe^{3+} into the organic phase. It is interesting to note that there is reaction between pure $FeCl_3$ solution and LA-1. The salt is extracted from the aqueous phase and a brown scum forms at the aqueous/organic interface.

2.4.4 The Removal of Cations by Ion Exchange Resins

If all the cations could be removed by ion exchange prior to the acid entering the amine extraction step, all the problems would be solved. Unfortunately, it is not possible to remove Fe^{3+} from concentrated acid solution by this means.

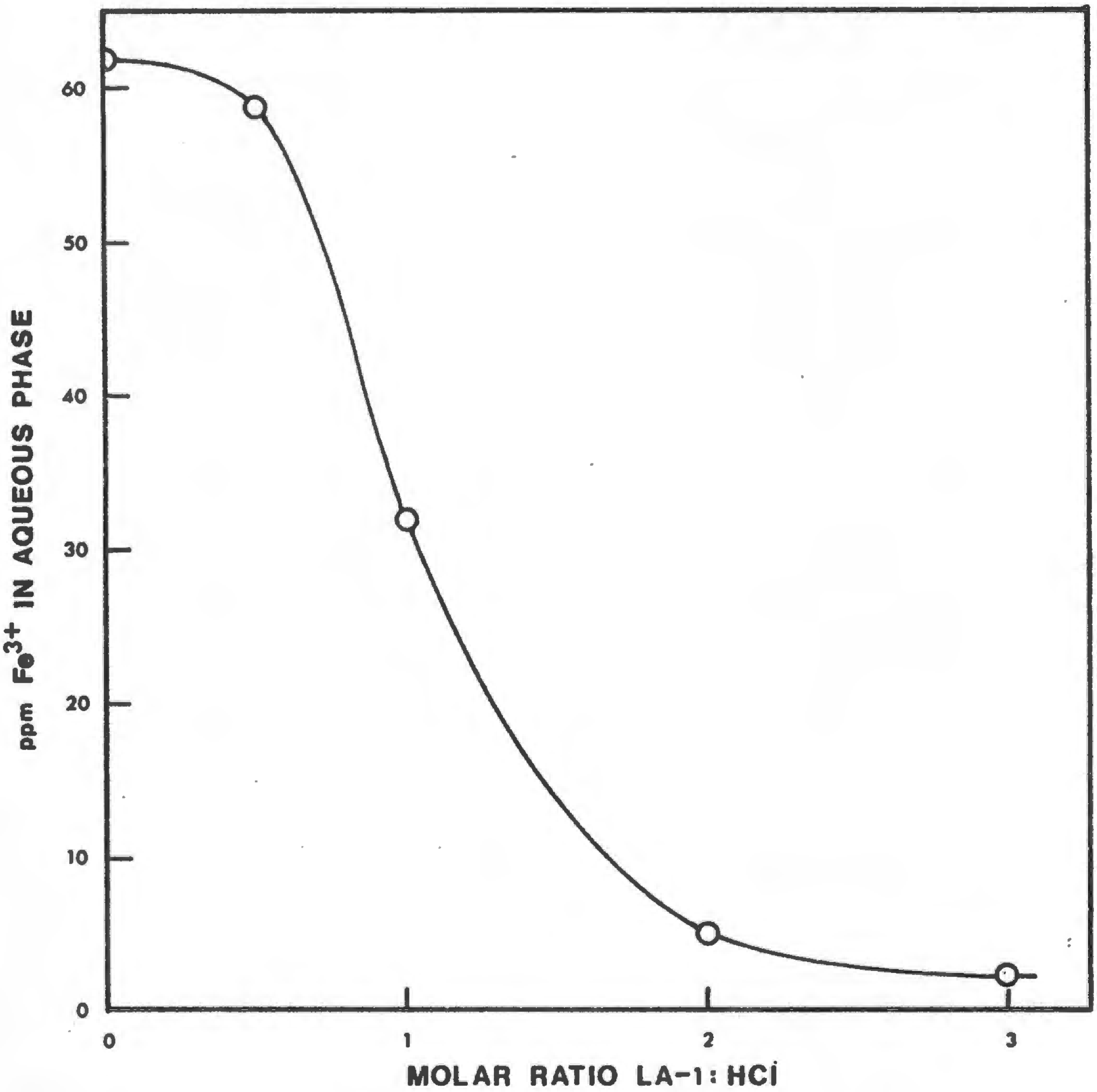

FIG. 2.2

Extraction of Fe^{3+} into the organic phase. (10% LA-1 by volume in kerosene, no decanol.)

The reason is not just competition from H^+ ions, but also phosphate complexing again. With a dilute acid, however, Fe^{3+} can be removed, but the dilution needed is very great indeed. Fig. 2.3 shows the breakthrough curves for both Fe^{3+} and Mg^{2+} with 0,5 M acid containing 145 ppm[1] of the former and 760 ppm[1] of the latter cation. It is evident that Mg^{2+} is effectively removed, but Fe^{3+} breaks through very early, and its curve rises steadily. The reason why it rises above the concentration for the feed solution, is that loaded Fe^{3+} is eventually eluted by Mg^{2+}. No doubt, it would be possible to remove Fe^{3+} at still greater dilutions, but this is really no help, because LA-1 cannot extract H_3PO_4 at such great dilution without precipitation of the amine phosphate, and evaporation is out of the question.

Anion exchange was also tried, using the strong base resin Amberlite IRA-68, but this showed only a very limited affinity for the Fe^{3+}-phoshate complexes.

Resinous ion exchangers were then ruled out as possible purifying agents for wet process H_3PO_4.

2.4.5 Extraction of Phosphate Values from Impure Acids

The only remaining possibility for establishing a viable process is to extract the impure acid with LA-1, relying on the partial rejection of Fe^{3+} to effect purification in a number of countercurrent stages.

The acid used must not be too impure, however, otherwise precipitation and scum formation may occur. The evaporated acid whose composition is given in Table 1.1 is suitable, and this composition was taken as typical for the feed acid in a hypothetical process. Since evaporated acid is readily available, it is not necessary to find a way of utilising the much dirtier, unevaporated acid, with all its attendant complications.

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[1] Unless otherwise stated, parts per million (ppm) is equivalent to mg/litre (weight/volume basis).

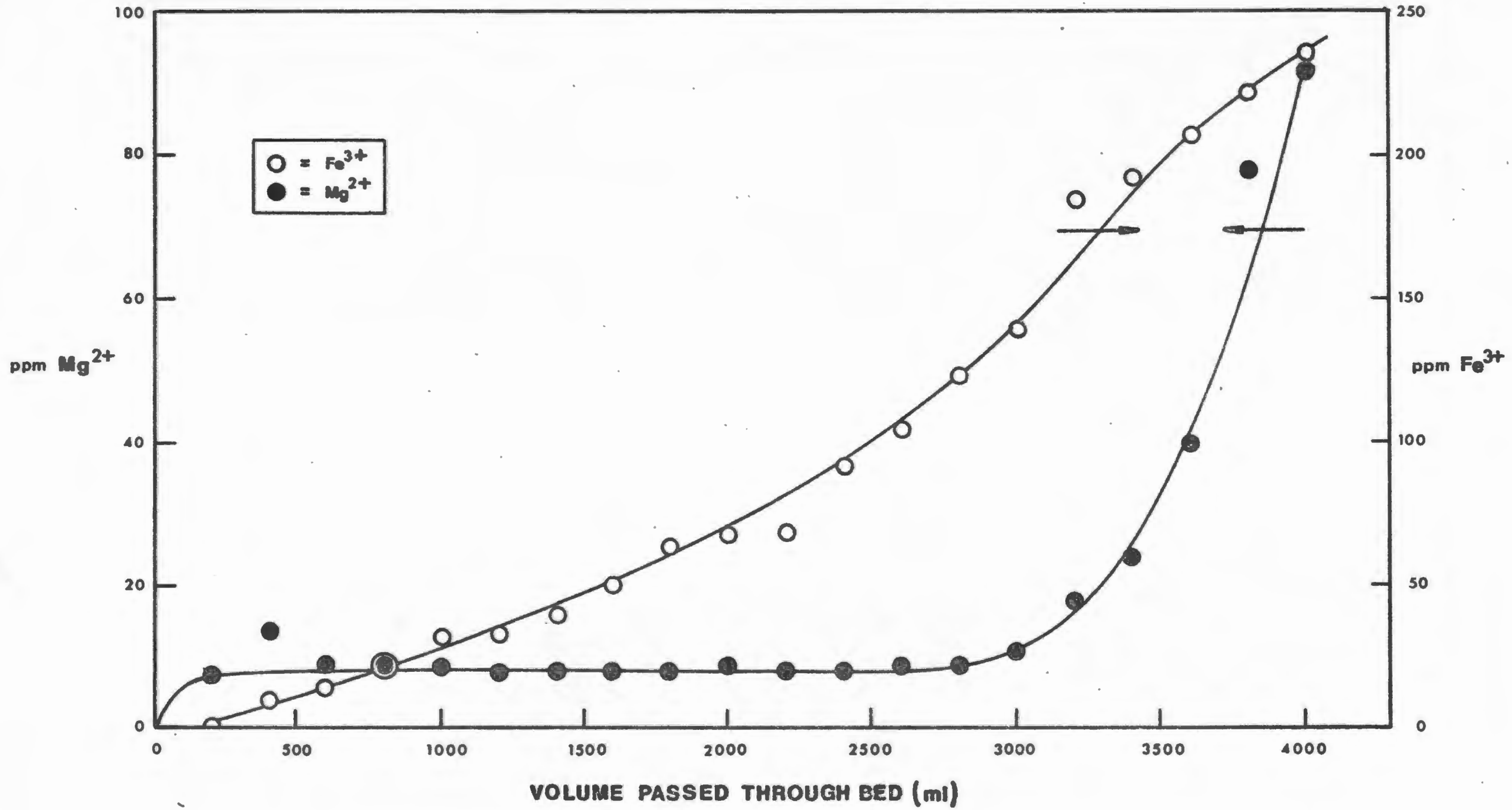

FIG. 2.3

Breakthrough curves for Fe^{3+} and Mg^{2+} removed from 0,5 M H_3PO_4 by Amberlite IRA-120. Resin in H^+ form. Bed volume 207 ml, height 39 cm, capacity 390 milliequivalents.

2.4.6 Setting up a Process Flow Sheet

In a simple countercurrent liquid-liquid contact system, the best organic composition in terms of Fe^{3+} and H_3PO_4 which can be obtained, is that which is in equilibrium with the feed acid. Since this gives no great purification with respect to Fe^{3+}, an extract washing section must be incorporated in which the loaded organic phase is washed countercurrently with clean water. In the water feed stage, the aqueous phase contains a certain amount of acid which has been stripped from the LA-1, and as long as this acid concentration is maintained at a high enough level, no amine phosphate precipitation problem will occur. The washing section utilises the selectivity of LA-1 for H_3PO_4 over Fe^{3+}, since the former is less readily stripped than the latter. By using enough stages, any desired level of purification may be obtained.

The organic phase leaving the washing section is thus free of cations, but still contains most of the anionic impurities. It is then stripped countercurrently with NaCl, so that these impurities are retained in the organic phase, while an exchange of Cl^- and $H_2PO_4^-$ ions takes place between the two phases, resulting in a product solution of NaH_2PO_4 which is both highly pure and also concentrated, since the concentration is fixed by that of the brine used for stripping.

Care has to be taken that the product contains neither an excess of H_3PO_4 nor of NaCl, but this should not be too difficult a technical problem. It may even be possible to produce some disodium salt, when this is required, or a mixture of the mono- and disodium salts suitable for calcining to the complex phosphates, such as sodium tripolyphosphate.

Before the organic phase enters the stripping section, extra LA-1 solution has to be added, because the product of the washing section will still have an H_3PO_4 to LA-1 molar ratio higher than 1 to 1 whereas, for efficient stripping, this ratio should not be exceeded.

After stripping, the LA-1 is regenerated with a lime slurry, after which it is back in the free base form, and may be used again.

A layout of the process is given in Fig. 2.4.

2.4.7 A Simple Two-Stage Test

The effectiveness of a water wash for purifying the loaded organic phase with respect to Fe^{3+} and Mg^{2+} was tested in separating funnels. The extractant used was 5% LA-1 with 2½% decanol, as at the time when the test was performed, the desirability of using more decanol was not appreciated.

400 ml of LA-1 solution was contacted with 50 ml of 11,4 M H_3PO_4 containing 990 ppm Fe^{3+} and 5190 ppm Mg^{2+}. The organic phase was separated and washed with 20 ml of water, which took up acid to reach a concentration of 3,42 M. The organic phase concentration in equilibrium was 0,124 M. The organic phase was again separated, 100 ml of fresh LA-1 solution was added to it, and then the mixture was stripped with 9,4 ml of saturated (5,47 M) NaCl. The aqueous product NaH_2PO_4 still contained some H_3PO_4, as the pH was 1,75. Fe^{3+} was 84 ppm, and Mg^{2+} was 149 ppm, indicating percentage purifications of 82% and 94% for the two species respectively. On the basis of this result, it was decided to work on the process depicted in Fig. 2.4.

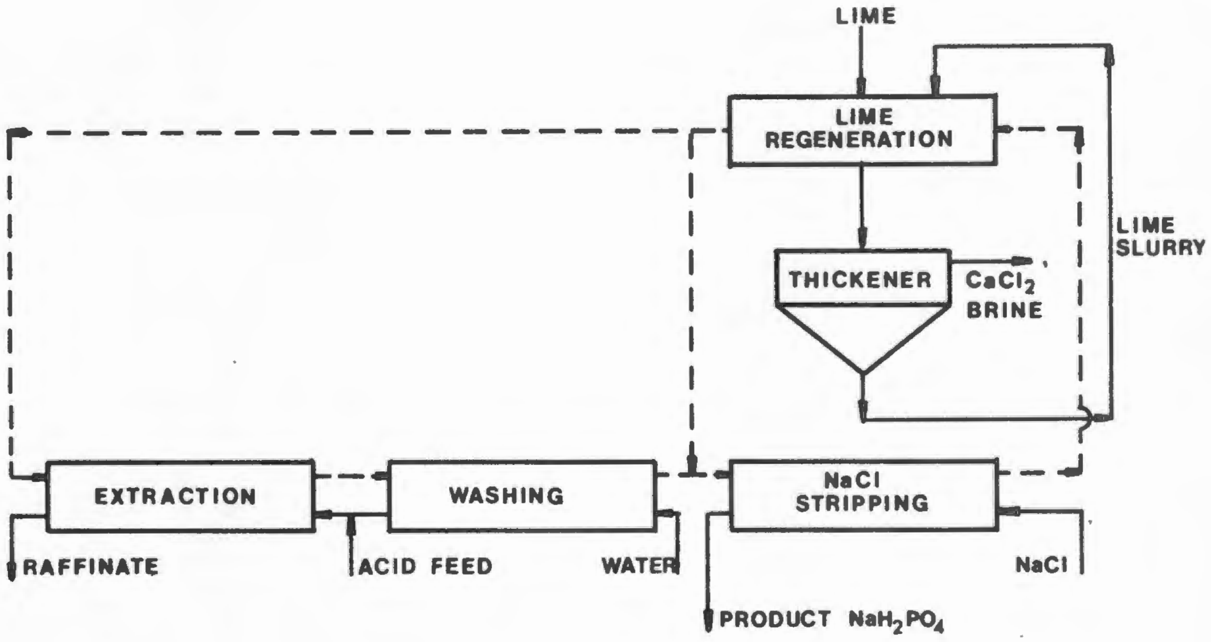

FIG. 2.4

Proposed process for the production of NaH_2PO_4 from NaCl and wet process H_3PO_4.

——— Aqueous streams. – – – – Organic streams.

CHAPTER 3

EXPERIMENTAL RESULTS

3.1 OUTLINE OF SUBSEQUENT EXPERIMENTAL WORK

A food grade phosphoric acid should have an iron concentration of no more than 5 ppm in 85% H_3PO_4 (49). This is very low indeed, and the question arises as to how many theoretical stages would be necessary to achieve such a level of purification. Therefore, it was necessary to study the distribution of Fe^{3+} between the aqueous and organic phases under various conditions. Other cations were not studied, since their removal is more effective than the removal of iron.

For the anionic impurities, sulphate was studied in detail, and its effect on the distribution of phosphate and iron. The other anionic impurities, fluorosilicate and arsenate, were not studied.

The basis of the work, then, was the system containing H_3PO_4, H_2SO_4 and Fe^{3+}, and how an organic phase containing virtually no Fe^{3+} could be obtained.

3.2 ANALYTICAL METHODS

In the preliminary tests, H_3PO_4 concentration was determined by titration using a pH meter. For organic samples, standard NaOH was added with stirring after each aliquot, and the pH of the aqueous layer taken. The procedure takes a long time. When both H_3PO_4 and H_2SO_4 are present, analysis cannot be done by this method and, in fact, presents a difficult problem, especially with regard to the organic phase.

For iron, atomic absorption was used at first. This method can be applied to both aqueous and organic solutions, although aqueous solutions are easier. Accuracy is fair, but a great deal of labour is involved, since the solutions must be carefully diluted, typically to the order of 1000 times.

Standardisation of the machine is also awkward, as the zero tends to drift, and restandardisation has to be done after every sample.

Because of these difficulties, it was decided to use radiochemical methods, especially since suitable isotopes of the elements iron, phosphorus and sulphur are readily available. ^{59}Fe is a strong γ-emitter, and so can be counted on a γ-counting machine, while ^{32}P and ^{35}S are strong and weak β-emitters respectively, and can be determined by scintillation counting. The difference in energy of the β-emissions makes it possible to differentiate between ^{32}P and ^{35}S in solutions containing both these nuclides, so that samples containing only one nuclide need be made up only in the case of iron. This is a major time-saving advantage.

Radiochemical assays may be obtained with good accuracy, since the standard deviation resulting from the randomness of radioactive disintegration is the square root of the number of counts, or 1% for a sample giving 10000 counts during its counting time. However, it was soon realised that the scatter was greater than could be explained on this basis. It was found that in the case of γ-counting, the geometry of the sample and the exact position of the sample in the counting machine have a profound effect. In scintillation counting, the source of variation is the phenomenon known as 'quenching', whereby counts may be lost or downgraded to a lower energy channel according to the exact physical and chemical makeup of the scintillator sample.

For the best results, a great deal of care is necessary, and accuracy increases as the analyst becomes more experienced with the system being studied.

A more complete discussion of the radiochemical methods is given in Appendix A.

3.3 AQUEOUS AND ORGANIC PHASE COMPOSITIONS FOR TESTING

Compositions for each test were decided upon with a view to optimal coverage of the whole range of interest, which is large when three components (H_3PO_4, H_2SO_4 and Fe^{3+}) are involved.

Without knowing much about the characteristics of the extraction system, it is difficult to determine beforehand the most suitable points to test. Table 3.1 shows the points eventually chosen.

As regards the organic phase, two compositions were used, one being 5% LA-1, 10% decanol, and the other 10% LA-1, 20% decanol, by volume, in kerosene. This corresponds to 0,11 M and 0,22 M in amine respectively.

3.4 SAMPLE PREPARATION

3.4.1 Techniques and Volumes

Aqueous samples were made up in 10 ml volumetric flasks. This small size was chosen because it is important, when working with radioactive materials, to use as little as possible, on account of both expense and radiation hazard.

Phosphoric acid was added with the flask on a balance, and the amount checked by weighing to an accuracy of better than 0,005 g. Care was taken to prevent the concentrated acid, which is hygroscopic, from picking up too much water. The same method was used for sulphuric acid in the high concentration test of 1 to 8 M.

Other ingredients were added with hand-held automatic pipettes with disposable plastic tips.

Where ^{59}Fe was required, this was first added to the Fe^{3+} solution to be used for supplying the iron content of the samples.

In the case of ^{32}P and ^{35}S on the other hand, each 10 ml flask was spiked with its own small aliquot of radioactive solution delivered from an automatic pipette. 4 ml Aliquots of organic phase were delivered by an automatic dispenser into small bottles, and 4 ml of the appropriate aqueous solution was added to each bottle with a hypodermic syringe, a new syringe being used for each 10 ml flask of aqueous solution. Shaking was done for 5 minutes on a shaking table, and the phases were allowed to settle thoroughly for at least a day.

TABLE 3.1

AQUEOUS SOLUTIONS FOR RADIOCHEMICAL ANALYSIS

System	Tracers	H_3PO_4 concs (M)	H_2SO_4 concs (M)	Fe^{3+} concs (ppm x 10^{-3})
H_2SO_4	^{35}S	--------	1;2;3;4;5;6;7;8	-------
H_3PO_4/Fe^{3+}	^{32}P	1;2;3;4;5;6;7;8	-------	0;6
H_3PO_4/Fe^{3+}	^{59}Fe	1;2;3;4;5;6;7;8	-------	1,14; 2,28; 3,42; 4,56; 5,70; 6,84
H_3PO_4/H_2SO_4	^{32}P, ^{35}S	3;5;6;7;8	0,0316;0,0632;0,1127; 0,1612;0,2423;0,3223	--------
$H_3PO_4/H_2SO_4/Fe^{3+}$	^{59}Fe	5;8	0,1612; 0,3223	1;2;3;4;5;6
$H_3PO_4/H_2SO_4/Fe^{3+}$	^{32}P, ^{35}S	5;8	0,1612; 0,3223	1;2;3;4;5;6

Aliquots of each settled phase were taken by automatic pipette and delivered, in the case of ^{59}Fe, into counting tubes or, in the case of ^{32}P and ^{35}S, into counting bottles containing 7 ml of scintillator solution.

A more detailed description of sample preparation, with a discussion of accuracy and sources of error, is given in Appendix B.

3.4.2 Problems of Preparing Iron Solutions

When Fe^{3+} is added to an H_3PO_4 solution, some anion must be added as well. If the solution is to contain sulphate, the Fe^{3+} may be added as $Fe_2(SO_4)_3$, as long as the sulphate so added does not exceed the total required. If sulphate must be excluded, as in the H_3PO_4/Fe^{3+} system, the Fe^{3+} must be added in the form of an $FePO_4$ solution. Ferric phosphate in the form of $FePO_4.2H_2O$ is available, and can be dissolved in H_3PO_4 solution by heating, but it is insoluble in water. The prepared solution is unstable, and slowly precipitates $FePO_4$ in a form which cannot be redissolved by heating. This precipitation continues slowly over days and weeks, and never appears to come to an end, although the rate decreases. Consequently, the solution must be used soon after standardisation, and in all the present work, care was taken that not more than one day should elapse before use.

In some preliminary Fe^{3+} distribution tests, using atomic absorption for analysis, it was found that the amount of Fe^{3+} extracted decreased considerably if the solution was allowed to stand for, say, two weeks, even if the actual Fe^{3+} concentration was relatively low, for example 1000 ppm. No precipitate was visible in such cases, but it is possible that Fe^{3+} and $PO_4{}^{3-}$ ions could combine to form a colloid, which would be extracted less readily than charged, phosphate complexed Fe^{3+} ions. The presence of a certain amount of sulphate does not eliminate the effect.

3.5 IRON - PHOSPHATE DISTRIBUTION

The results of this test indicate that at low aqueous H_3PO_4 concentrations, a great deal of Fe^{3+} is extracted into the organic phase, but increasing H_3PO_4 suppresses this effect up to a concentration of about 7 M. More concentrated acids tend to increase the Fe^{3+} takeup above the minimum at 7 M, this phenomenon being associated with the rapidly increasing upward trend of the H_3PO_4 extraction isotherm in the high concentration region (see Fig. 2.1).

Increasing Fe^{3+} concentration in the aqueous phase increases Fe^{3+} extraction, but not in proportion. The higher concentrations are extracted proportionately less.

The actual data was rather scattered, and so a method of smoothing was required. Also, it was necessary to express the organic Fe^{3+} concentratration as a function of aqueous Fe^{3+} and H_3PO_4, in order to simulate a multi-stage extraction process on a computer.

The general shape of the curves suggested an equation of the form:

$$[Fe]_{org} = A(e^{-D[H_3PO_4]_{aq}} + C)(1 - e^{-B[Fe]_{aq}}) \text{ ----- } 3.1$$

At constant $[H_3PO_4]_{aq}$, $[Fe]_{org}$ is 0 at $[Fe]_{aq} = 0$, and increases with increasing $[Fe]_{aq}$, approaching a limit. At constant $[Fe]_{aq}$, $[Fe]_{org}$ is large at $[H_3PO_4]_{aq} = 0$, being equal to (A + AC) x (second bracket), while at high $[H_3PO_4]_{aq}$, it approaches (AC) x (second bracket). Thus equation 3.1 gives curves of the general form required. It still does not take into account such deviations as the upward trend of the curves after $[H_3PO_4]_{aq} = 7$ M, but this can be remedied by expanding equation 3.1 in a power series, truncating the series at some convenient point and allowing each coefficient to vary independently.

Expansion gives:

$$\begin{array}{llll}
[Fe]_{org} = & a_{11}[Fe]_{aq} & + a_{12}[Fe]_{aq}^{2} & + \cdots + a_{1n}[Fe]_{aq}^{n} \\
& + a_{21}[Fe]_{aq}[H_3PO_4]_{aq} & + a_{22}[Fe]_{aq}^{2}[H_3PO_4]_{aq} & + \cdots + a_{2n}[Fe]_{aq}^{n}[H_3PO_4]_{aq} \\
& \vdots & & \vdots \\
& + a_{m1}[Fe]_{aq}[H_3PO_4]_{aq}^{(m-1)} & + a_{m2}[Fe]_{aq}^{2}[H_3PO_4]_{aq}^{(m-1)} & + \cdots + a_{mn}[Fe]_{aq}^{n}[H_3PO_4]_{aq}^{(m-1)}
\end{array}$$

----- 3.2

Fitting was done by a packaged subroutine which selects only the statistically most significant terms in equation 3.2. Values of 5 and 4 were given to m and n respectively. For detailed tables of fitted results, see Appendix C.

Graphs of the fits are shown in Fig. 3.1 for 5% LA-1 and in Fig. 3.2 for 10% LA-1. The latter curves are raised to about double the height of the former.

Perhaps a more meaningful method of plotting these curves is to use as ordinate the selectivity for H_3PO_4 over Fe^{3+}, which is equal to $\frac{[H_3PO_4]_{org}}{[H_3PO_4]_{aq}} \cdot \frac{[Fe]_{aq}}{[Fe]_{org}}$. Plots of this quantity appear in Figs. 3.3 and 3.4. The curves were constructed from the computer fits, and are rather irregular in form. Probably, neither the data nor the fit is good enough to produce accurate selectivity curves, but the general trend is still clear.

The presence of Fe^{3+} does effect the extraction of H_3PO_4, but not to a very great extent. This was checked by testing H_3PO_4 extraction both from pure solution, and from a solution which contained 6000 ppm of Fe^{3+}. No intermediate Fe^{3+} concentrations were taken, but no great inaccuracy would result from interpolating linearly between 0 and 6000 ppm. For comparison, the curves have been plotted in Fig. 3.5.

3.6 EXTRACTION OF SULPHURIC ACID

In order to gain information about the extraction of sulphate from wet process H_3PO_4, extraction isotherms for pure H_2SO_4 were determined, for aqueous concentrations up to 8 M, even though the actual concentrations found in wet process H_3PO_4 are very low.

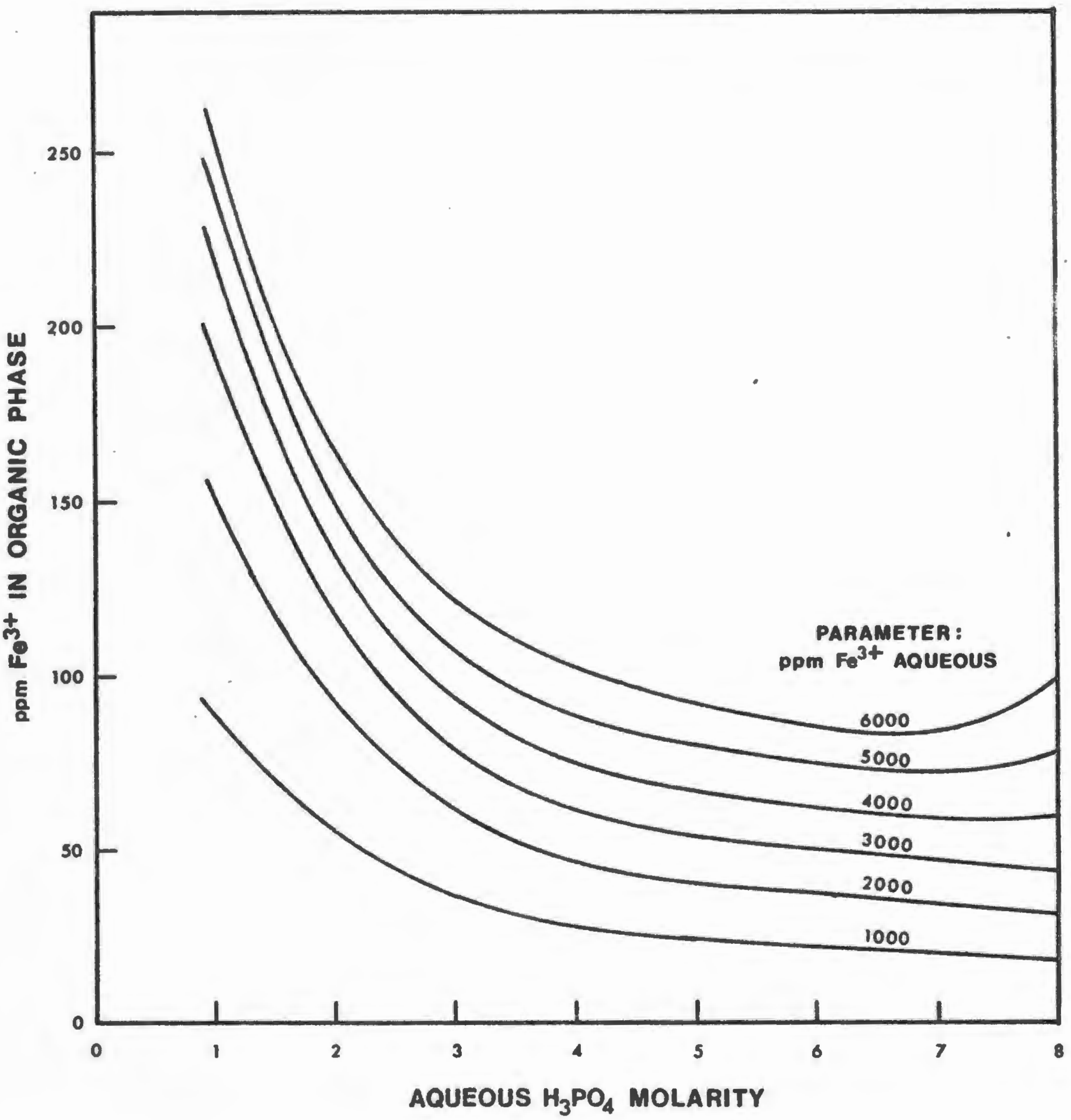

FIG. 3.1

Distribution of Fe^{3+} between H_3PO_4 solution and 5% LA-1, 10% decanol in kerosene. (Volume %.) The data has been fitted to a polynomial for smoothing.

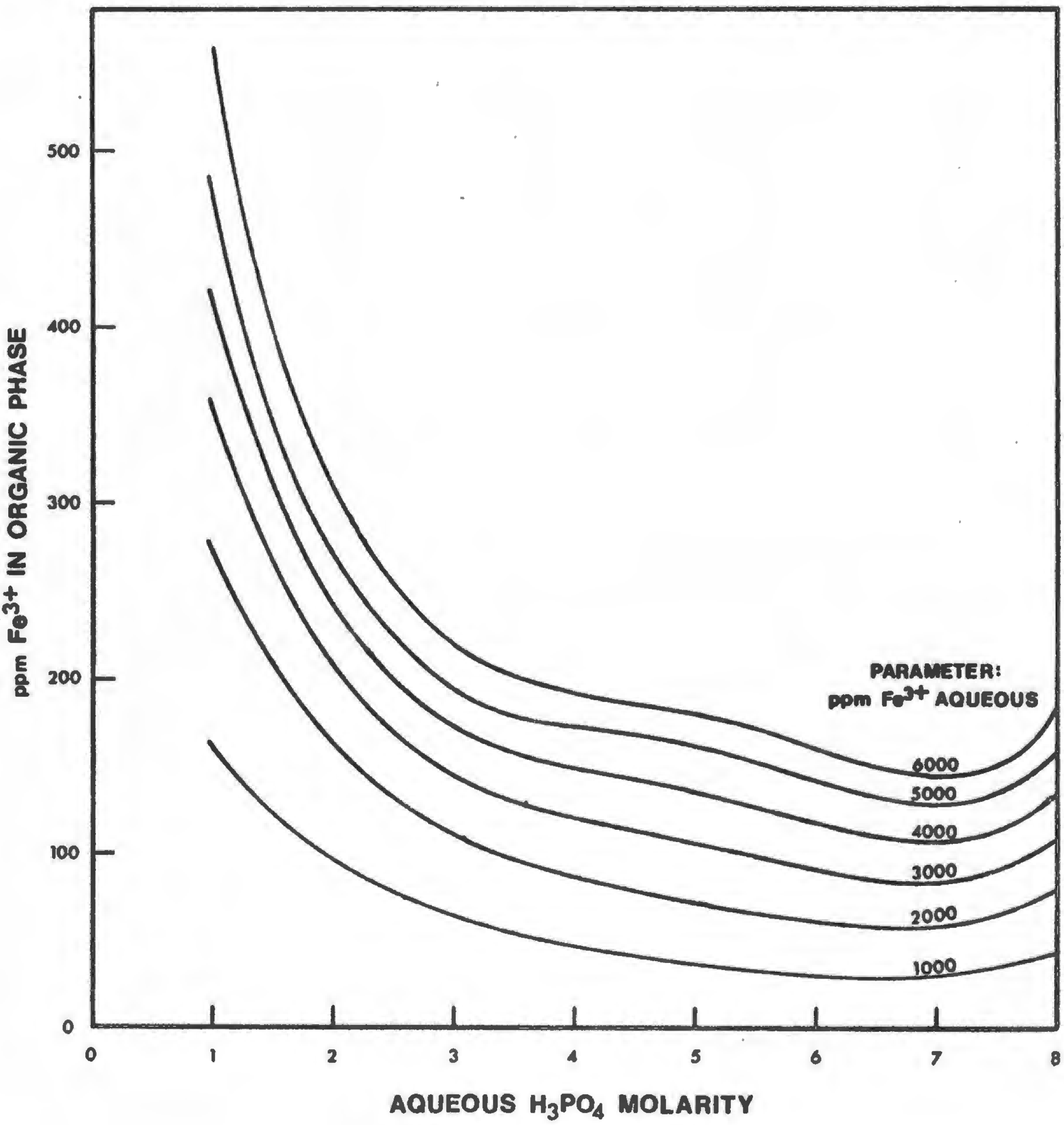

FIG. 3.2

Distribution of Fe^{3+} between H_3PO_4 solution and 10% LA-1,20% decanol in kerosene. (Volume %.) The data has been fitted to a polynomial for smoothing.

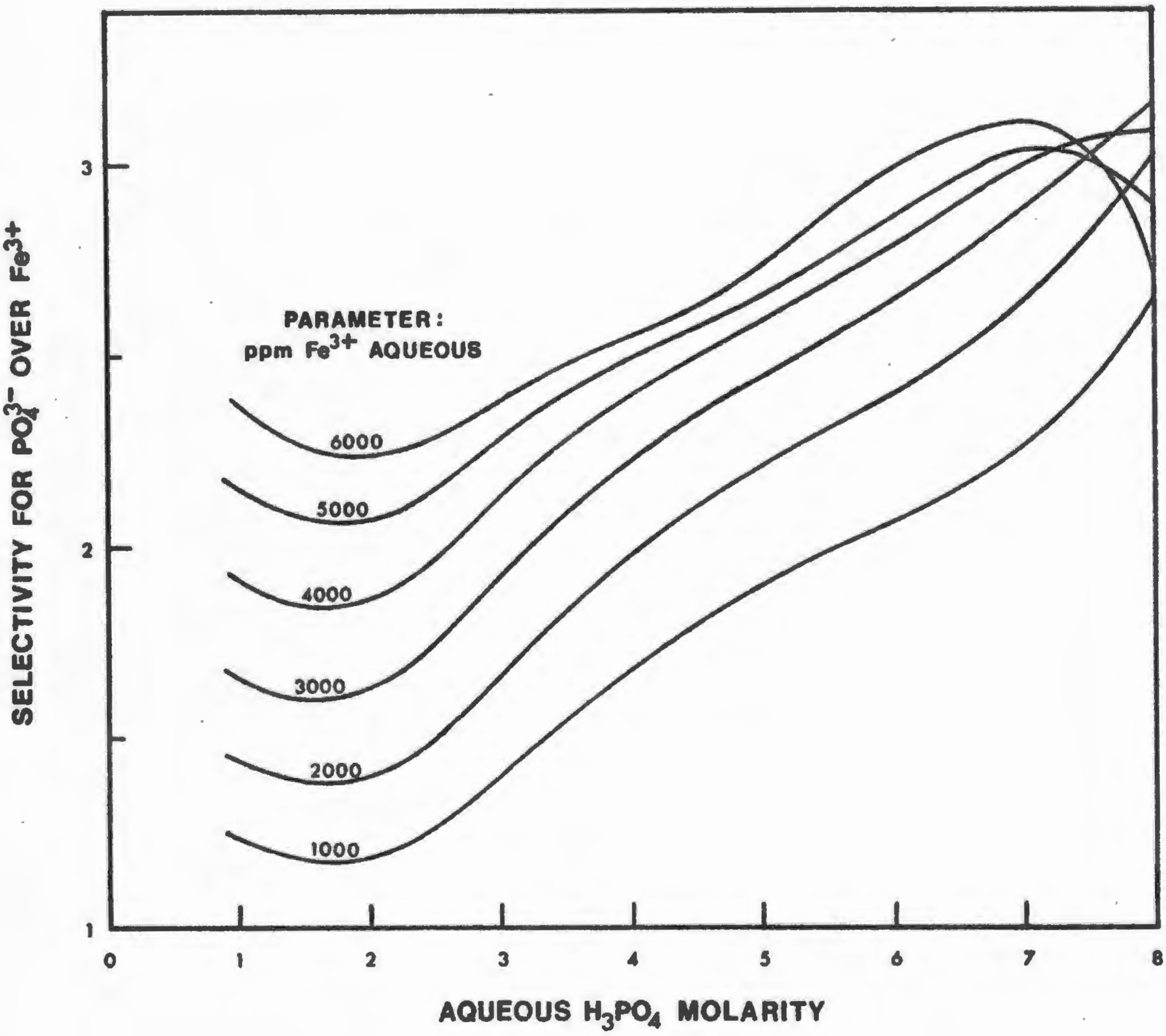

FIG. 3.3

Selectivity for phosphate over iron $\dfrac{[H_3PO_4]_{org}\,[Fe^{3+}]_{aq}}{[H_3PO_4]_{aq}\,[Fe^{3+}]_{org}}$ for 5% LA-1, 10% decanol in kerosene. (Volume %.) Values were calculated from the fit given in Fig. 3.1.

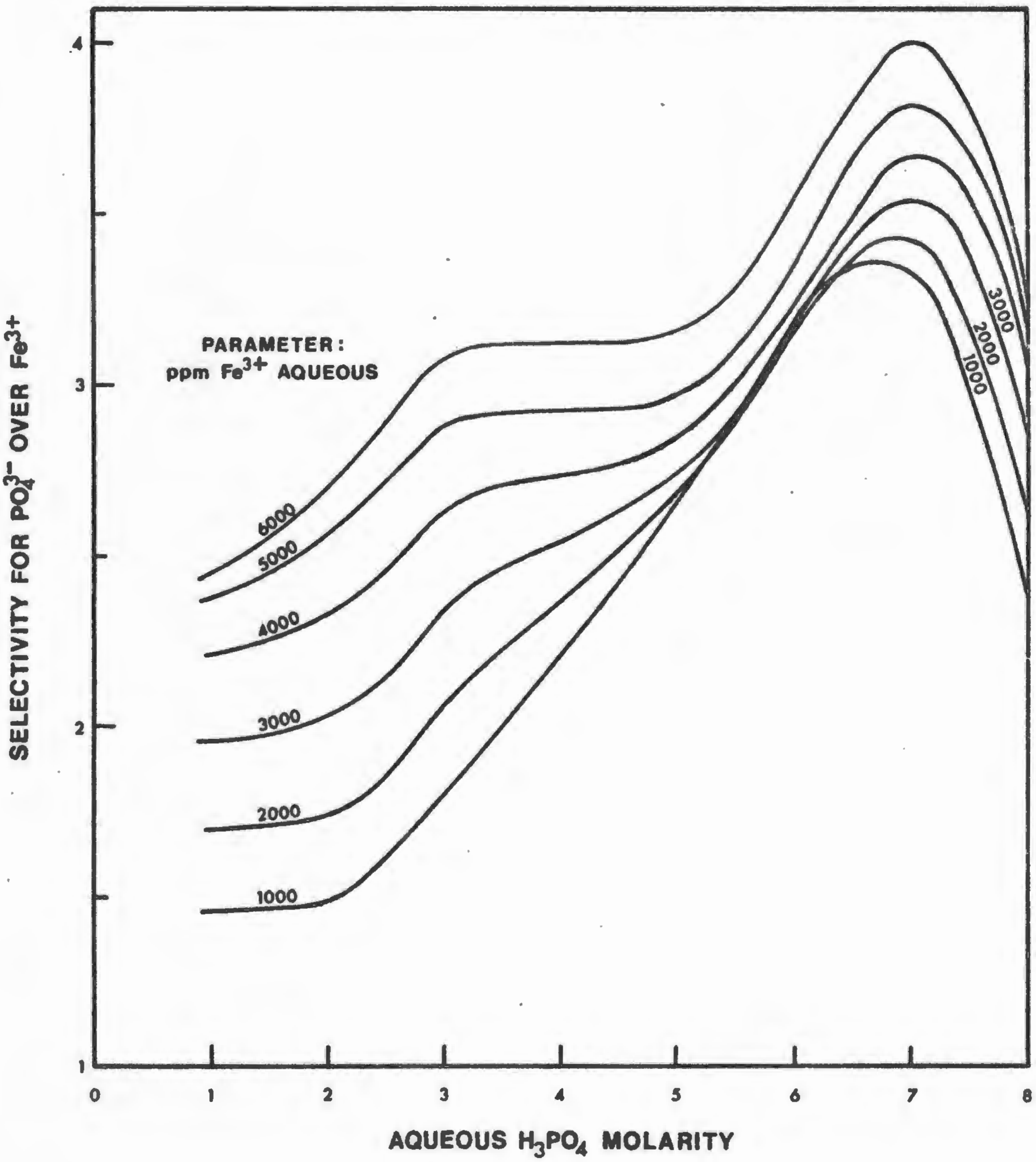

FIG. 3.4

Selectivity for phosphate over iron $\dfrac{[H_3PO_4]_{org}\,[Fe^{3+}]_{aq}}{[H_3PO_4]_{aq}\,[Fe^{3+}]_{org}}$ for 10% LA-1,20% decanol in kerosene. (Volume %.) Values were calculated from the fit given in Fig. 3.2.

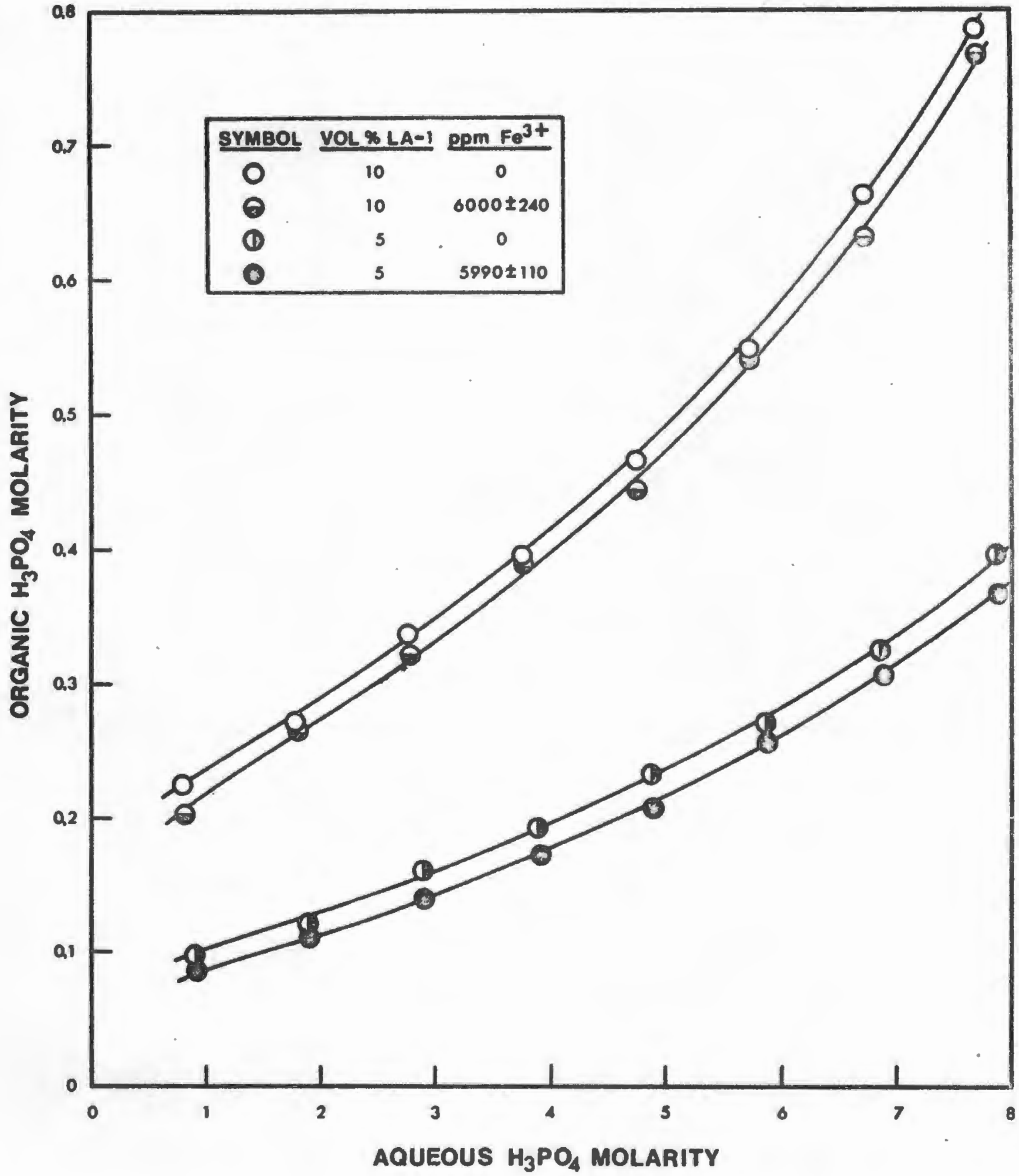

FIG. 3.5

Extraction of H_3PO_4 with and without Fe^{3+} present.

The isotherms, as determined using ^{35}S, are presented in Fig. 3.6 together with the pure H_3PO_4 isotherms for comparison.

It was at first a cause for some concern that the H_2SO_4 curves lay below the corresponding H_3PO_4 curves, whereas the literature indicates that amines are much more selective for H_2SO_4 (42). However, the very low concentration region was not studied, and it is here that the high selectivity effects occur. With a strong acid like H_2SO_4, a low aqueous concentration may be in equilibrium with a high organic concentration. Further increase in the aqueous concentration results in addition of H_2SO_4 molecules to already formed amine salts, and in the region where this takes place, the high selectivity for a strong acid over a weaker acid disappears. In fact, it seems that the weaker acid is preferred.

The minimum slope of the sigmoid isotherms for H_2SO_4 is less than the corresponding slope for H_3PO_4, and this is another interesting difference which depends on the strength of the acid. Some systems, such as HCl/tri-n-octylamine in benzene, have a virtually flat middle portion of the curve (55), which takes a sudden upward swing somewhere in the high concentration region. The stronger the acid, the higher the concentration at which this point occurs. In fact, $HClO_4$ is such a strong acid that there is no upward swing even at an aqueous concentration of 10 M (55).

3.7 PHOSPHATE - SULPHATE DISTRIBUTION

The study of this distribution confirmed that LA-1 is far more selective for sulphate than for phosphate, especially at low sulphate concentrations. Thus for the initial neutralisation of the amine, H_2SO_4 is much more effective than H_3PO_4, but for subsequent additions of acid molecules, this selectivity is reduced. At very low aqueous H_2SO_4 concentrations, selectivity for sulphate is very high, since amine neutralisation accounts for most of the extracted acid. Low H_3PO_4 concentration also increases the sulphate selectivity, since the binding of further acid molecules to amine salts

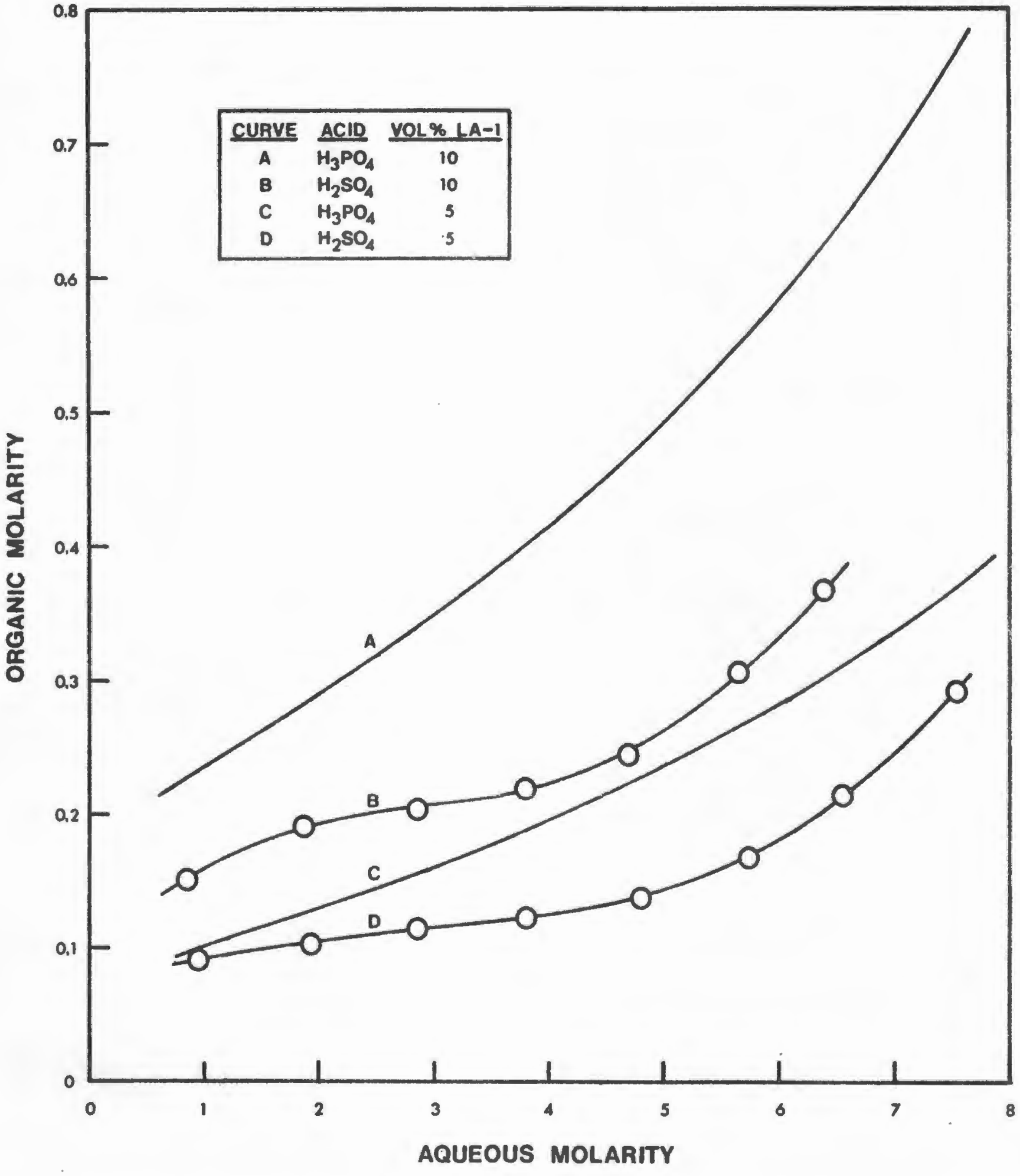

FIG. 3.6

Comparison of extraction isotherms for pure solutions of H_3PO_4 and H_2SO_4.

predominates mostly at high concentrations.

For the 5% LA-1 solution, the selectivity for sulphate over phosphate at an aqueous H_3PO_4 concentration of 2,97 M was measured as 166 at aqueous $[H_2SO_4]$ = 0,0054 M, whereas at aqueous $[H_2SO_4]$ = 0,260 M, it was only 22. In the case of 10% LA-1, very similar results were recorded. As regards the actual organic H_3PO_4 concentrations, these are lowered sharply when a small amount of sulphate is present, but the rate of lowering decreases with increasing sulphate concentration.

Figs. 3.7 to 3.12 show organic phosphate and sulphate concentrations and selectivities for 5% and 10% LA-1. The data points were plotted and the curves drawn by eye, since the attempt to fit an equation (see Section 4.7.2) did not give results suitable for constructing these graphs. The variation in aqueous H_3PO_4 concentration, used as the parameter, is small along any one curve (see Tables C.7 and C.8 in the Appendix).

The results of the phosphate-sulphate distribution test confirm the literature on the extent of the selectivity for sulphate over phosphate, and also show how difficult it is to predict such selectivities from the individual extraction isotherms for H_3PO_4 and H_2SO_4 (Fig. 3.6).

3.8 PHOSPHATE - SULPHATE - IRON DISTRIBUTION

In this test, unexpected results were obtained. The presence of Fe^{3+} changes the phosphate-sulphate distribution in a complex way, which can produce the paradoxical effect of an increase in aqueous H_2SO_4 concentration enhancing the extraction of H_3PO_4, instead of suppressing it. Table 3.2 gives a sample of the results for 5% LA-1, together with figures reflecting the situation in the absence of Fe^{3+} for comparison. The full results appear in Tables C.9 and C.10 in the Appendix.

TABLE 3.2

SAMPLE RESULTS FROM THE $H_3PO_4/H_2SO_4/Fe^{3+}$ DISTRIBUTION WITH 5% LA-1

Column headings: A - $[H_3PO_4]_{aq}$ (M)
B - $[H_3PO_4]_{org}$ (M)
C - $[H_2SO_4]_{aq}$ (M)
D - $[H_2SO_4]_{org}$ (M)
E - $[Fe^{3+}]_{aq}$ (ppm)
F - $[Fe^{3+}]_{org}$ (ppm)
G - Selectivity for SO_4^{2-} over PO_4^{3-}
H - Selectivity for PO_4^{3-} over Fe^{3+}

A	B	C	D	E	F	G	H
4,96	0,086	0,108	0,0540	0	0,0	28,9	-
4,96	0,085	0,113	0,0483	1020	3,3	24,8	5,3
4,96	0,086	0,115	0,0464	2980	7,0	23,3	7,3
4,96	0,078	0,116	0,0457	5970	11,0	24,9	8,6
7,94	0,210	0,118	0,0450	0	0,0	14,5	-
7,97	0,135	0,113	0,0491	1010	5,9	25,7	3,0
7,97	0,126	0,115	0,0473	2990	16,0	26,2	2,9
7,98	0,117	0,117	0,0449	6120	27,7	26,1	3,2
4,98	0,064	0,259	0,0645	0	0,0	19,3	-
4,94	0,112	0,266	0,0585	1020	2,1	9,7	11,0
4,94	0,108	0,265	0,0591	2940	4,2	10,2	15,3
4,94	0,108	0,266	0,0587	6040	6,3	10,2	20,9
7,95	0,167	0,264	0,0613	0	0,0	11,0	-
7,95	0,183	0,266	0,0596	1010	4,1	9,7	5,7
7,95	0,189	0,267	0,0594	2970	11,0	9,4	6,4
7,95	0,168	0,268	0,0578	6020	19,9	10,2	6,4

The salient features of the table are listed below:

1) For aqueous $[H_3PO_4]$ = 5 M and $[H_2SO_4]$ = 0,11 M, the presence of Fe^{3+} does not greatly alter the extraction of H_3PO_4 and H_2SO_4. Increasing the Fe^{3+} concentration tends to lower the amounts of both acids extracted, but not by much.
2) For aqueous $[H_3PO_4]$ = 5 M and $[H_2SO_4]$ = 0,26 M, the presence of Fe^{3+} causes the amount of H_3PO_4 extracted to be almost doubled, although the higher Fe^{3+} concentrations produce this effect to a lesser extent than the lower ones. H_2SO_4 extraction is somewhat reduced. The selectivity for H_3PO_4 is almost halved.
3) For aqueous $[H_3PO_4]$ = 8 M and $[H_2SO_4]$ = 0,12 M, the presence of Fe^{3+} suppresses the extraction of H_3PO_4, the effect increasing with increasing Fe^{3+} concentration. The extraction of H_2SO_4 is increased at the lower Fe^{3+} concentrations. The selectivity for H_2SO_4 over H_3PO_4 is increased.
4) For aqueous $[H_3PO_4]$ = 8 M and $[H_2SO_4]$ = 0,27 M, H_3PO_4 extraction is about the same for no Fe^{3+} and $[Fe^{3+}]$ = 6000 ppm. At lower Fe^{3+} concentrations, H_3PO_4 extraction is enhanced. For $[H_3PO_4]$ = 8 M, considerably more H_3PO_4 is extracted at $[H_2SO_4]$ = 0,27 M than at $[H_2SO_4]$ = 0,12 M.
5) The selectivity for H_3PO_4 over Fe^{3+} increases with both Fe^{3+} and H_2SO_4 concentration. The selectivity is considerably higher for 5 M than for 8 M H_3PO_4. This is somewhat similar to the case of sulphate free H_3PO_4, when the selectivity is often greater for 7 M than for 8 M acid, although up to 7 M, the selectivity tends to increase with increasing acid concentration. It is interesting to note the high selectivity of 20,9 which was obtained with 5% LA-1 for $[H_3PO_4]$ = 4,94 M, $[H_2SO_4]$ = 0,266 M and $[Fe^{3+}]$ = 6040 ppm. In the absence of sulphate, no directly calculated selectivity exceeded 4.

When 10% LA-1 is used, the extraction picture is similar, as can be verified from Tables C.9 and C.10 in the Appendix.

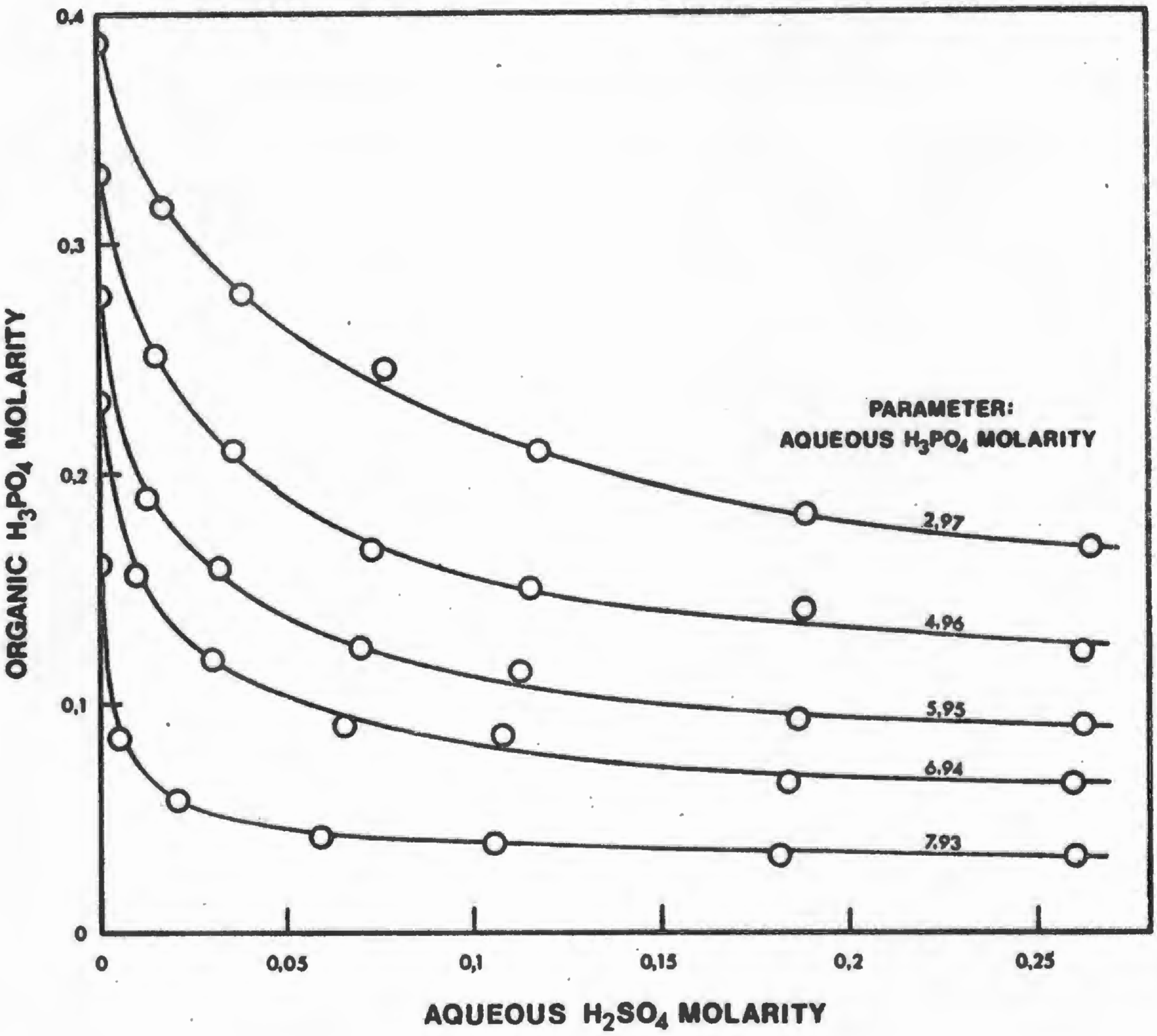

FIG. 3.7

The effect of sulphate on the extraction of H_3PO_4 by 5% LA-1, 10% decanol in kerosene. (Volume %.) No Fe^{3+} is present.

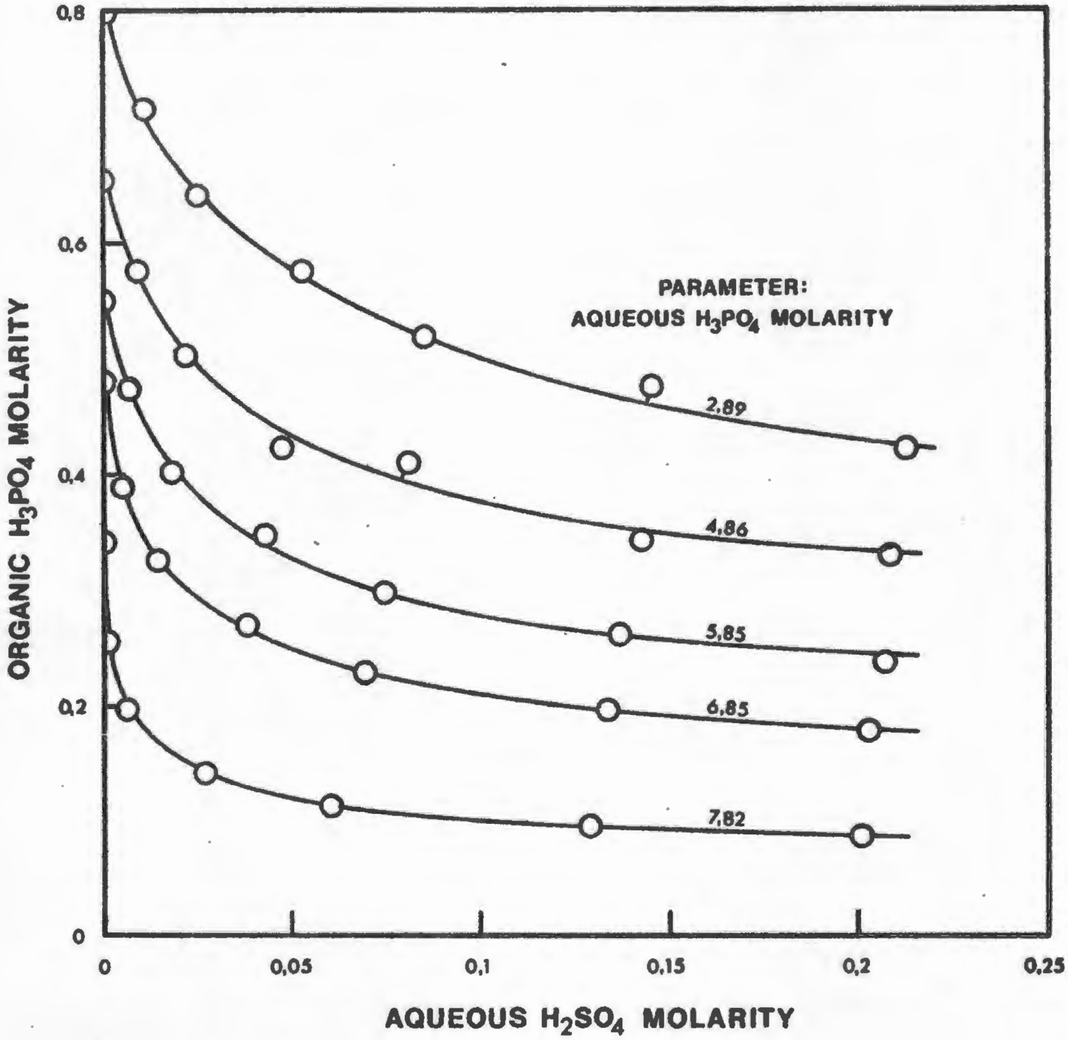

FIG. 3.8

The effect of sulphate on the extraction of H_3PO_4 by 10% LA-1, 20% decanol in kerosene. (Volume %.) No Fe^{3+} is present.

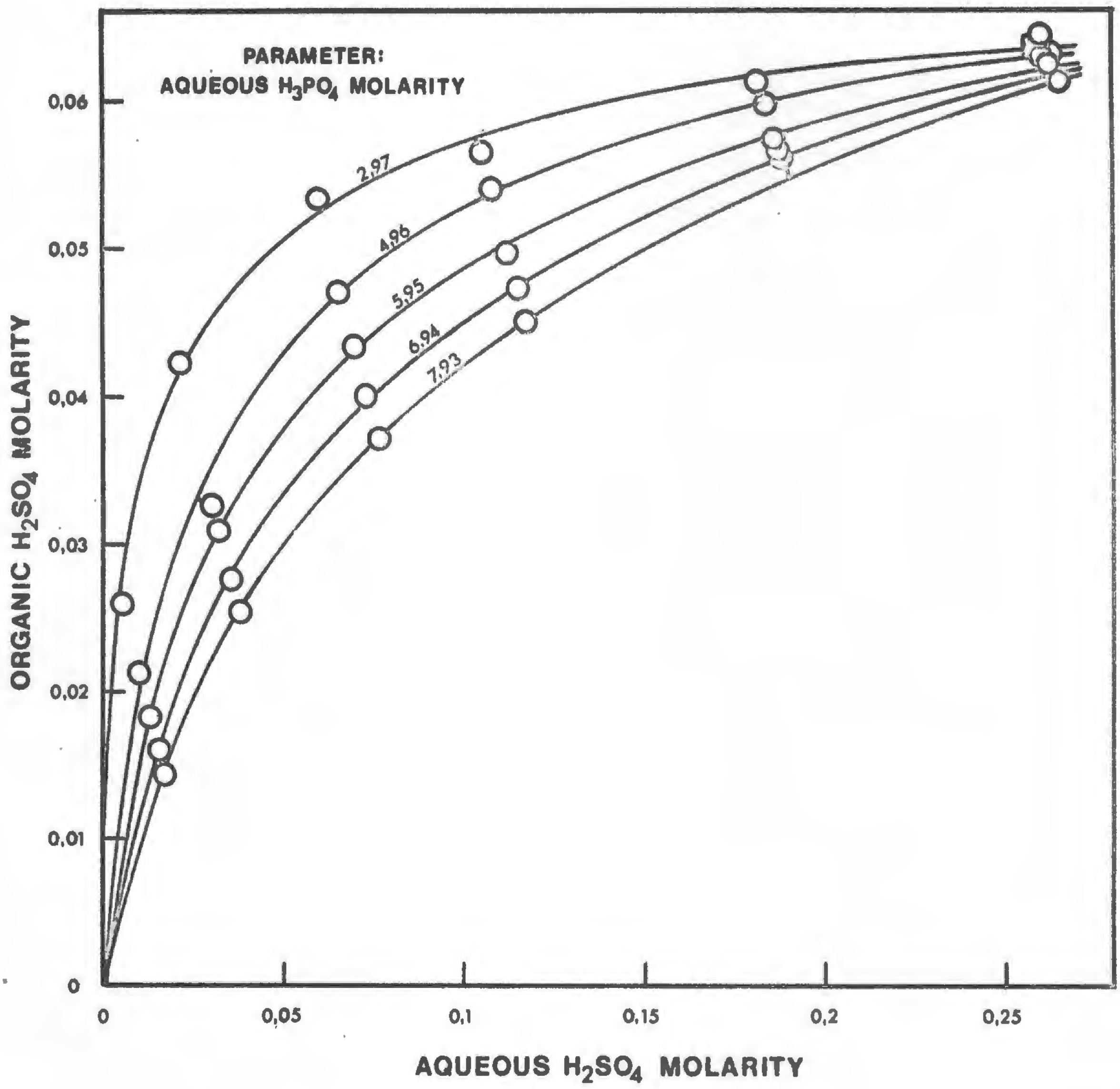

FIG. 3.9

Extraction of sulphate from H_3PO_4 solution by 5% LA-1, 10% decanol in kerosene. (Volume %.) No Fe^{3+} is present.

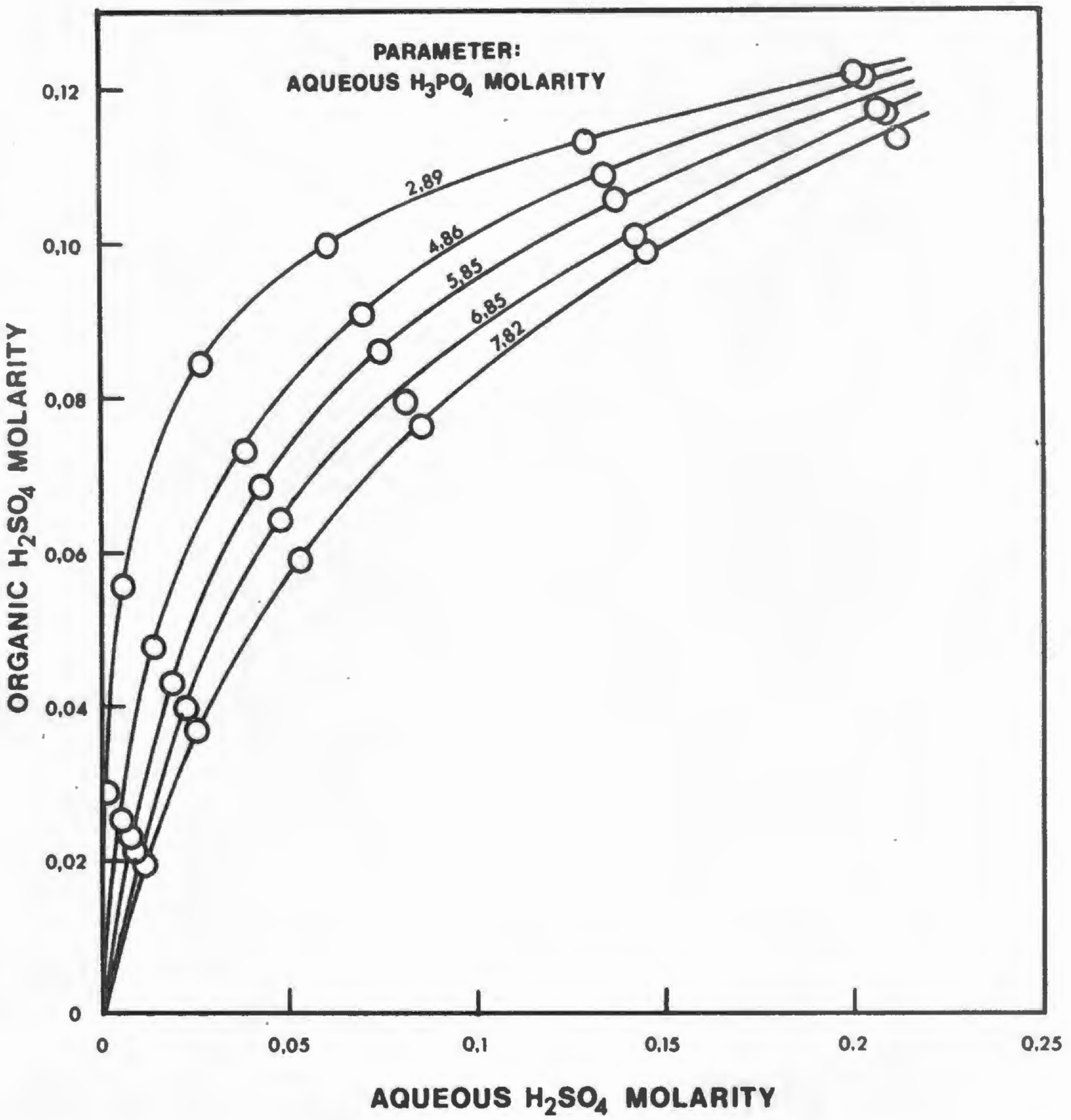

FIG. 3.10

Extraction of sulphate from H_3PO_4 solution by 10% LA-1, 20% decanol in kerosene. (Volume %.) No Fe^{3+} is present.

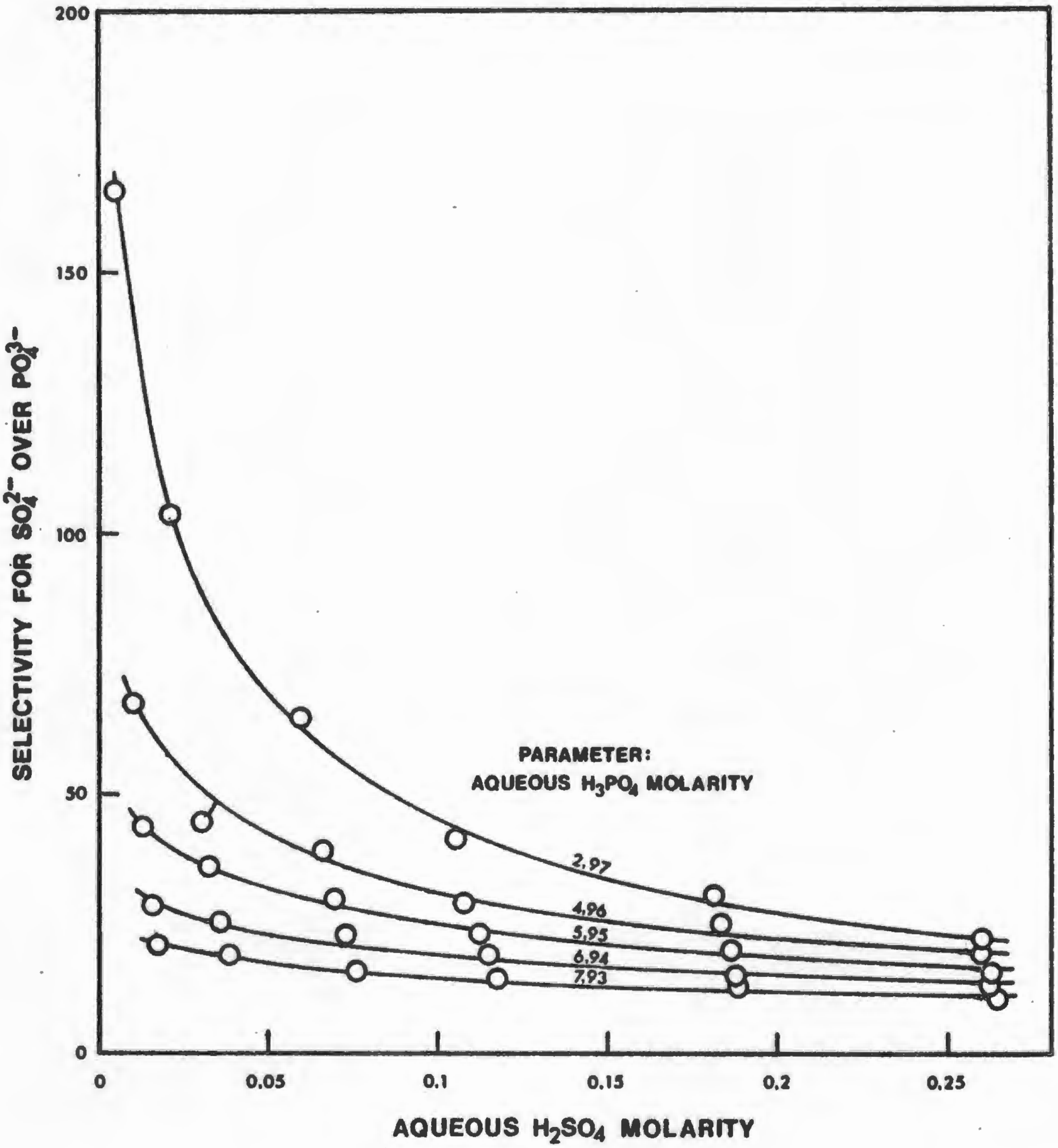

FIG. 3.11

Selectivity for sulphate over phosphate $\frac{[H_2SO_4]_{org}\,[H_3PO_4]_{aq}}{[H_2SO_4]_{aq}\,[H_3PO_4]_{org}}$ for 5% LA-1, 10% decanol in kerosene. (Volume %.) No Fe^{3+} is present.

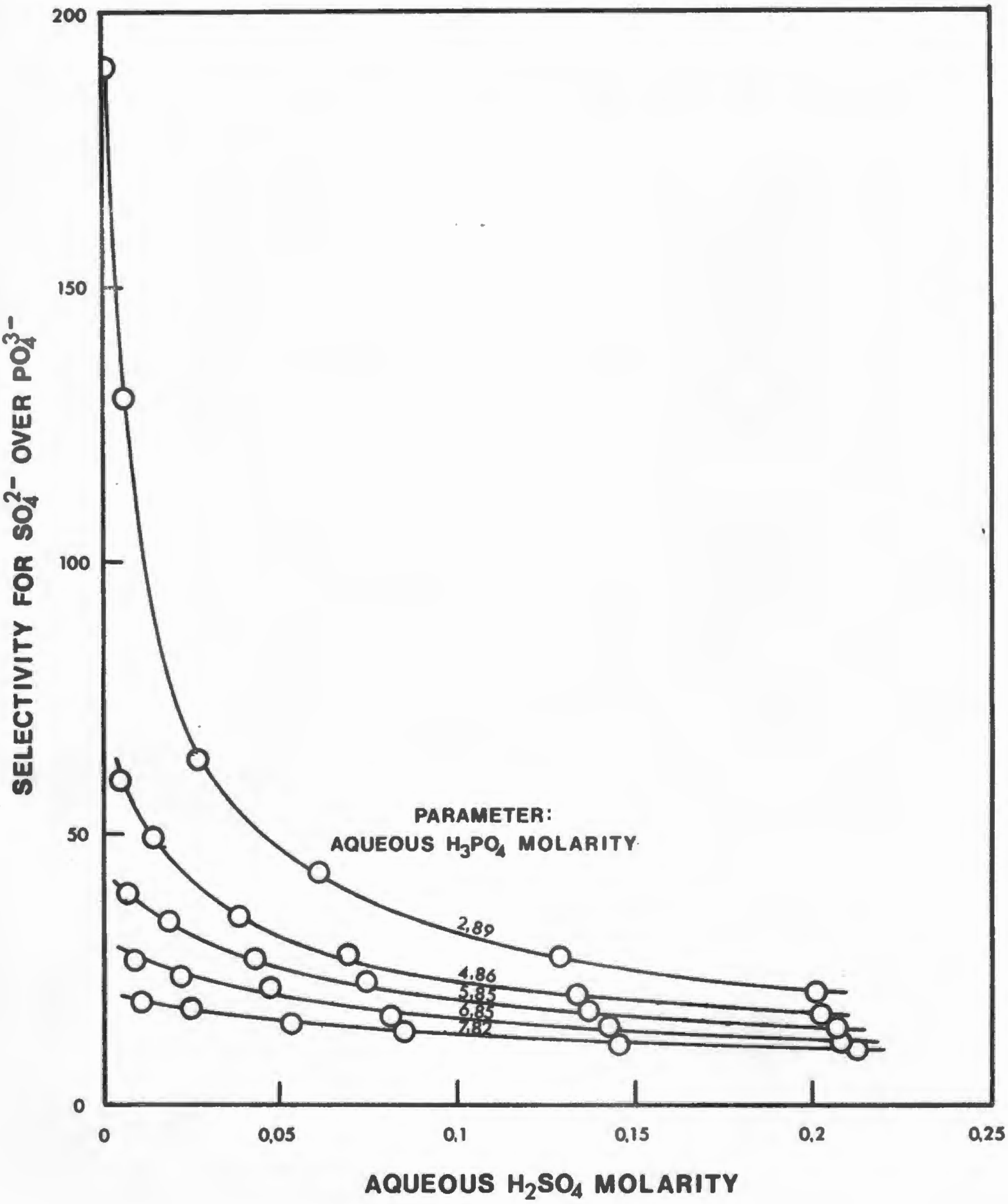

FIG. 3.12

Selectivity for sulphate over phosphate $\frac{[H_2SO_4]_{org}[H_3PO_4]_{aq}}{[H_2SO_4]_{aq}\ [H_3PO_4]_{org}}$ for 10% LA-1, 20% decanol in kerosene. (Volume %.) No Fe^{3+} is present.

Figs. 3.13 and 3.14 show the actual Fe^{3+} curves obtained, while Figs. 3.15 and 3.16 show how the selectivity for H_3PO_4 over Fe^{3+} varies with H_3PO_4, H_2SO_4 and Fe^{3+} concentration.

It would be very difficult to explain these results on a theoretical basis, and indeed, more information on the system is needed, especially in the region of low Fe^{3+} concentration. The lowest used was 1000 ppm, at which concentration the effects of Table 3.2 are already fully established, whereas there must be a continuous transition from the situation with no Fe^{3+} present.

3.9 EXTRACTION OF WATER

When LA-1 extracts H_3PO_4 from aqueous solution, some water is taken up as well. Most amine/acid systems behave in this way. It is important to determine the amount of water extracted, because otherwise a material balance for a multistage process cannot be effectively done.

Water extraction by 5% LA-1 with pure H_3PO_4 solution was studied by carefully separating the organic phase and weighing it, the excess weight being attributable to extracted water. Blanks were done to account for the organic phase lost by adherence to the inside of the separating funnels used. The method is more fully described in Appendix B.

Fig. 2.1 shows the extraction curve obtained, together with the H_3PO_4 extraction curve. It can be seen that water extraction is considerable and has a profound effect on the material balance.

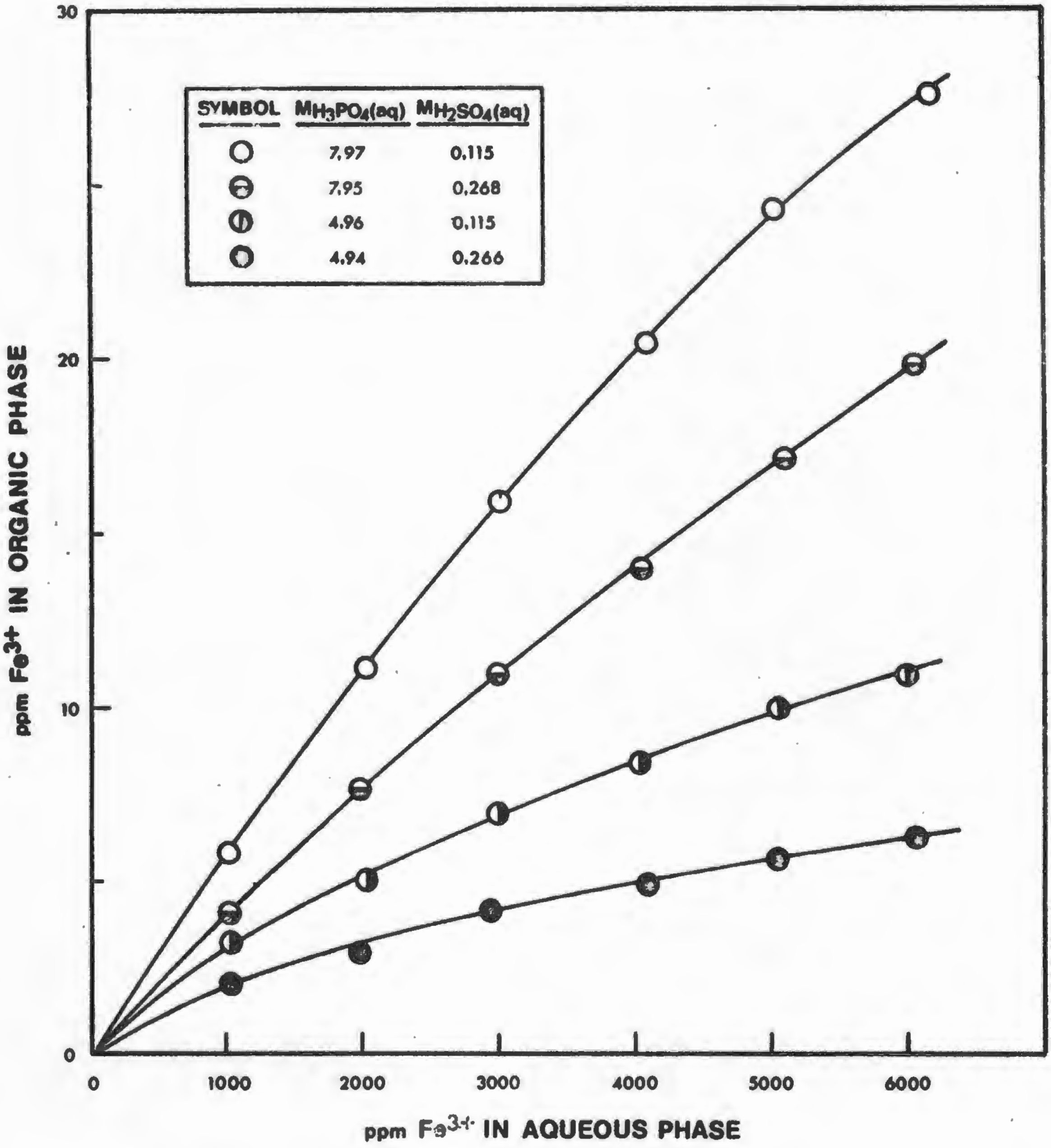

FIG. 3.13

Extraction of Fe^{3+} from H_3PO_4/H_2SO_4 solution by 5% LA-1, 10% decanol in kerosene. (Volume %.)

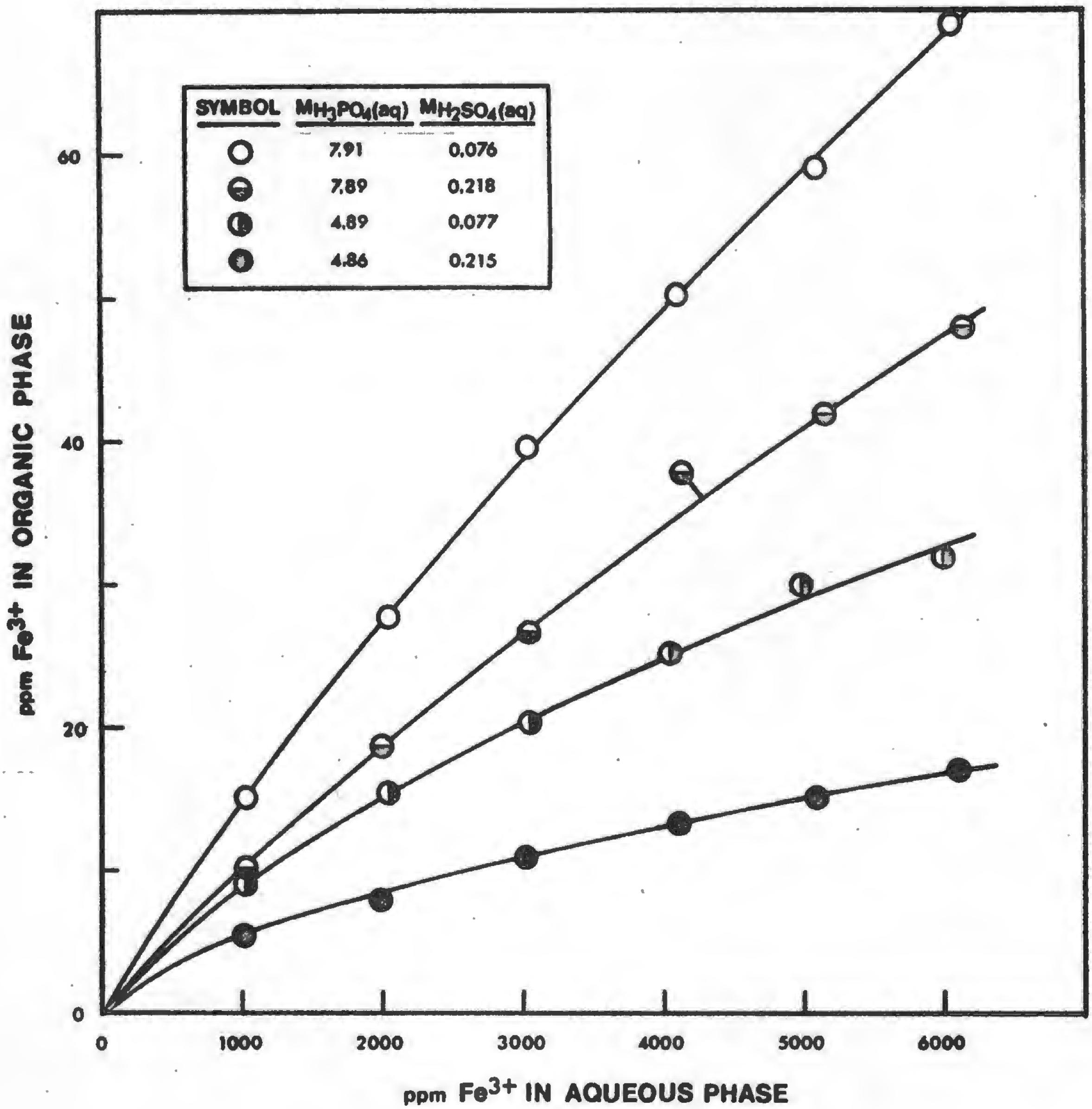

FIG. 3.14

Extraction of Fe^{3+} from H_3PO_4/H_2SO_4 solution by 10% LA-1, 20% decanol in kerosene. (Volume %.)

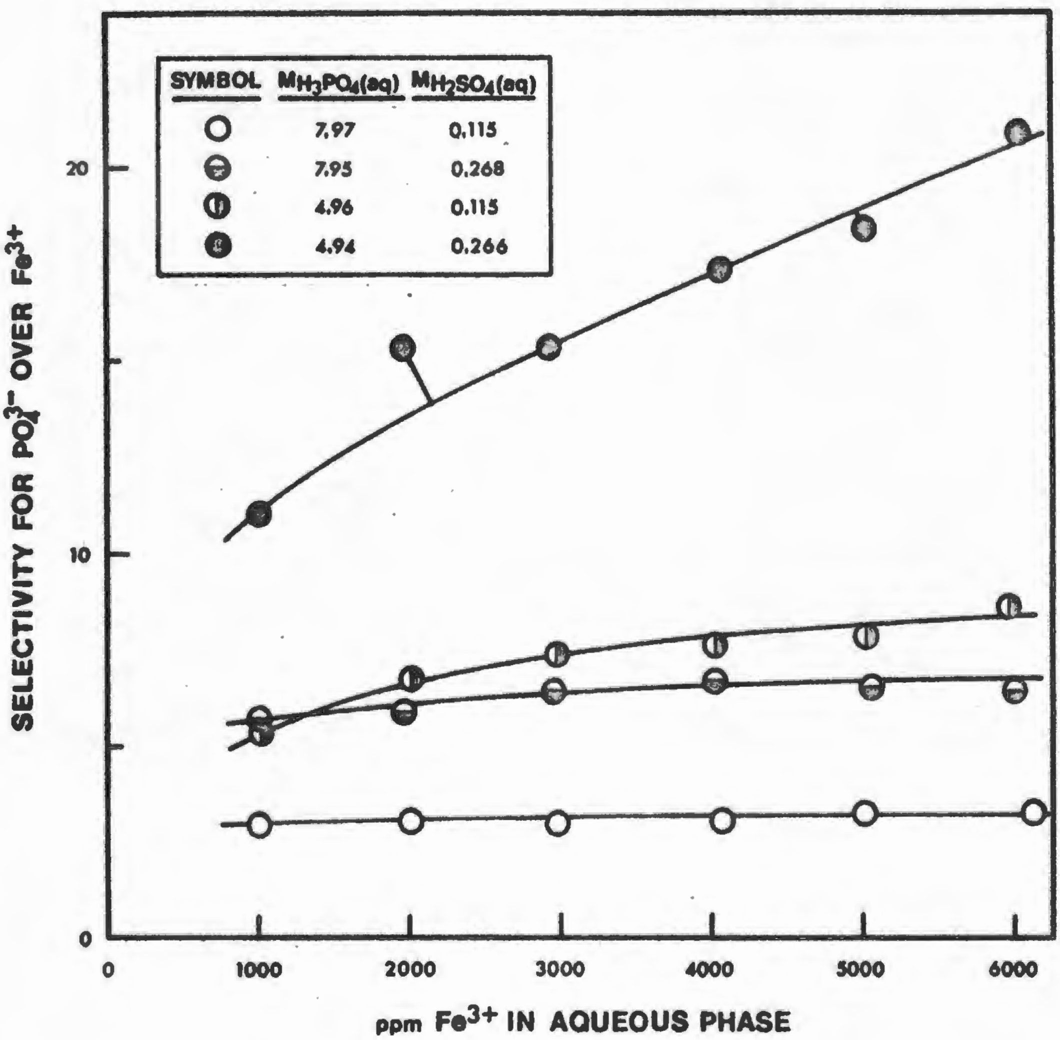

FIG. 3.15

Selectivity for phosphate over iron $\frac{[H_3PO_4]_{org}\,[Fe^{3+}]_{aq}}{[H_3PO_4]_{aq}\,[Fe^{3+}]_{org}}$ with sulphate present, for 5% LA-1, 10% decanol in kerosene. (Volume %.)

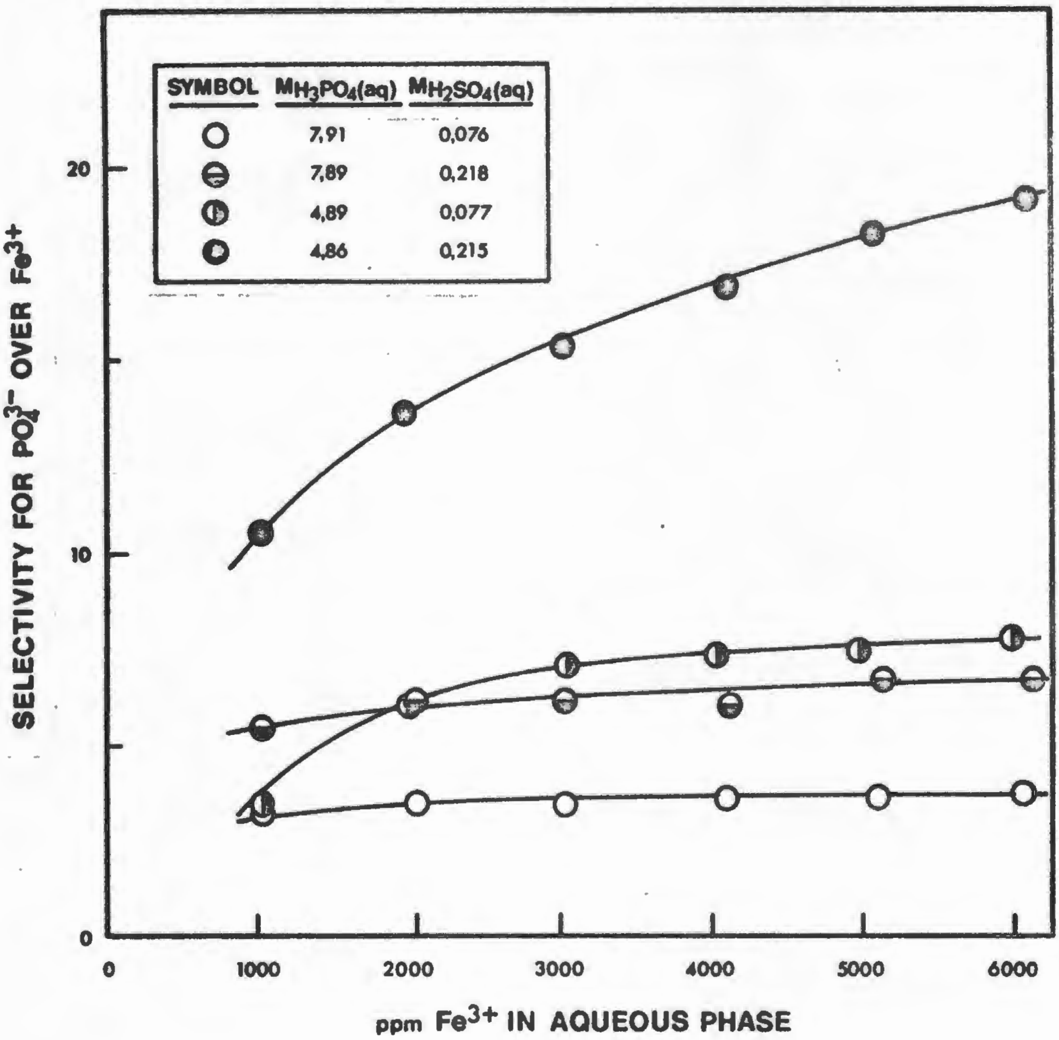

FIG. 3.16

Selectivity for phosphate over iron $\frac{[H_3PO_4]_{org}\,[Fe^{3+}]_{aq}}{[H_3PO_4]_{aq}\,[Fe^{3+}]_{org}}$ with sulphate present, for 10% LA-1, 20% decanol in kerosene. (Volume %.)

CHAPTER 4

THEORETICAL ASPECTS OF AMINE EXTRACTION

4.1 EXTRACTION OF ACIDS BY AMINES

Since the early work of Smith and Page (38), many amine/acid systems have been studied, and various theories put forward to explain their behaviour. Table 4.1 lists a few of the systems for which information is available.

Excellent reviews on amine extraction have been written by Schmidt (64) and Frolov, Ochkin and Sergievsky (65).

Investigators in this field tend to use the simplest systems possible, namely, an amine dissolved in a pure diluent extracting one acid from aqueous solution. Solubilisers and mixtures of acids are generally avoided, because of the complications they add. It is considered wiser to attempt to understand the more simple cases before tackling the more complex, and indeed, these 'simple' systems exhibit behaviour which is often very difficult to fit to a theory (65).

4.2 THEORIES BASED ON CHEMICAL EQUILIBRIA

The standard method of describing acid distribution is by means of mass-action type equations, using activities rather than concentrations where applicable. A good example of this method is the work of Allen (50), who studied the extraction of H_2SO_4 by solutions of tri-n-octylamine (TOA) in benzene, in the region of less than unity molar ratio acid to amine in the organic phase.

He assumed that at low acid concentrations, only the normal sulphate would be formed:

$$K_1 = \frac{\left[R_2H_2SO_4\right]}{a_{H_2SO_4}\left[R\right]^2} \qquad \text{------ } 4.1$$

where R represents the amine and $a_{H_2SO_4}$ is the activity of

TABLE 4.1

SOME TYPICAL AMINE/ACID EXTRACTION SYSTEMS WHICH HAVE BEEN STUDIED

Amines	Acids	Diluents	Ref.
TOA	H_2SO_4	benzene	(50)
TOA	HCl	benzene	(51)
TOA	HF, HCl, HBr, HI	toluene, xylene, nitrobenzene, 2-nitropropane, cyclohexane	(52)
TOA	HF, HCl, HNO_3, H_2SO_4	xylene	(53)
TOA	HNO_3	benzene, nitrobenzene, chloroform, dodecane, dodecane with 6% n-octanol	(54)
TOA	HCl, HNO_3, $HClO_4$, H_2SO_4, H_3PO_4	benzene	(55)
TOA, THA	H_2SO_4	benzene	(56)
TAA	HCl, HBr, HI, HNCS	benzene, nitrobenzene, chloroform, cyclohexane, carbon tetrachloride	(57)
TAA	$HClO_4$, $HReO_4$	benzene, nitrobenzene, chlorobenzene, anisole, o-dichlorobenzene, mesitylene, sym-triethylbenzene, tetrachloroethylene	(58)
TNA	HF	none, benzene	(59)
TLA	HNO_3	benzene	(60)
MDOA	HF, HCl, HBr, HI, HNO_2, HNO_3, HCN, $HClO_4$, H_2SO_4, H_2SeO_4, $(COOH)_2$	chloroform	(61)
LA-1	HNO_3	benzene, chloroform	(62)
LA-2	HCl, HBr, HI	carbon tetrachloride	(63)

TOA = tri-n-octylamine

TAA = triaurylamine

THA = tri-n-hexylamine

TNA = tri-n-nonylamine

TLA = trilaurylamine (n-dodecyl)

MDOA = methyldi-n-octylamine

H_2SO_4 in aqueous solution. A log-log plot of the data according to equation 4.1 fitted to a straight line of unit slope at values of $[R_2H_2SO_4]$ below 0,02 M with $K_1 = 1,90 \times 10^8$ moles l^{-1}. It was postulated that aggregation of the organic species was responsible for the deviations which occurred above 0,02 M. Such aggregation, or colloid formation, is a common phenomenon in amine systems (65,66,67).

Bisulphate formation now had to be considered. This is best studied at organic phase acid to amine molar ratios of more than 0,5 to 1, where the free amine concentration $[R]$ may be considered negligible. In this region, where organic species are well aggregated, it was found best to treat bisulphate formation along similar lines to sulphate-bisulphate ion exchange in a solid resin. The exchange equation is:

$$2HSO_4^- + R_2H_2SO_4 \rightleftharpoons 2RH_2SO_4 + SO_4^{2-} \quad \text{-----} \; 4.2$$

Organic phase activities of $R_2H_2SO_4$ and RH_2SO_4 were taken as their mole fractions:

$$X = X_{RH_2SO_4} = \frac{[RH_2SO_4]}{[RH_2SO_4] + 2[R_2H_2SO_4]} \quad \text{-----} \; 4.3$$

$$X_{R_2H_2SO_4} = 1 - X \quad \text{-----} \; 4.4$$

Equation 4.2 indicates the equilibrium

$$K_2' = \frac{X^2}{a_{H_2SO_4}(1-X)} \quad \text{------} \; 4.5$$

but the empirical result leads to

$$K_2'' = \frac{X^2}{a_{H_2SO_4}^{2/3}(1-X)} \quad \text{------} \; 4.6$$

$$\text{or} \quad K_2 = \frac{X^3}{a_{H_2SO_4}(1-X)^{3/2}} \quad \text{------} \; 4.7$$

Apparently, this type of deviation from the normal exponents is common in ion exchange systems, and equation 4.7 was accepted without a specific attempt to explain it theoretically.

The next step was to apply equation 4.1, making allowance for the influence of bisulphate on the free amine concentration. To do this, X was found from equation 4.7 using the known aqueous H_2SO_4 activity, and then $[R]$ could be obtained from the total organic sulphate concentration. Equation 4.1 should still apply, if $[R_2H_2SO_4]$ is taken as the concentration in true solution, as opposed to the overall concentration, which includes the colloidal material. This true solution concentration was considered to be constant in the presence of colloid, if this contained salt of constant activity. The assumption seems rather dubious, since the activity of $R_2H_2SO_4$ in the colloid has already been taken as its mole fraction. Also, the possible presence of RH_2SO_4 was not considered at all. Nevertheless, the treatment led to equations which satisfactorily fitted the data.

In the presence of colloid, equation 4.1 becomes

$$K_3 \quad = \quad a_{H_2SO_4}[R]^2 \qquad \text{------ } 4.8$$

This equation fitted sets of data in which total amine concentration was constant, but if this concentration was changed, K_3 also changed. To account for this, it was assumed that not all the free amine was in true solution, but that some was associated with the colloid. The fraction in true solution is designated α, and the rest is in the colloid at an activity proportional to its equivalent fraction there. This gives

$$D \quad = \quad \frac{(1-\alpha)[R]}{\left([\Sigma R] - \alpha[R]\right)\alpha[R]} \qquad \text{------ } 4.9$$

where D is a constant, and $[\Sigma R]$ is total amine concentration. When $[R]$ is very small, equation 4.9 becomes

$$D \quad = \quad \frac{1}{[\Sigma R]}\left(\frac{1}{\alpha_0} - 1\right) \qquad \text{------ } 4.10$$

where the subscript 0 implies infinite dilution of R. For two total amine concentrations $[R]'$ and $[R]''$

$$D = \frac{1}{[\Sigma R]'}\left(\frac{1}{\alpha_0'} - 1\right) = \frac{1}{[\Sigma R]''}\left(\frac{1}{\alpha_0''} - 1\right) \qquad \text{----- } 4.11$$

The object of the calculation is to obtain a value for D such that the free amine concentration in true solution is a constant. Thus, for the two total amine concentrations above,

$$\alpha'[R]' = \alpha''[R]'' \quad \text{or} \quad \frac{\alpha'}{\alpha''} = \frac{[R]''}{[R]'} \qquad \text{----- } 4.12$$

From the data, the limiting ratio $\frac{[R]''}{[R]'}$ was found, and hence D could be calculated from equation 4.11, and α from equation 4.9.

This now enabled all the data to be fitted by equations. It must be remembered that further extraction of H_2SO_4 beyond the amount required to convert all the amine to bisulphate, is not explained by the theory. Some investigators have calculated equilibrium constants for subsequent addition of acid molecules to amine salts. For, example, Bullock et al (61) obtained values for the equilibrium constant of the first addition of HNO_3, HF, HCl and HBr to the corresponding salts of methyldioctylamine (MDOA) in chloroform. These 'constants' were found to vary considerably with total amine concentration, and so could not be regarded as theoretically satisfactory. Investigators tend to concentrate more on the salt formation region than the excess acid region, the latter, if treated at all, usually receiving not much more than qualitative discussion.

Fig. 4.1 shows a set of extraction isotherms for 0,4 M MDOA in chloroform with various acids. It can be seen how different acids follow widely differing isotherms, and how important the region of excess acid is.

Several workers have used infrared and other forms of spectroscopy to gain insight into the nature of the bonding

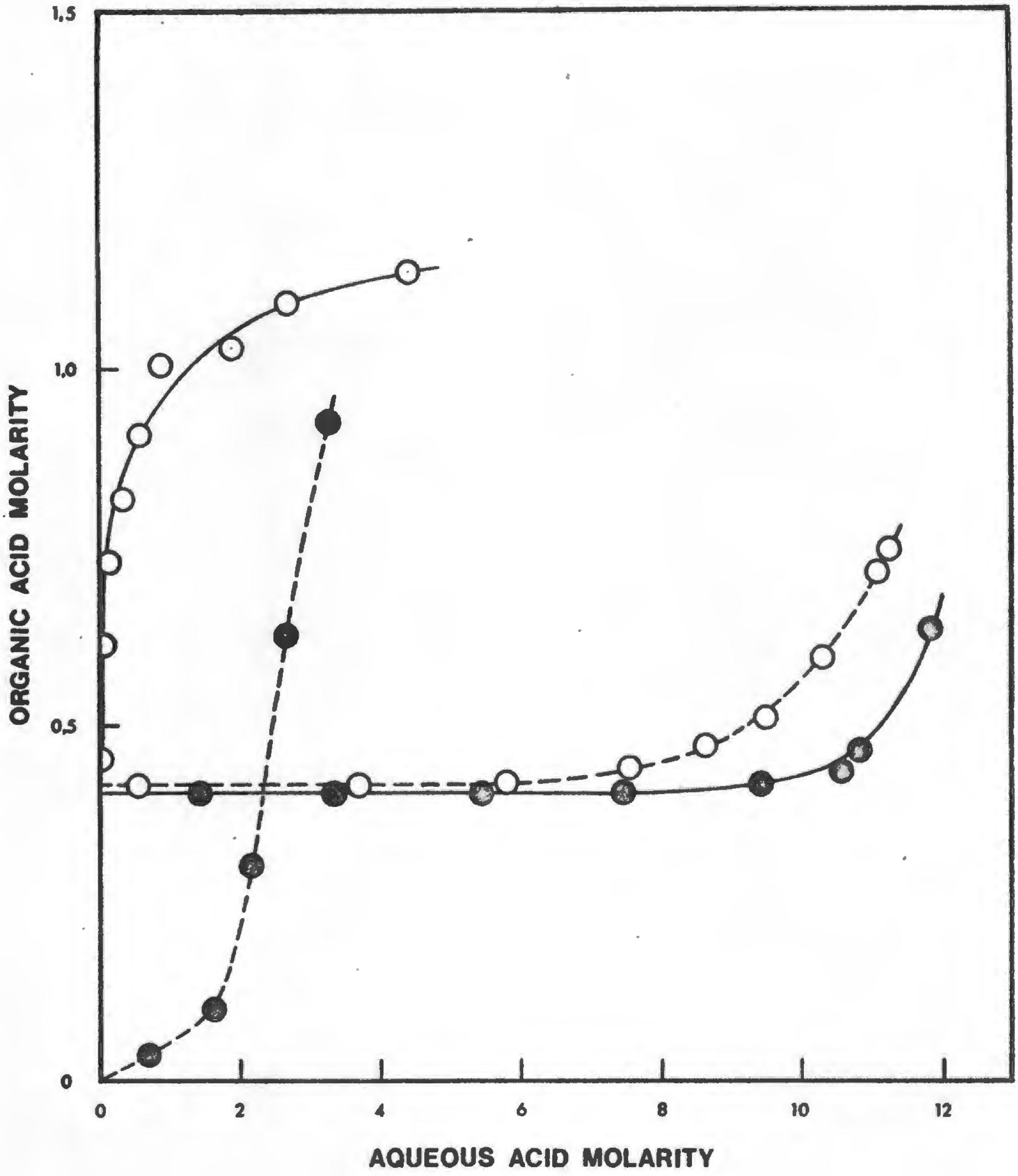

FIG. 4.1

Extraction of hydrocyanic acid and hydrohalic acids by ~0,4 M MDOA in chloroform. (See reference (61).) Initial MDOA concentrations:
o——o, HF, 0,397 M; o---o, HCl, 0,415 M;
●——●, HBr, 0,392 M; ●---●, HCN, 0,395 M.

which occurs in organic species (54,55,56,60,61,63,68). This gives useful information on the compounds which are formed, but the derivation of theories to describe the behaviour of these compounds is difficult.

4.3 INSTABILITY IN AMINE EXTRACTION SYSTEMS

There is reason to believe that equilibria in amine extraction systems may change with conditions of loading or stripping, and with the vigour of agitation. Allen and McDowell (69) have shown that in the extraction of uranyl sulphate by tri-n-octylamine sulphate and di-n-decylamine sulphate, the equilibrium is affected by the vigour of agitation. The theory suggested is that complexes form by adsorption at the liquid-liquid interface, and the larger the interface, the greater the effect. On settling, these complexes may enter the organic phase in a metastable condition, and persist for a very long time.

The situation could also be envisaged whereby the difference between extraction and stripping produces a similar effect. In the present work, all equilibrium curves were obtained by extraction with vigorous shaking, and no study of hysteresis effects produced by unstable or metastable species was attempted. However, an investigation of these phenomena is suggested as a possible project for the future.

4.4 SIMILARITY OF AMINE EXTRACTION AND GAS ADSORPTION

Since an adequate model of an amine/acid extraction system was not readily forthcoming from the literature, the idea of applying gas adsorption theory was tried. The inspiration for this came from the similarity of typical amine extraction isotherms, and the sigmoid type isotherms which are common in multi-layer gas adsorption.

The earliest theory explaining these sigmoid shapes was published by Brunauer, Emmett and Teller (70) in 1938, and is known as the BET theory. It is based on the kinetic approach of gas molecules attaching themselves to free adsorbent surface or other adsorbed molecules, while others break free and re-enter the gaseous phase, thus setting up an equilibrium. For a gas to have a sigmoid adsorption isotherm, it must be below its critical temperature, and so there will be a saturation pressure, p_0, at which condensation takes place. As this pressure is approached, the sigmoid isotherm tends to infinity.

The BET equation is

$$\frac{v}{v_m} = \frac{cp}{(p_0 - p)\left(1 + (c-1)\frac{p}{p_0}\right)} \qquad \text{------ 4.13}$$

where v is the volume of gas adsorbed (expressed at standard conditions)

v_m is the volume of gas needed to form a monolayer on the adsorbent

p is the pressure of the gas

p_0 is the saturation pressure

c is a constant, which depends on the eqilibrium between adsorbing and desorbing molecules, and also contains p_0 as a factor.

The BET equation is similar to the result which is obtained by applying mass action equilibria to an amine extraction system, assuming the first attachment of an acid molecule to an amine molecule has an equilibrium constant K_1, and all subsequent attachments a constant K_2. If at high acid concentration, the amine solution becomes miscible with the acid in all proportions, this condition corresponds to condensation at the saturation pressure in gas adsorption.

A set of BET isotherms appears in Fig. 4.2. It can be seen that the general shape is quite characteristic, and cannot be fitted to just any sigmoid curve. For instance, H_3PO_4 curves can be fitted much better than H_2SO_4 curves (see Fig. 3.6), since the latter has a flatter middle portion than the former. The BET treatment really assumes too much ideality to fit non-ideal systems, which need a thermodynamic approach.

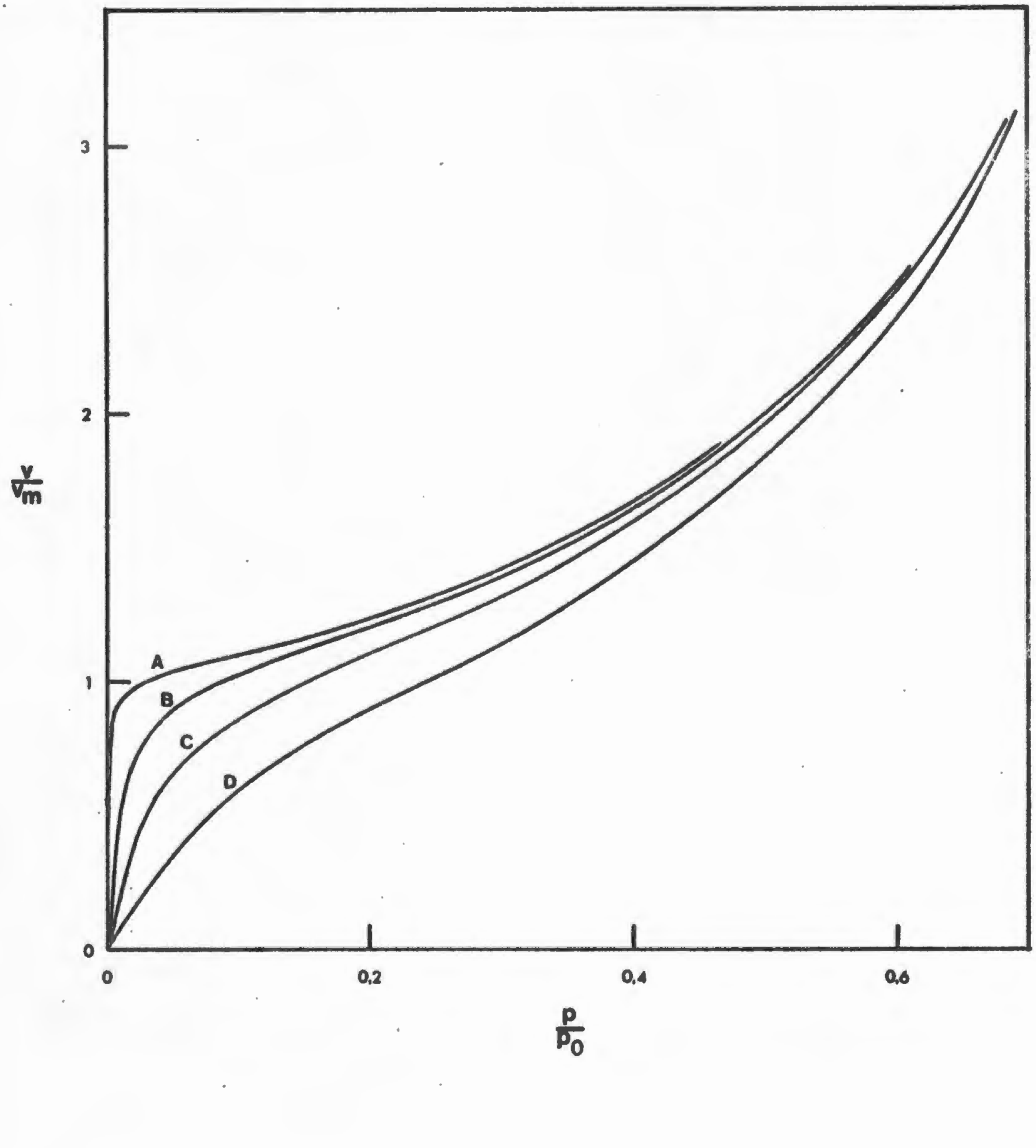

FIG. 4.2

BET isotherms (see equation 4.13).
(A) c=1000; (B) c=100; (C) c=30; (D) c=10.

4.5 SOME INTERESTING GAS ADSORPTION ISOTHERMS

Amine extraction isotherms of the sigmoid type exhibit one step for the first acid molecule addition, but some gas adsorption isotherms show many steps, one for each layer of molecules as it adds on (71,72,73). For this to be observed, it is necessary for the adsorbent surface to be highly uniform and for the temperature to be low. Such behaviour is followed by C_2H_5Cl, $CHCl_3$, $CFCl_3$ and C_6H_6 adsorbing on graphite (73). An interesting feature of the first three of these compounds is that they all show a sudden jump in the sub-monolayer region. The shape of the isotherms here looks like that for HCN in Fig. 4.1, and this may be significant. The explanation for the jump is that when the adsorbent surface accomodates relatively few adsorbate molecules, the latter may act as a '2-dimensional gas', but with the addition of more molecules, this 'gas' condenses to form a '2-dimensional liquid', and the isotherm jumps at this sudden phase change. Lateral interactions between molecules are important.

The steps themselves may be quite sharp and the plateaux between them quite flat, unlike the middle portion of a BET isotherm, which has an appreciable slope. The higher the number of the layer adding on, the more blurred the step becomes. Increase in adsorbent surface irregularity and increase in temperature both tend to blur the steps, and reduce the isotherm to something approaching the BET form.

4.6 THE APPLICATION OF THERMODYNAMICS

It was shown in the above section that phase changes can occur in gases adsorbed on a surface. The colloid formation postulated by Allen (see Section 4.2) to explain deviation from the simple mass-action equation 4.1 in the system tri-n-octylamine/H_2SO_4, is also akin to a phase change, since it begins suddenly at $[R_2H_2SO_4] = 0{,}02$ M.

Adsorption isotherms may be derived by considering the increments in the heat of condensation induced by the adsorbent surface for gas molecules in the various layers of an adsorbed film. Thus Halsey (74,75) has suggested the isotherm

$$\theta = \exp(\Delta E_0/\Delta E_m)\sum_{n=1}^{\infty} z^{n^3} \qquad \text{------ } 4.14$$

where θ is the number of monolayers adsorbed. (θ can be fractional or an integer plus a fraction.)

ΔE_0 is the increment in heat of condensation for the first adsorbed layer.

ΔE_m is the modulus of the distribution function $N_i(\Delta E)$ of site energies in the i'th layer, where

$$N_i(\Delta E) = \frac{1}{\Delta E_m}\exp\left(\frac{-\Delta E}{i^3 \Delta E_m}\right) \quad \text{and} \quad z = \left(\frac{p}{p_0}\right)^{RT/\Delta E_m}$$

Equation 4.14 is subject to the condition that each term z^{n^3} in the summation should be $\leq \exp(-\Delta E_0/\Delta E_m)$. If any term in the series becomes greater than this limit, it is replaced by the limit.

The equation can produce isotherms with steps of various sharpnesses, or it can produce BET shaped isotherms. It cannot account for the sudden jump during the filling of the first layer, which can occur in some systems (see Section 4.5).

Surface irregularities, both physical and in the adsorbent properties of the surface, tend to smooth the steps, as does increasing temperature, since the distinction between the different layers is reduced. Such blurring also occurs in amine extraction since, in the colloids which are formed, amine and acid molecules would be arranged somewhat randomly in a cluster, and the temperature is also quite high. This may be why amine extraction systems show only one step in their isotherms.

An extensive theoretical study of gas adsorption has been undertaken by Hill on the basis of statistical thermodynamics (76,77,78,79), and many aspects of the field are covered.

For instance, the number of ways X molecules can fill B sites is considered, as well as the number of ways (A-X) molecules may be placed on top of the X molecules in the first adsorbed layer (76). For mobile films ('2-dimensional gases'), a van der Waals equation of state is applied (77,78), and phase changes in the submonolayer portion of isotherms explained. Transitions from mobile to localised films are analysed, as well as multilayer adsorption on top of a mobile film (77). A treatment for diatomic molecules in which rotation is restricted, is given (79).

In general, thermodynamic adsorption isotherms are highly complex and would, no doubt, require a great deal of modification for application to amine extraction. Information on the subject may be found in Gregg's 'The Surface Chemistry of Solids' (80) and Adamson's 'Physical Chemistry of Surfaces' (81).

4.7 EXTRACTION OF MIXED ACIDS

4.7.1 A Simple Extension of the BET Equation

The BET equation can be extended to include more than one gas. The following derivation uses gas adsorption symbols, but the same argument applies to acid extraction. The assumption made is that, for all layers other than the first, the proportion of each gas adsorbing is constant, and does not depend on the composition of the previous layer. This assumption is bad, but was used as a first approximation, and leads to the situation of having to add only two constants, p_{GO} and c_G, for each gas G added to the system. It is also assumed that the gases have molecules of approximately the same size, so that a mixed layer is reasonably flat.

Adsorption of gases A and B

Adsorption/desorption equilibria:

For gas A

$$\left.\begin{aligned} a_1p_AS_0 &= c_1S_A\,e^{-E_{A1}/RT}\\ a_2p_AS &= c_2S_{A2}e^{-E_{A2}/RT}\\ a_3p_AS_2 &= c_3S_A\,e^{-E_{A3}/RT}\\ \vdots\qquad &\qquad\vdots \end{aligned}\right\} \text{----- 4.15}$$

For gas B

$$\left.\begin{aligned} b_1p_BS_0 &= d_1S_B\,e^{-E_{B1}/RT}\\ b_2p_BS &= d_2S_{B2}e^{-E_{B2}/RT}\\ b_3p_BS_2 &= d_3S_B\,e^{-E_{B3}/RT}\\ \vdots\qquad &\qquad\vdots \end{aligned}\right\} \text{----- 4.16}$$

where S_0 is surface area not covered by adsorbed gas
S_i is surface area covered by i layers ($i = 1\cdots\cdot n$)
S_{Ai} is the portion of S_i covered by gas A in the i'th layer ($i = 1\cdots\cdot n$)

Similar definitions apply for gas B.

All a_i, b_i, c_i, d_i, are constants.

E_{Ai}, E_{Bi} are activation energies for adsorption/desorption of gases A and B in the i'th adsorbed layer.

Assume

$$\left.\begin{aligned} a_2 &= a_3 = a_4 = \cdots\cdot\\ b_2 &= b_3 = b_4 = \cdots\cdot\\ c_2 &= c_3 = c_4 = \cdots\cdot\\ d_2 &= d_3 = d_4 = \cdots\cdot\\ E_{A2} &= E_{A3} = E_{A4} = \cdots\cdot\\ E_{B2} &= E_{B3} = E_{B4} = \cdots\cdot \end{aligned}\right\} \text{----- 4.17}$$

Now $S_{A1} + S_{B1} = S_1$
$S_{A2} + S_{B2} = S_2$ and so on.

$$S_{A1} = \frac{a_1p_AS_0}{c_1e^{-E_{A1}/RT}} = K'_AS_0p_A$$

(replacing $\dfrac{a_1}{c_1e^{-E_{A1}/RT}}$ by one constant K'_A)

Similarly $$S_{A2} = \frac{a_2 p_A S_1}{c_2 e^{-E_{A2}/RT}} = K_A S_1 p_A$$

$$S_{Ai(i\geqslant 2)} = K_A S_{(i-1)} p_A$$

Also $$S_{B1} = K'_B S_0 p_B$$

$$S_{Bi(i\geqslant 2)} = K_B S_{(i-1)} p_B$$

Now $$\begin{aligned} S_{A2} &= K_A p_A (S_{A1} + S_{B1}) \\ &= K_A p_A (K'_A S_0 p_A + K'_B S_0 p_B) \\ &= K_A p_A (K'_A p_A + K'_B p_B) S_0 \end{aligned}$$

$$\begin{aligned} S_{A3} &= K_A p_A S_2 \\ &= K_A p_A (K_A p_A + K_B p_B)(K'_A p_A + K'_B p_B) S_0 \end{aligned}$$

and in general,

$$S_{Ai(i\geqslant 2)} = K_A p_A (K_A p_A + K_B p_B)^{(i-2)} (K'_A p_A + K'_B p_B) S_0 \qquad \text{-----}\ 4.18$$

Let $$K'_A p_A + K'_B p_B = x$$

$$K_A p_A + K_B p_B = y$$

Then $$S_{A1} = K'_A p_A S_0$$

$$S_{Ai(i\geqslant 2)} = K_A p_A x y^{(i-2)} S_0$$

Let the volume of gas A adsorbed under standard conditions be v_A, and the volume needed to form a monolayer on the adsorbate be v_{Am}. For any pair of p_A and p_B values, the fraction of each layer from the second up composed of gas A has been assumed to be constant.

Therefore:

$$\frac{v_A}{v_{Am}} = \frac{\left(\sum_{i=1}^{\infty} S_i\right)\frac{S_{A1}}{S_1} + \sum_{i=2}^{\infty} (i-1) S_{Ai}}{\sum_{i=0}^{\infty} S_i}$$

$$= \frac{(1-y) K'_A p_A + x K_A p_A}{(1-y)(1-y+x)}$$

$$= \frac{K'_A p_A - K'_A p_A K_B p_B + K_A p_A K'_B p_B}{(1-K_A p_A-K_B p_B)(1-K_A p_A-K_B p_B+K'_A p_A+K'_B p_B)} \qquad \text{----- } 4.19$$

In the absence of gas B, v_A must be infinite when $p_A = p_{AO}$. Therefore, $1-K_A p_{AO} = 0$, from which $K_A = \frac{1}{p_{AO}}$. Also, $K_B = \frac{1}{p_{BO}}$.

Let $c_A = \frac{K'_A}{K_A}$ and $c_B = \frac{K'_B}{K_B}$. Substitute these relationships into equation 4.19 to give

$$\frac{v_A}{v_{Am}} = \frac{p_A(c_A + \frac{p_B}{p_{BO}}(c_B-c_A))}{(p_{AO}-p_A-\frac{p_{AO}}{p_{BO}}p_B)(1+(c_A-1)\frac{p_A}{p_{AO}}+(c_B-1)\frac{p_B}{p_{BO}})} \qquad \text{----- } 4.20$$

Equation 4.20 may be extended to include many gases, A, B, C, ..., as follows:

$$\frac{v_A}{v_{Am}} = \frac{p_A(c_A + \frac{p_B}{p_{BO}}(c_B-c_A) + \frac{p_C}{p_{CO}}(c_C-c_A) + \cdot\cdot)}{(p_{AO}-p_A-\frac{p_{AO}}{p_{BO}}p_B-\frac{p_{AO}}{p_{CO}}p_C\cdot\cdot)(1+(c_A-1)\frac{p_A}{p_{AO}}+(c_B-1)\frac{p_B}{p_{BO}}+(c_C-1)\frac{p_C}{p_{CO}}+\cdot\cdot)} \qquad \text{----- } 4.21$$

Similar isotherms may be written to give v_B, v_C, etc.

It can readily be seen that mixed acid extraction will give equivalent isotherms, if similar assumptions are made. Pressure is replaced by acid concentration, and surface areas by fractions of the amine associated with a certain number of acid molecules. For example, S_O becomes the fraction of amine which may be regarded as unassociated or 'free', and so forth. Colloid formation is not specifically taken into account, but if most of the organic species are in colloid form, the equation parameters should fit adequately over a wide range of conditions. Large discrepancies may come in, however, in the low concentration region, where there is a transition from true solution to colloid.

Equation 4.20 was fitted to the 5% LA-1 H_3PO_4/H_2SO_4 distribution data, by the Nelder and Mead Simplex method (82), and the results are summarised in Table 4.2. The equation parameters v_A, v_{Am}, p_{AO}, p_{BO}, c_A, c_B take on the following meanings:

v_A - organic phase H_3PO_4 concentration
v_{Am} - amine molarity
p_{AO} - H_3PO_4 concentration at which acid and organic phase just become mutually miscible
p_{BO} - as for p_{AO}, only H_2SO_4 is involved
c_A, c_B - dimensionless constants describing the equilibrium

It can be seen that the results of Table C.15 do not represent a good fit of the experimental data. Convergence of the parameters was also bad, since the programme often changed their values by large amounts with only a minimal improvement in the standard deviation of the fit. Apparently, two constants per acid are insufficient to describe the system, and so a better equation was sought.

4.7.2 Extended BET Treatment of T.L. Hill

In 1946, Hill published a method of extending the BET equation to two or even more gases (83), taking into account the effect of the composition of lower layers on the adsorption taking place in higher layers. Molar heats of adsorption of the two gases, A and B, are defined as follows:

q_A - heat of adsorption of A on adsorbent surface
q_B - of B on adsorbent surface
q_{AA} - of A on a layer of pure A
q_{BB} - of B on a layer of pure B
q_{AB} - of A on a layer of pure B
q_{BA} - of B on a layer of pure A
q_{AN_A} - of A on a layer of (mole fraction A) = N_A
q_{BN_A} - of B on a layer of (mole fraction A) = N_A

A complex expression for the isotherm was derived, and approximated to give three versions, each of a different level of accuracy, which could be used for practical calculations. The most accurate form is given below, and was used to fit the H_3PO_4/H_2SO_4 data:

$$\frac{v_A}{v_{Am}} = \frac{E_0X}{1 + E_0Y} \qquad \text{-----}\ 4.22$$

$$X = \gamma_{A1} + (\gamma_{A1}+\gamma_{A2})E_1 + (\gamma_{A1}+\gamma_{A2}+\gamma_{A3}+\frac{E\gamma_A}{1-E})\frac{E_1E_2}{1-E} \qquad \text{-----}\ 4.23$$

$$Y = 1 + E_1 + \frac{E_1E_2}{1-E} \qquad \text{-----}\ 4.24$$

$$E_0 = x_AQ_A + x_BQ_B \qquad \text{-----}\ 4.25$$

$$E_{i(i\geqslant1)} = x_Af_A(N_{Ai}) + x_Bf_B(N_{Ai}) \qquad \text{-----}\ 4.26$$

$$E = (E_3E_\infty)^{\frac{1}{2}} \qquad \text{-----}\ 4.27$$

$$E_\infty = x_Af_A(N_{A\infty}) + x_Bf_B(N_{A\infty}) \qquad \text{-----}\ 4.28$$

$$\gamma_A = (\gamma_{A4}\gamma_{A\infty})^{\frac{1}{2}} \qquad \text{-----}\ 4.29$$

$$N_{A1} = \frac{x_AQ_A}{E_0} \qquad \text{-----}\ 4.30$$

$$N_{Ai(i\geqslant2)} = \frac{x_Af_A(N_{A(i-1)})}{E_{(i-1)}} \qquad \text{-----}\ 4.31$$

$$N_{A\infty} = \frac{x_Af_A(N_{A\infty})}{x_Af_A(N_{A\infty}) + x_Bf_B(N_{A\infty})} \qquad \text{-----}\ 4.32$$

$$Q_A = \exp\left[(q_A-q_{AA})/RT\right] \qquad \text{-----}\ 4.33$$

$$Q_B = \exp\left[(q_B-q_{AA})/RT\right] \qquad \text{-----}\ 4.34$$

$$f_A(N_{Ai}) = \exp\left[(q_{AN_{Ai}}-q_{AA})/RT\right] \qquad \text{----- } 4.35$$

$$f_B(N_{Ai}) = \exp\left[(q_{BN_{Ai}}-q_{BB})/RT\right] \qquad \text{----- } 4.36$$

$$x_A = \frac{p_A}{p_{AO}} \qquad \text{----- } 4.37$$

$$x_B = \frac{p_B}{p_{BO}} \qquad \text{----- } 4.38$$

Equation 4.22 is the basic form of the isotherm, which can be seen to be of the BET pattern. The equations which follow after define the right hand side of 4.22, in terms of p_A, p_{AO}, p_B, p_{BO} and the eight q values which are heats of adsorption. γ_{Ai} is the area of the i'th layer taken up by gas A, and in the application of the isotherm to the acid/amine system, was approximated by setting it equal to N_{Ai}.

For $q_{AN_{Ai}}$ and $q_{BN_{Ai}}$, values were approximated by linear interpolation between q_{AA} and q_{AB} in the first case, and q_{BB} and q_{BA} in the second.

The use of the isotherm given above involves a great deal of computer calculation, and it is still simple compared to a full thermodynamic treatment. This indicates that more complex equations may not be worth developing, since the computing time would multiply rapidly with increasing complication. The isotherm was fitted to both the 5% and 10% LA-1 data on H_3PO_4/H_2SO_4 distribution, by the Nelder and Mead simplex method (82), and the results appear in Tables C.17 and C.18 in the Appendix. The greatest inaccuracies are in the region of low H_2SO_4 concentration.

4.8 THE EXTRACTION AND INFLUENCE OF IRON

The extraction of all cations is influenced by the formation of complexes, and so a theoretical treatment would be even more difficult than for mixtures of acids. In H_3PO_4 solution, Fe^{3+} forms the complex $FeHPO_4^+$ (84), and a consideration of this species would be a good first line of approach.

The general principle can be stated that, in phosphate solution, H_3PO_4 and Fe^{3+}, in whatever complexed forms it is present, compete for entry into the organic phase, with the selectivity for H_3PO_4 over Fe^{3+} increasing with H_3PO_4 concentration, and perhaps falling off again at aqueous concentrations greater than 7 M. When H_2SO_4 is present, extra complexing takes place. For instance, it has been reported that $(FeOHSO_4)_2.2(R_2NH_2)_2SO_4$ may be formed in the organic phase (85). In view of such complications, the H_3PO_4/Fe^{3+} distribution data was fitted only to a polynomial function as explained in Section 3.5, rather than to an equation of theoretical significance.

As for the phenomena which were observed with the phosphate/sulphate distribution in the system $H_3PO_4/H_2SO_4/Fe^{3+}$ (see Table 3.2), the Hill isotherm in Section 4.7.2 goes some way towards explaining how such a situation can arise, at least on a qualitative basis. What needs to be explained is how, in the presence of Fe^{3+}, an increase in H_2SO_4 increases the amounts of both H_2SO_4 and H_3PO_4 extracted whereas, without Fe^{3+}, an increase in H_2SO_4 always reduces the amount of H_3PO_4 extracted. Hill's isotherm shows that a gas A, which adsorbs more readily on to a surface than gas B, may not adsorb so readily on to attached molecules of A. However, gas B may adsorb quite readily on to adsorbed A, leading to a situation where an increase in adsorbed A promotes the adsorption of B, in spite of the selectivity of the surface itself favouring A. In the amine extraction case, it seems that the presence of Fe^{3+}, through complexing, alters the q values in Hill's isotherm in such a way as to produce a similar effect.

This explanation is only qualitative, as can be seen from Table C.19 in the Appendix, which presents the results of an attempt to fit the data for 5% LA-1. By altering the parameters, in particular q_{BB}, the trend at least of the data can be produced.

CHAPTER 5

APPLICATION OF DISTRIBUTION DATA TO PROCESS DESIGN

5.1 STAGE TO STAGE CALCULATIONS

A multistage process with an extraction and a washing section as in Fig. 2.4, was modelled on a computer for phosphoric acid containing only Fe^{3+} as an impurity. The object was to determine the number of stages necessary for purification to the food grade level, and how this number depends on the various flow rates.

Fig. 5.1 shows a typical liquid-liquid contact stage, which need not necessarily represent a mixer-settler. The flow and concentration symbols, which are listed individually in the figure, are built up on the basis of the following:

G - flow rate
C - concentration
Subscripts: i - inlet stream
o - discharge stream
A - phosphoric acid
W - water
F - iron
Superscript: prime (') - indicates organic phase.
No prime indicates aqueous phase.

The method for determining all flows and concentrations is to start at the raffinate end and assume the process variables for this aqueous stream. Iron is ignored for the moment; the first step is to determine how acid and water pass through the system. It is also necessary to assume the variables for the aqueous discharge from the washing section, which is combined with the incoming impure acid to form the feed to the extraction section of the plant. The organic feed into the extraction

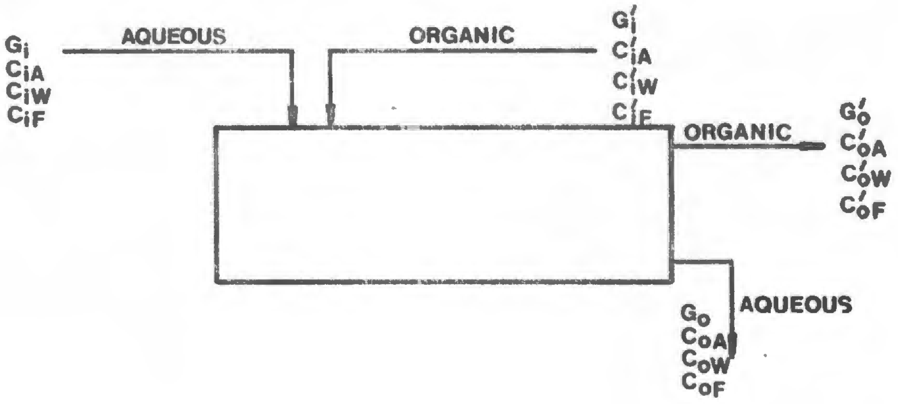

FIG. 5.1

A countercurrent extraction stage.

Meanings of symbols:

G_i = flow rate of aqueous stream entering
C_{iA} = conc. of acid in aqueous stream entering
C_{iW} = conc. of water in aqueous stream entering
C_{iF} = conc. of iron in aqueous stream entering
G_o = flow rate of aqueous stream leaving
C_{oA} = conc. of acid in aqueous stream leaving
C_{oW} = conc. of water in aqueous stream leaving
C_{oF} = conc. of iron in aqueous stream leaving
G'_i = flow rate of organic stream entering
C'_{iA} = conc. of acid in organic stream entering
C'_{iW} = conc. of water in organic stream entering
C'_{iF} = conc. of iron in organic stream entering
G'_o = flow rate of organic stream leaving
C'_{oA} = conc. of acid in organic stream leaving
C'_{oW} = conc. of water in organic stream leaving
C'_{oF} = conc. of iron in organic stream leaving

section is regenerated LA-1 solution having a known flow rate, and so the other two streams flowing into and out of the stage may be calculated by material balance and the equilibrium curves. Similar calculations are done from stage to stage until the feed stage is reached, when the resulting estimate for the acid entering this stage is compared with that from the combining of the impure feed and wash streams. The closeness of the estimate provides the basis for varying the assumed raffinate composition, and the iteration is repeated until close agreement is reached.

For the washing section, calculations were at first done from the feed entry point towards the wash water entry point, but this method was found to break down if the number of wash stages was more than about eight. The reason is that if the number of wash stages is large the differences in process stream parameters between stages close to the feed point are small, but as the end of the line of stages is approached, the changes become large, as the wash water stream drops from an acid concentration which may be about 5 M, to zero for the inflowing wash water. The method of iteration was to make small changes to the assumed aqueous outlet washings, until the corresponding wash water composition came very close to zero acid. It was found that if the assumed washings concentration was too high, and was then lowered by small amounts, the resulting calculated inlet wash water composition would decrease, slowly at first, and then much faster as zero was approached. If the number of stages in the washing section was large, a very small adjustment in the outlet composition might cause the wash water stream to fall to below zero concentration several stages before the wash entry point was reached. Sometimes, a close approach to the desired zero value was obtained, only to find that the iteration started to cycle, without getting any closer. Eventually it was decided to iterate in the opposite direction, from wash water entry to feed point, estimating the washed organic phase composition and working back to the organic entering the washing section, and comparing this with the value obtained from the extraction section calculations. The method involves a longer computer programme, but the calculating time is effectively used, since the iterations converge rapidly.

When the washing section has converged, the value of the calculated aqueous discharge composition is compared to that originally chosen for use with the extraction section calculations, and if there is too much deviation, the whole procedure of iterations is repeated using the new value.

When the H_3PO_4/H_2O system has converged, the Fe^{3+} impurity is considered in a similar way. It is assumed that Fe^{3+} does not appreciably affect either the H_3PO_4 and H_2O equilibria, or the overall material balance. Since the Fe^{3+} concentration profile from stage to stage slopes down rapidly at first and then more slowly, going from the acid feed point to the wash water inlet, the iterations in the washing section were done in this direction. No trouble at all was experienced with convergence.

5.2 MATERIAL BALANCE EQUATIONS

Using the symbols defined in Fig. 5.1, the material balance equations needed for the computer programme are derived. The equations apply to any stage. Concentration of H_3PO_4 and water are expressed as parts per million on a weight/weight basis (i.e. milligrams Fe^{3+} per kilogram of solution).

The organic phase was taken to be the 5% LA-1 solution, and the relevant extraction curves for H_3PO_4 and water were fitted to polynomials, designated here by f_1 for H_3PO_4 and f_2 for water.

We have $C'_{oA} = f_1(C_{oA})$ ----- 5.1

$C'_{oW} = f_2(C_{oA})$ ----- 5.2

Let $C'_{iA}G'_i - C_{oA}G_o = A$ ----- 5.3

$C'_{iW}G'_i - C_{oW}G_o = B$ ----- 5.4

$G'_i - G_o = C$ ----- 5.5

Then, if the aqueous outflow and organic inflow are known, A, B and C are known. This corresponds to calculations starting at the raffinate end of the plant.

Acid balance gives: $C'_{oA}G'_o - C_{iA}G_i = A$ ------ 5.6

Water " " $C'_{oW}G'_o - C_{iW}G_i = B$ ------ 5.7

Overall " " $G'_o - G_i = C$ ------ 5.8

Also: $C_{iA} + C_{iW} = 1$ ------ 5.9

From 5.6 and 5.9 $G'_o(C'_{oA}-C_{iA})+C_{iA}C = A$ ------ 5.10

From 5.7, 5.8 and 5.9 $G'_o(C'_{oW}-1+C_{iA})+C-C_{iA}C = B$ ---- 5.11

Therefore $$G'_o = \frac{A-C_{iA}C}{C'_{oA}-C_{iA}} = \frac{B-C+C_{iA}C}{C'_{oW}-1+C_{iA}}$$ ------ 5.12

$$C_{iA} = \frac{C'_{oA}(B-C) - A(C'_{oW}-1)}{A + B - C(C'_{oA}+C'_{oW})}$$

$$= \frac{(f_1(C_{oA}))(B-C) - A(f_2(C_{oA})-1)}{A + B - C(f_1(C_{oA})+f_2(C_{oA}))}$$ ---- 5.13

Hence G'_o can be found from equation 5.12, G_i from 5.8 and C_{iW} from 5.9, and so all the streams entering and leaving the stage are determined.

For the washing section calculations, the starting quantities are the aqueous inflow and organic outflow, and here some complications arise. It is desirable to use the same equilibrium curves f_1 and f_2, and not to introduce any others. Thus, if the concentration C'_{oA} is assumed, C'_{oW} is not immediately known, because a direct relationship between the two concentrations is not being used. It is also necessary to know C'_{oW} in order to have G'_o. The method used was to find C_{oA} from the equilibrium $C'_{oA} = f_1(C_{oA})$ by iteration, and then to find C'_{oW} from $C'_{oW} = f_2(C_{oA})$.

The problem now is to calculate C'_{iA} and the rest of the unknowns, but again, the lack of a direct relationship between C'_{iA} and C'_{iW} makes it necessary to use an iterative method based on the aqueous concentration with which C'_{iA} and C'_{iW} are in equilibrium. This concentration is designated C_2, and is equal to the acid concentration in the aqueous stream leaving the next stage upstream, with organic flow, from the one under consideration.

From the equilibrium relationships f_1 and f_2 we have:

$C'_{iA} = f_1(C_2)$ ----- 5.14

$C'_{iW} = f_2(C_2)$ ----- 5.15

Let $C'_{oA}G'_o - C_{iA}G_i = D$ ----- 5.16

$C'_{oW}G'_o - C_{iW}G_i = E$ ----- 5.17

$G'_o - G_i = F$ ----- 5.18

All the LHS quantities are known, so D, E and F are known.

Acid balance gives: $C'_{iA}G'_i - C_{oA}G_o = D$ ----- 5.19

Water " " $C'_{iW}G'_i - C_{oW}G_o = E$ ----- 5.20

Overall " " $G'_i - G_o = F$ ----- 5.21

Also: $C_{oA} + C_{oW} = 1$ ----- 5.22

From 5.14, 5.19 and 5.21,

$f_1(C_2)G'_i - C_{oA}G'_i + C_{oA}F = D$ ----- 5.23

From 5.15, 5.20, 5.21 and 5.22,

$f_2(C_2)G'_i - G'_i + F + C_{oA}G'_i - C_{oA}F = E$ ----- 5.24

Eliminating G'_i between 5.23 and 5.24 gives:

$f_1(C_2)(F-E-C_{oA}F)+f_2(C_2)(D-C_{oA}F) = D-C_{oA}(D+E)$ ---- 5.25

C_2 is now found from equation 5.25 by iteration, and then the solution of the other unknowns is straightforward.

The material balance for Fe^{3+} is much simpler, since all flow rates are known, and all the calculations are done in one direction from stage to stage.

The equlibrium function is expressed as follows:

$C'_{oF} = g(C_{oA}, C_{oF})$ ----- 5.26

Fe^{3+} balance: $C'_{oF}G'_o-C_{iF}G_i = C'_{iF}G'_i-C_{oF}G_o = H$ ---- 5.27

Therefore $$C_{iF} = \frac{g(C_{oA}, C_{oF})G'_o - H}{G_i} \qquad \text{-----} \; 5.28$$

5.3 ESTIMATION OF THEORETICAL STAGES

The acid composition given in Table 1.1 was taken as the basis for the composition supplied to the computer programme. The acid was assumed to be diluted somewhat to give a composition by weight of 60% H_3PO_4 and 0,22% Fe. The acid feed rate was given a value of one unit, while other flows and also the plant layout were altered to study their effect on the operation as a whole, and in particular, on the purification with respect to Fe^{3+}.

The important parameters are:

1) Number of stages.
2) The way these stages are divided into the extraction and washing sections.
3) The organic flow rate to the extraction section.
4) The wash water flow rate.

Table 5.1 summarises the results of a number of runs. With up to eleven stages, the H_3PO_4/H_2O material balances were done in one direction throughout the system, and in order to make the attempt for eleven stages converge, the accuracy criteria were slackened a little. From twelve stages up, the extraction and washing section calculations were done in opposite directions, and these results are consequently more accurate.

The table contains much useful information about the process variables. For instance, in the case of twelve stages, it is most efficient in terms of purification to have three extraction stages. If there are either two or four extraction stages, purification is less efficient. With fifteen stages, three is still the optimum number.

A useful figure in these calculations is the percentage of the feed acid recovered in the organic product stream. The process depends on the raffinate being a fairly concentrated acid which can carry the Fe^{3+} impurity, and so it is important

TABLE 5.1

PROCESS OPERATING CHARACTERISTICS

One unit of flow is equal to the flow rate of the acid feed stream expressed on a mass basis.

Column headings:
A - Total stages
B - Extraction stages
C - Washing stages
D - Organic feed flow rate
E - Wash water flow rate
F - % acid recovery
G - % Fe^{3+} purification

A	B	C	D	E	F	G
4	2	2	20	0,25	79,4	56,0
4	2	2	15	0,25	58,9	72,7
5	2	3	20	0,25	77,4	65,6
6	2	4	20	0,25	76,2	72,3
7	2	5	20	0,25	75,8	77,0
8	2	6	20	0,25	75,3	80,9
8	2	6	15	0,25	50,3	92,6
8	2	6	15	0,20	60,2	90,6
8	3	5	15	0,20	66,7	92,4
8	3	5	10	0,20	32,5	95,0
8	3	5	10	0,15	43,0	94,5
11	3	8	15	0,20	62,3	97,2
12	2	10	15	0,25	47,8	97,95
12	3	9	15	0,25	51,6	98,51
12	4	8	15	0,25	53,9	98,16
13	3	10	15	0,25	51,0	98,87
15	3	12	15	0,25	50,0	99,49
15	4	11	15	0,25	51,8	99,29
17	3	14	15	0,25	49,4	99,75
17	4	13	15	0,25	50,9	99,55
19	3	16	15	0,25	48,9	99,87

to decide how much acid the raffinate should contain. This acid is not lost, as it can be returned to the evaporators of the wet process plant. It was found that an acid recovery of about 50% is a reasonable figure on which to work. At very high acid recoveries, i.e. well over 80%, the situation sometimes developed where the aqueous Fe^{3+} concentration in the raffinate stage was lower than the concentration closer to the feed point, because the dilute raffinate acid was not able to carry the Fe^{3+} adequately. Such situations are extreme cases, however, and a 'normal' stage to stage organic Fe^{3+} profile is shown in Fig. 5.2, the points being taken from Table 5.2, which gives the printout for the 19-stage run.

The criterion for iron in food grade acid is 5 ppm in 85% H_3PO_4 (49), and the most important result of Table 5.1 is an estimate of the number of theoretical stages needed to achieve such a purity. It seems that 18 or 19 are likely to be required.

5.4 THE EFFECT OF SULPHATE ON THE NUMBER OF REQUIRED STAGES

It was shown in Section 3.8 that the presence of sulphate increases the selectivity of the LA-1 solution for H_3PO_4 over Fe^{3+}, and this increase can be quite remarkable under certain conditions. (Compare the selectivities in Tables C.4 and C.5 in the Appendix with those in Tables C.9 and C.10.) Under process conditions, however, the small amount of residual H_2SO_4 present in wet process H_3PO_4 is unlikely to make a great difference. Since the ratio of organic to aqueous flow rates is high, typically about 15 to 1 in the case of 5% LA-1, most of the sulphate will be taken up, leaving a very low aqueous concentration. The presence of sulphate would probably make the purification process slightly more efficient, and reduce the extent to which the organic phase can be loaded with H_3PO_4, but it can be stated that there is no hope of reducing significantly the rather large number of theoretical stages required in the absence of sulphate.

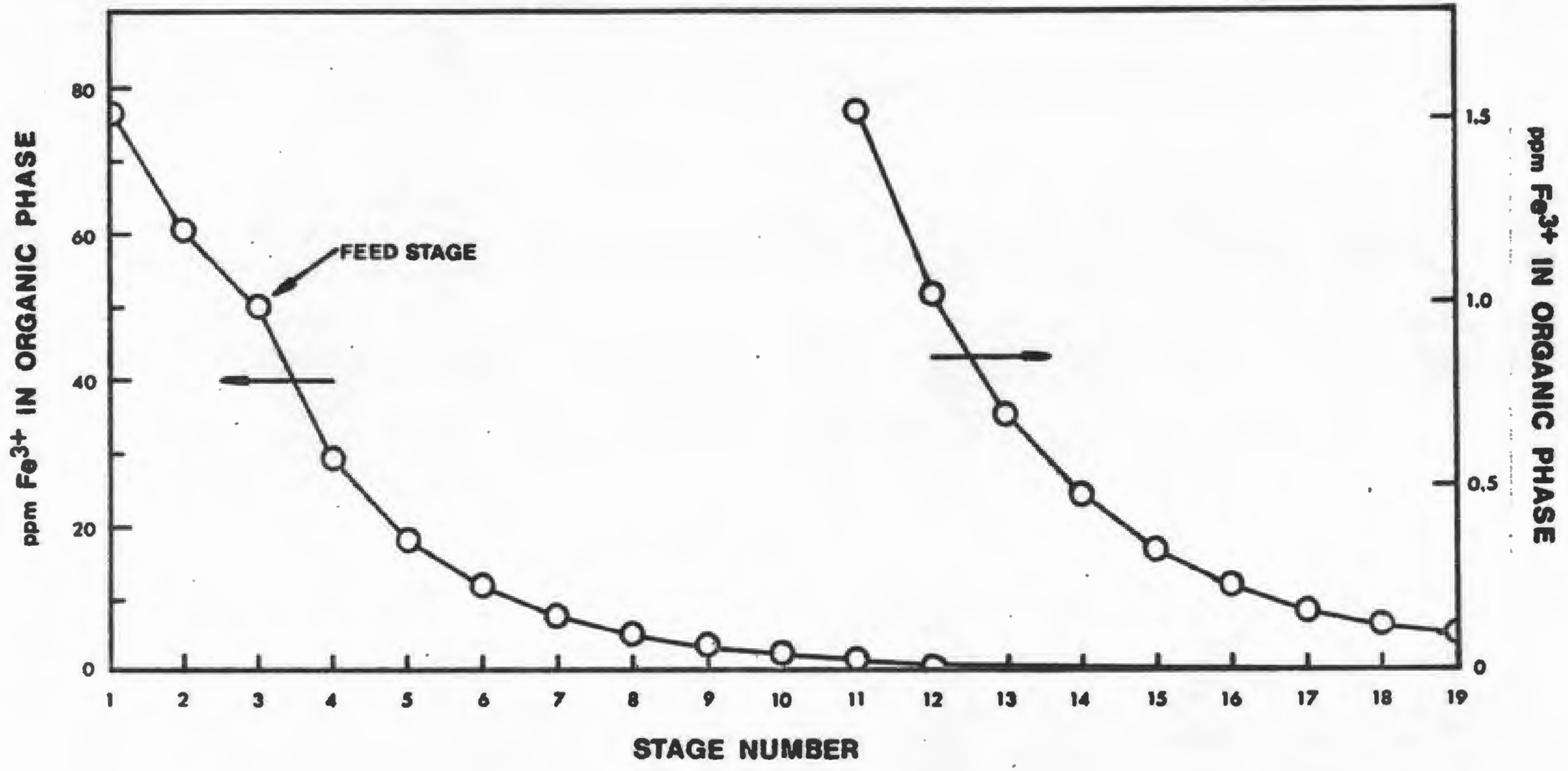

FIG. 5.2

Stage to stage Fe^{3+} concentration profile in a countercurrent process for extracting H_3PO_4 from an aqueous solution contaminated only by Fe^{3+}. The results were obtained by computer simulation. For details of flows and concentrations, see Section 5.4 and Table 5.2.

TABLE 5.2

STAGE TO STAGE ANALYSIS OF 19-STAGE PLANT

Acid feed rate = 1 unit, organic rate = 15 units, wash water rate = 0,25 units. All units are on a weight basis. Stage numbers increase from raffinate end to wash water inlet. E refers to the extraction section, W to the washing section.

Column headings: A - Stage number
B - Aqueous flow leaving stage
C - Acid fraction of above stream
D - Iron fraction of above stream x 10^7
E - Organic flow leaving stage
F - Acid fraction of above stream x 10^4
G - Water fraction of above stream x 10^4
H - Iron fraction of above stream x 10^8

A	B	C	D	E	F	G	H
E 1	0,803	0,381	27400	15,615	271	124	7660
E 2	1,419	0,513	23900	15,874	400	151	6050
E 3	1,678	0,561	18800	15,995	462	160	5000
W 1	0,799	0,557	9990	15,984	456	160	2920
W 2	0,788	0,552	5900	15,972	450	159	1810
W 3	0,777	0,548	3710	15,960	444	158	1170
W 4	0,764	0,543	2420	15,947	437	157	764
W 5	0,751	0,537	1600	15,932	430	156	507
W 6	0,737	0,531	1080	15,917	422	154	338
W 7	0,721	0,524	728	15,899	413	153	227
W 8	0,704	0,516	494	15,880	403	151	153
W 9	0,684	0,506	335	15,858	392	149	103
W 10	0,662	0,495	227	15,832	379	147	70
W 11	0,637	0,481	153	15,802	364	144	48
W 12	0,606	0,464	102	15,765	345	140	33
W 13	0,569	0,440	67	15,719	322	135	23
W 14	0,523	0,406	43	15,657	291	129	16
W 15	0,462	0,352	26	15,571	249	118	12
W 16	0,376	0,251	13	15,445	190	98	9

5.5 SUGGESTIONS FOR LIQUID-LIQUID CONTACTING EQUIPMENT

In view of the large number of stages needed, mixer-settlers can be ruled out as possible contacting equipment, at least for the majority of the stages in the plant. However, there is a wide variety of alternative equipment available, and this has been summarised briefly in a paper by Hanson (86). The basic types are as follows:

1) Unagitated columns. These include spray columns, packed columns and perforated plate columns.
2) Pulsed columns. The efficiency of plate or packed columns can be increased by pulsing the flow of liquids through the system.
3) Mechanically agitated columns. Agitation may be by means of rotating paddles or discs, and many variations have been devised. The Graesser raining bucket contactor (87) falls into this category, in spite of having a horizontal rather than a vertical column, and it is this device which seems most suited to H_3PO_4 extraction.

In selecting suitable equipment, attention must be paid to the mass-transfer and settling characteristics of the system. In the present case, mass transfer is rapid while settling is poor, with the possibility of the formation of stable emulsions and scums at the interface. In the early stages of the work, a rough mass transfer test was done by performing extractions on H_3PO_4 samples containing Fe^{3+}, and measuring Fe^{3+} extraction for various agitation times. It was found that shaking for one minute was sufficient to attain equilibrium, and any longer shaking time caused no more Fe^{3+} to be extracted. The rapid rate of mass transfer can even be detected by eye, for if an H_3PO_4 solution with a layer of regenerated LA-1 on top is gently shaken so as to disturb the interface, and then observed against a bright background, the change in the refractive index of the organic phase as H_3PO_4 dissolves in it can be clearly seen.

All the mixing done in the distribution tests was vigorous, resulting in the formation of a highly dispersed emulsion. This emulsion sometimes took a long time to settle, especially the secondary dispersion, and all samples were allowed to settle for at least a day. Sometimes, with 10% LA-1, a small amount of emulsion remained at the interface for days. The 10% LA-1 solution settled with far greater difficulty than the 5%, in keeping with the principle that the closer the two phases are in polarity, the more slowly they settle. This imposes a limit on the concentration of the amine solution which can be used with any given degree of phase dispersion.

Hanson's paper (86) indicates that the best way of dealing with a system having rapid mass transfer, but poor settling characteristics, is with the Graesser raining bucket contactor. This piece of equipment consists of a horizontal cylinder through which runs a central rotating shaft, to which a number of equally spaced discs is fixed. These discs are not much smaller in diameter than the internal diameter of the cylinder, and they each carry several buckets around their circumference. The aqueous and organic streams are passed countercurrently through the contactor, in such a way that the interface lies at the middle of the cylinder. As the buckets revolve, they trap liquid from each phase and carry it into the other phase, where it is released. The action is unusual in that each phase is dispersed in the other. The bubbles formed are large, so that settling is rapid, and this large bubble size is also the reason why the contactor works well only if the mass transfer coefficient is high.

The Graesser contactor is cheap and simple in operation, and can be made to give a large number of theoretical stages. It appears to be eminently suited to H_3PO_4 extraction with an amine solution, and should be seriously considered if such a process is to be studied at the pilot plant stage.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

6.1 THE VIABILITY OF THE PROCESS

The amine process for the production of NaH_2PO_4 was shown in Chapter 1 to have several advantages over other processes. These advantages include cost of raw materials and consumption of energy. The process itself is quite simple, and involves little more than liquid-liquid contacting, thus making for a relatively cheap plant.

A very important aspect of all amine extraction processes is loss of amine through its small but finite solubility in aqueous solutions, or by entrainment of the organic phase. It has been shown that in the case of uranium extraction, the loss by solubility in the aqueous phase is not serious (40), whereas loss by entrainment can be minimised by careful design.

As shown in the previous chapter, an amine process would require liquid-liquid contacting equipment giving many theoretical stages, but this need not be a disadvantage if a suitable contactor is used.

Process control may prove to be difficult in the NaCl stripping section, since the product should contain neither excess NaCl nor H_3PO_4, but again, this should not be a serious difficulty, or one which cannot be overcome with modern methods of control.

In view of the limited extent to which the present study has covered the whole problem, it has not been possible to design a plant and go into detailed economics. It has, however been shown that wet process H_3PO_4 can be used in an amine extraction process giving effective separation from cationic impurities, and also dealing with sulphate. Other anionic impurities were not studied, but they are not expected to cause difficulty. The process as a whole is workable, and suitable for further investigation.

6.2 THE APPLICATION OF THEORY TO PROCESS DESIGN

Such a complex system as amine/wet process H_3PO_4 is not readily amenable to a complete theoretical treatment, and so any solution theory which may emerge is not likely to provide a neat package of equations upon which the design of a whole plant can be based. The application of gas adsorption isotherms to multi-acid systems is interesting, but the results can only be regarded as general guidelines. The best way to study such isotherms would be in systems made to be as simple as possible, without the large number of interfering ingredients which are present in wet process H_3PO_4, and the results are likely to be mainly of academic interest.

In process design, therefore, empirical observations are of great value, and the information obtained from a pilot plant would be of certain practical use, although little may be learned of the complex interactions which produce the observed behaviour.

6.3 SUGGESTIONS FOR FUTURE WORK

The field of amine extraction is vast indeed, and this project itself has produced ideas for much possible investigation.

On the theoretical side, work could be done on the organic phase solution chemistry of the amine/H_3PO_4 + impurities system, perhaps on the basis of the thermodynamic extraction isotherms mentioned in Section 4.6.

Since the main objective of the project was to put forward a viable chemical process, the most important suggestions for future work must involve study leading to a better understanding of the practical workings of the process, and to optimisation of the many variables involved. These suggestions are listed below:

1) A study of the fluorine- and arsenic-containing anionic impurities.

2) Cationic impurities other than Fe^{3+}, such as Mg^{2+} and Ca^{2+}, may be investigated for completeness.
3) The effect of temperature on the extraction equilibria.
4) The relative merits of different amines, solvents and solvaters.
5) A more detailed look at the presence of sulphate (and perhaps other anionic impurities) on the extraction of Fe^{3+} (and perhaps other cationic impurities).
6) The reproducibility of results and possible hysteresis effects. The effect of the degree of agitation on the equilibria.
7) A detailed study of the NaCl stripping and CaO regeneration sections of the plant.
8) A look at the mixing/settling characteristics of the system, and how they change with organic phase composition.
9) Multistage simulations with separating funnels, and the building and operating of a pilot plant.

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APPENDIX A

RADIOCHEMICAL METHODS

A.1 γ-COUNTING WITH ^{59}Fe

The isotope ^{59}Fe, which has a half-life of 45,1 days, emits γ-rays of two energies, namely 1,10 and 1,29 MeV. The 1,10 MeV rays are the more frequent, being emitted at 1,27 times the rate of the 1,29 MeV rays. Compton scattering causes the energies of many γ-photons to be downgraded, so that the γ-ray spectrum of ^{59}Fe contains counts at energies other than 1,10 and 1,29 MeV, although these are still distinguished by peaks (see Fig. A.1).

The γ-counting machine which was used had a germanium/lithium detector cooled by liquid nitrogen, and the whole γ-spectrum was divided into 400 energy channels, the count for each channel being recorded on magnetic tape. This tape was then read by a computer, which printed out the whole spectrum and calculated the size of each peak.

The main advantage of distinguishing peaks in a γ-spectrum is in measuring the amounts of different γ-emitting isotopes in a mixed sample. In the present case, however, only one isotope was present, and so there was little advantage to be gained by measuring the peaks. Consequently, later determinations summed the counts over a wide range of energies, using a sodium iodide/thallium detector with which the counting machine was also provided. The switch to this detector was, in fact, necessitated by the failure of the germanium-lithium crystal during the course of the work.

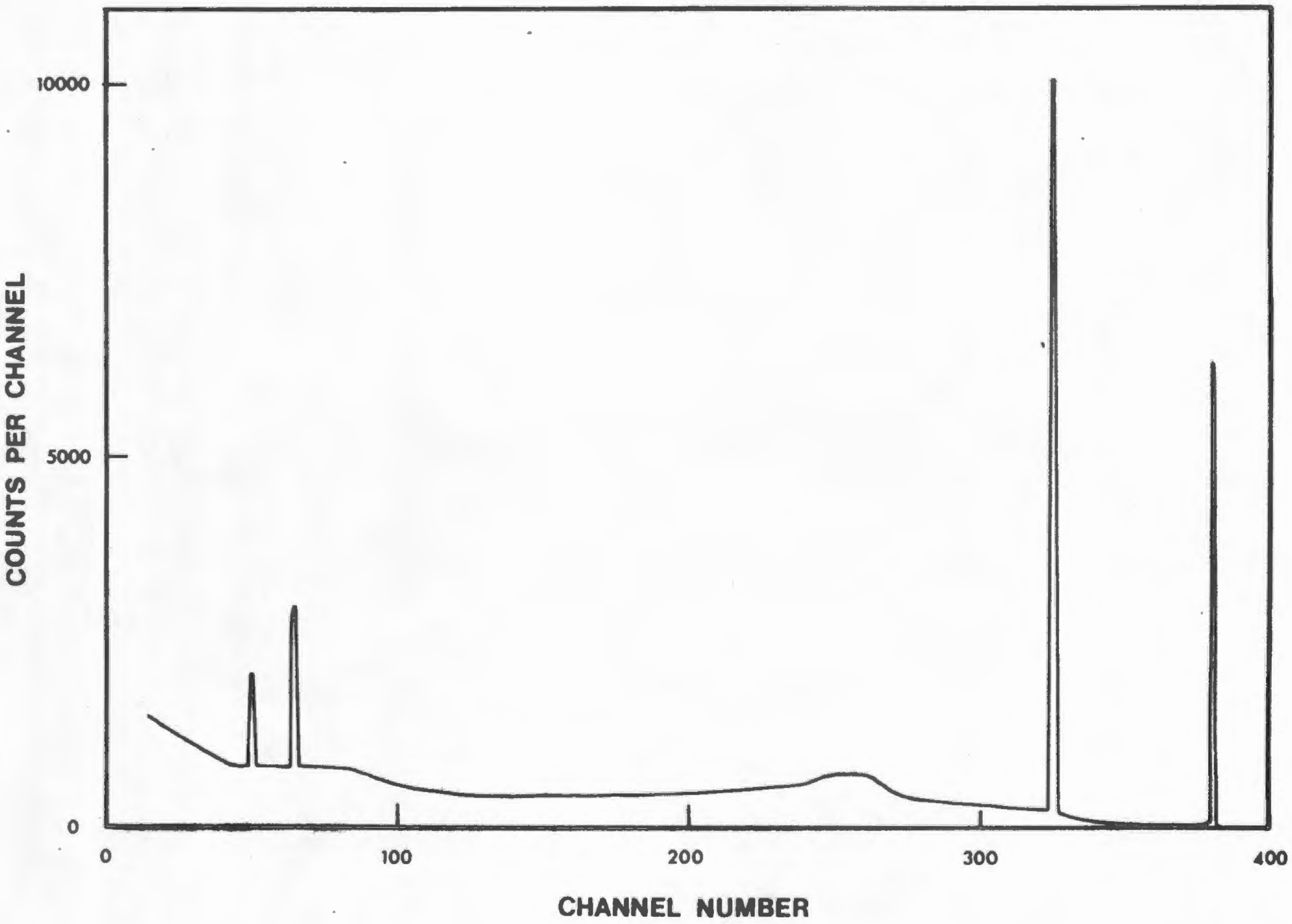

FIG. A.1

A typical γ-spectrum for ^{59}Fe.

When only one isotope is being counted, there is in fact an advantage in taking in the whole spectrum, since the number of counts is greatly increased, and hence the error due to randomness is reduced. The standard deviation of a count is equal to its square root, as stated in Section 3.2, so that for a sample giving n counts, the standard deviation expressed as a percentage is $\frac{100}{\sqrt{n}}$.

It was also stated in Section 3.2 that the greatest source of error in γ-counting is the exact shape and position of the sample with respect to the detector. The counting tubes were long and thin, and sometimes hung rather loosely in their holders, so that the sample may not always have been at the same distance from the detector. There may even have been some variation in the depth to which the sample was lowered into the lead-shielded counting chamber by the automatic changer.

The preparation of the samples themselves is also a source of inaccuracy, since splashing on the inside of the counting tube increases the mean distance of the sample from the detector. Such splashing is almost unavoidable. All the organic samples were 1 ml in volume, and were delivered by automatic pipette into the counting tubes with no dilution. The aqueous samples, however, had to be diluted, since the iron concentration in the aqueous phase was much higher than in the organic phase. Consequently, a very much smaller volume than 1 ml had to be taken, which was then added to a volume of water pipetted into the counting tube, so as to make the whole volume up to 1 ml. It was necessary to have the total volume of each sample the same, because of the influence of sample geometry on the count rate. The shaking necessary for dilution always caused splashing on the walls of the tube, and this must have introduced a certain amount of error. Another source of error was water evaporating from the aqueous samples and condensing in the upper part of the tube, thus reducing the sample volume and reducing its average distance from the detector.

Apart from the uncertainty associated with an individual count, there is the bias which applies to a whole set of counts, caused by errors in counting the standards which were used in the γ-counting tests. In radiochemical analysis, it is necessary to relate count numbers to concentrations, and one method is to use a standard, made up by diluting the radioactive tracer solution and preparing counting tubes containing aliquots of this dilute solution. Obviously, errors in counting these standards produce bias in the whole batch of concentrations determined by their means. For this reason, standards were prepared in duplicate or triplicate, and counted many times over in order to obtain a good average. In most of the scintillation counting tests, different methods of standardisation were used.

The efficiency of γ-counting, that is, the ratio of disintegrations detected to total disintegrations, is very low, being generally less than 1%. However, this is not a serious hindrance, since the sample can be made up with enough activity to give a reasonable count rate. For samples of equal geometrical proportions accurately positioned with respect to the detector, the efficiency of counting is virtually constant, and varies to a negligible extent with the composition and density of the solution in the counting tube.

Since, in all ^{59}Fe tests, only the one nuclide was present, the calculation of results was simple, involving only subtraction of background, half-life correction and comparison with the standard.

A.2 SCINTILLATION COUNTING WITH ^{32}P AND ^{35}S

In scintillation counting, the radioactive sample is dissolved or emulsified in a solution containing a scintillator, which emits pulses of light on being stimulated by the energy of radioactive emissions. The scintillator used was a commercial solution known as 'Instagel', which contains the active ingredients PPO and POPOP. The method is suitable for β-emitters, especially weak β-emitters such as ^{35}S (half-life 87,1 days), which has a maximum energy of 0,17 MeV. ^{32}P (half-life 14,3 days) is a strong β-emitter with a maximum energy of 1,71 MeV.

The scintillation counter records the scintillations with almost 100% efficiency, but errors may result from a varying efficiency of transmission of β-particle energies to the scintillator. Some emissions are 'quenched', and either do not cause scintillations at all, or result in scintillations of a reduced energy. Unfortunately, the quenching properties of a scintillator sample are difficult to control, and two samples made up to almost the same specifications may quench to significantly different extents.

There are two ways of correcting for quench, both of which were available on the scintillation counter used in the tests. One method uses an external radioactive standard which is viewed through the scintillator sample, its count rate providing a measure of the quench. An empirical correlation between the external standard and the quenching must be obtained by testing a number of samples made up to have the same amount of activity in each.

The other method depends on the ability of the scintillation counter to resolve the counts into a number of energy channels, three being the usual number, as on the machine used. The greater the quenching, the greater the number of counts which are downgraded to the lower channels, so that, if the sample contains only one nuclide, the ratio of the counts in any two channels provides a measure of the quenching. If more than one nuclide is present, as in most of the tests done, this method cannot be used, and so the external standard method was adopted.

It was soon evident that the higher energy nuclide, ^{32}P, suffered far more from quenching than ^{35}S. The aqueous samples suffered more than the organic samples in this respect, and the ^{32}P aqueous counts were so bad that it was decided not to use them, but to deduce aqueous H_3PO_4 concentrations from the organic concentrations. In the case of ^{35}S, quenching did not appear to alter appreciably the accuracy of the counts, and no correction was made.

In samples containing both nuclides, ^{32}P could be determined from the counts in the high energy channel, as this was not penetrated by ^{35}S at all. However, in order to determine ^{35}S in the presence of ^{32}P, allowance had to be made for interference in the two lower energy channels in which the ^{35}S counts appear. This was found to be impossible to do accurately, since the correlation between the external standard test and channel ratio was very poor with ^{32}P, especially for the aqueous solutions. Consequently, ^{35}S was determined by recounting after a period of 17 weeks, after which most of the ^{32}P had decayed, owing to its short half-life. What remained could be allowed for without the danger of discrepancies in the channel ratios of ^{32}P producing large errors in the ^{35}S determination.

Difficulty was also experienced with standards, especially in the case of ^{32}P. Eventually, the prepared standards were dispensed with, and H_3PO_4 standardised from the distribution obtained with 5% LA-1 by titration (see Fig. 2.1). In the case of ^{35}S, reliable aqueous counts were available, and so the ratio of H_2SO_4 concentration in the two phases was known. From this and a knowledge of the amount of H_2SO_4 originally present in the aqueous phase before extraction, an estimate of the final concentrations in both phases could be obtained. Of course, during the extraction process the organic phase increases in volume, while the aqueous phase decreases, and a knowledge of the extent of these changes improves the accuracy of the above method of H_2SO_4 determination. Consequently, the information obtained from the water distribution test was used (see Sections 3.9, B.3 and Fig. B.1). This only takes H_3PO_4 into account, but since the level of H_2SO_4 is generally low by comparison, the volume changes associated with the latter should be correspondingly small. Fig. B.1 shows the volume change in the organic phase; aqueous phase volume changes were deduced from data on the density of aqueous solutions of H_3PO_4.

Fig. B.1 was also used in the determination of aqueous H_3PO_4 concentrations in the ^{32}P tests. The pure H_2SO_4 distribution (see Fig. 3.6), however, was obtained by the use of radioactive standards.

In spite of the errors inherent in scintillation counting, the results were good, and it was possible to draw smooth curves through plotted points without the points lying too far from the curves. The complete set of these curves is shown in Figs. 3.6 to 3.12.

APPENDIX B

ANALYTICAL PROCEDURES

B.1 THE ACCURACY OF THE EQUIPMENT

A great deal of the preparation of solutions was done with the aid of hand-held automatic pipettes. These had disposable plastic tips which were not wetted by water, and so, with care, quick and accurate dispensing of aqueous solutions was possible. Organic solutions, however, wetted the tips, making it necessary to allow time for draining. Also, the pipettes had to be restandardised for use with organic solutions.

Table B.1 gives the nominal volumes, actual volumes and standard deviations of the pipettes used, as found by weighing pipetted aliquots of water or LA-1 solution.

TABLE B.1

PARTICULARS OF THE AUTOMATIC PIPETTES

Nominal Vol. (μl)	Aq. Vol.	S.D.	Org. Vol.	S.D.
10	9,86	0,04		
25	24,54	0,20		
50	49,78	0,28		
100	100,1	0,2		
200	200,6	0,7		
250	257,3	0,4	257,1	0,9
500	511,2	1,0	509,2	2,3
2 x 500			1016,9	9,1

The 2 x 500 µl row in Table A.1 refers to the dispensing of 1 ml of organic solution into γ-counting tubes. The first 500 µl are sucked into a clean plastic tip, while for the second 500 µl, the tip is wet.

Disposable plastic syringes were used to dispense 4 ml aliquots of radioactive aqueous solutions into bottles already containing 4 ml of LA-1 solution. Each syringe was discarded after use with one aqueous solution. The syringe technique was tested for accuracy by delivering and weighing 1 ml aliquots of water. The mean volume was found to be 1,006 ml with a standard deviation of 0,017 ml.

Aliquots of LA-1 solution were dispensed by means of an automatic plunger-type dispenser, which could be adjusted to deliver from almost 0 up to 10 ml. It was also used for the scintillator solution. Although it had a scale, it was set to the desired volume of 4 ml by weighing aliquots of water, since this gave greater accuracy. It was not tested for standard deviation, as it was known to be much more constant than the syringes.

Radioactive aqueous solutions were made up in 10 ml 'B' grade volumetric flasks. Since the dissolution of H_3PO_4 is exothermic, the flasks were allowed to cool thoroughly before finally making them up to the mark.

Phosphoric acid was measured out by weighing, taking care that it picked up a minimum of atmospheric moisture in the process. Standardisation was by titration with NaOH using a pH meter, while standardisation of H_2SO_4 was done by titration using phenolphthalein. Iron solutions were standardised by atomic absorption, taking care to obtain an accurate reading from the machine.

Inaccuracies in the results were found to be more the result of γ- and scintillation counting errors than errors in sample preparation.

B.2 SAMPLE PREPARATION PROCEDURES

For the range of concentrations tested, see Table 3.1. Below follow the systematic procedures used in the various tests:

1) H_3PO_4/Fe^{3+} with ^{59}Fe

A standard solution of $FePO_4$ in H_3PO_4 was made up, its density measured and a certain quantity weighed out into a 100 ml volumetric flask. 0,5 mCi[1] of Fe tracer solution was added, and the flask made up to the mark with water. The Fe^{3+} contents of the flasks could then be made up by adding the correct number of aliquots to each one.

After extraction and settling, 1 ml of organic phase from each sample was placed in a counting tube, using the 500 µl pipette. For aqueous phase counting, the volumes taken were 500 µl for 1000 ppm Fe^{3+} samples, 200 µl for 2000 - 4000 ppm samples, and 100 µl for 5000 and 6000 ppm samples. Water was added to make the total volume of each sample up to 1 ml.

2) $H_3PO_4/H_2SO_4/Fe^{3+}$ with ^{59}Fe

Here the procedure was similar to that described above. The radioactive solution this time contained $Fe_2(SO_4)_3$, prepared in a 50 ml volumetric flask, to which 0,25 mCi[1] of ^{59}Fe was added. Since the addition of Fe^{3+} implied the addition of sulphate, extra H_2SO_4 was added to the 1000 - 5000 ppm Fe^{3+} samples, to make them up to the same level as the 6000 ppm samples. This addition was done with the 500 µl pipette, which was also used with a concentrated H_2SO_4

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[1] 1 mCi (milliCurie) = $3{,}7 \times 10^7$ disintegrations per second.

solution for the high sulphate set of samples.

3) All Tests with ^{32}P and ^{35}S

Whereas in the ^{59}Fe tests, the nuclide was added to the Fe^{3+} solution used for making up the iron content of the aqueous samples, ^{32}P and ^{35}S were added to each sample flask individually, in quantities of about 1 µCi for each nuclide. One reason for this is that the flasks could be made up with the correct amounts of H_3PO_4 and H_2SO_4 while awaiting the arrival of the nuclides, so that less time was lost in preparation for counting. This is an advantage in the case of ^{32}P with its fairly short 2-week half life. ^{32}P had to be added separately, in any case, since H_3PO_4 was dispensed from a large bottle by weighing, and not from a small flask by pipetting. With the samples containing Fe^{3+}, the $Fe_2(SO_4)_3$ solution was added immediately prior to the addition of ^{32}P and ^{35}S, since solutions of Fe^{3+} in the presence of phosphate do not keep well (see Subsection 3.4.2).

After phase contacting and separation, samples for counting were made up in scintillation counting bottles each containing 7 ml of Instagel. Aliquots of 250 µl for the organic and 50 µl for the aqueous phase were taken, although these quantities were varied for the pure H_2SO_4 distribution test. Some difficulty was experienced in making the more concentrated aqueous samples dissolve or emulsify in the Instagel, and eventually all the aqueous ^{32}P counts were found to be very scattered. Nevertheless, the counting was, on the whole, successful.

Note on Temperature

No temperature control was applied to the experiments, but the general range was about 20 - 23°C, rising to 25°C on rare occasions.

B.3 THE WATER DISTRIBUTION TEST

In Section 3.9 it was explained that a water distribution test was done for 5% LA-1 with pure aqueous solutions of H_3PO_4. Water, of course, is a component in the extraction system studied, and is carried along with the acid into the organic phase to an appreciable extent, but water extraction was not studied in any detail. The reason is because the main emphasis was on selectivities for H_3PO_4 and impurities, which are the basis for the viability or otherwise of the extraction process. Water does have its influence, since extraction of water increases aqueous phase concentrations, which in turn influence selectivities. However, the effect is secondary.

Nevertheless, it was necessary to have some knowledge of the water distribution, in view of material balances required for the computer simulation described in Chapter 5. Tests were done only with pure H_3PO_4 solutions, and the water distribution was assumed, in the simulation, not to depend on the Fe^{3+} impurity.

A quick and simple method for obtaining organic phase water concentrations was required, and so weighing of the loaded organic phase was adopted.

Weighed separating funnels were filled with 50 ml aliquots of LA-1 solution, and a more accurate estimate of the amount added obtained by reweighing the funnels. The density of the LA-1 was measured, so that the volume added was accurately known. Phosphoric acid solutions were added to the funnels, and also plain water in the case of two funnels, which were to provide blank readings. After shaking and settling, the aqueous layers were tapped off and samples retained for later determination by titration. Then the organic layers were run out into weighed beakers, so that the weight of the whole organic phase could be obtained. Densities were also taken. The blanks provided a measure of the volume lost from organic solution sticking to the walls of the funnels, and this fractional volume loss was assumed to be constant for the other funnels.

From the known aqueous phase H_3PO_4 concentration, the organic concentrations were determined from the curve in Fig. 2.1. From the density and weight of the organic phase, its volume was known, and so the weight of H_3PO_4 extracted was known. The extra weight was then attributable to extracted water.

The results of the determination are also presented in Fig. 2.1, along with the H_3PO_4 curve, and tabulated results appear in Table C.11. The scatter seems rather excessive, but the method could certainly be made to yield more accurate results with practice on the part of the operator.

Fig. B.1, which shows organic phase volume increase as a function of organic H_3PO_4 concentration, was also derived from the water distribution test, and was used as an aid in determining concentrations from scintillation counter results.

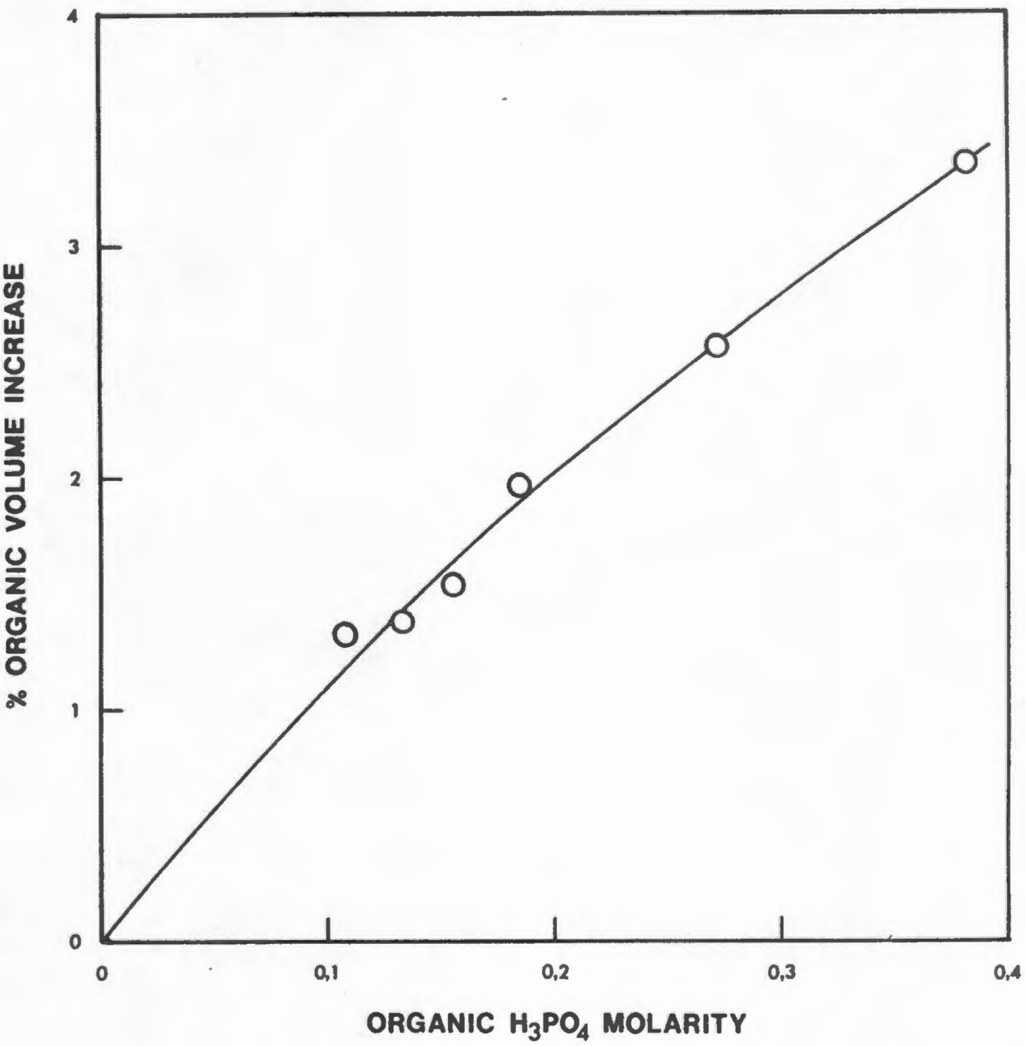

FIG. B.1

Volume increase of the organic phase. Extraction of pure aqueous H_3PO_4 by 5% LA-1, 10% decanol in kerosene.

APPENDIX C

TABLES OF RESULTS

TABLE C.1

PHOSPHORIC ACID DISTRIBUTION

5% LA-1, 10% decanol in kerosene. Analysis by titration.

$[H_3PO_4]_{aq}$ (M)	$[H_3PO_4]_{org}$ (M)
1,00	0,113
1,63	0,128
1,94	0,135
2,43	0,145
4,85	0,226
7,86	0,384

TABLE C.2

PHOSPHORIC ACID DISTRIBUTION

5% LA-1, 10% decanol in kerosene. With and without Fe^{3+} present. ^{32}P tracer.

$[H_3PO_4]_{aq}$ (M)	$[Fe^{3+}]_{aq}$ (ppm)	$[H_3PO_4]_{org}$ (M)
0,90	0	0,098
1,89	0	0,121
2,89	0	0,161
3,88	0	0,193
4,87	0	0,232
5,87	0	0,270
6,86	0	0,325
7,85	0	0,397
0,92	5780	0,086
1,91	5900	0,111
2,90	5960	0,140
3,91	6010	0,173
4,88	6030	0,207
5,88	6060	0,257
6,88	6080	0,307
7,88	6100	0,366

TABLE C.3

PHOSPHORIC ACID DISTRIBUTION

10% LA-1, 20% decanol in kerosene. With and without Fe^{3+} present. ^{32}P tracer.

$[H_3PO_4]_{aq}$ (M)	$[Fe^{3+}]_{aq}$ (ppm)	$[H_3PO_4]_{org}$ (M)
0,79	0	0,225
1,77	0	0,272
2,75	0	0,337
3,75	0	0,396
4,73	0	0,467
5,73	0	0,549
6,71	0	0,663
7,69	0	0,786
0,81	5520	0,203
1,78	5830	0,268
2,76	5950	0,322
3,76	6030	0,389
4,74	6070	0,445
5,73	6150	0,541
6,73	6210	0,632
7,70	6240	0,767

TABLE C.4

PHOSPHORIC ACID - IRON DISTRIBUTION

5% LA-1, 10% decanol in kerosene. ^{59}Fe tracer. Phosphoric acid concentrations found by calculation.

Column headings:
A - $[H_3PO_4]_{aq}$ (M)
B - $[H_3PO_4]_{org}$ (M)
C - $[Fe^{3+}]_{aq}$ (ppm)
D - $[Fe^{3+}]_{org}$ (ppm)
E - Selectivity for PO_4^{3-} over Fe^{3+}

A	B	C	D	E
0,90	0,107	1040	112	1,11
0,90	0,105	2070	158	1,53
0,91	0,103	3250	213	1,72
0,91	0,101	4320	232	2,06
0,91	0,100	5050	264	2,10
0,97	0,100	6360	264	2,48
1,90	0,131	1050	56	1,29
1,90	0,128	2170	97	1,51
1,90	0,126	3210	125	1,70
1,90	0,124	4360	144	1,97
1,90	0,121	5510	162	2,16
1,95	0,120	6560	172	2,35
2,89	0,154	1070	41	1,38
2,89	0,152	2130	69	1,62
2,89	0,149	3330	88	1,96
2,90	0,146	4470	102	2,22
2,90	0,143	5630	125	2,23
2,95	0,142	6600	141	2,25

Table continued overleaf.

TABLE C.4 continued

For column headings, see page C.4.

A	B	C	D	E
3,90	0,184	1130	33	1,62
3,91	0,181	2190	56	1,80
3,91	0,178	3380	71	2,17
3,91	0,175	4440	84	2,35
3,91	0,171	5560	99	2,45
3,95	0,169	6710	111	2,58
4,87	0,223	1110	27	1,86
4,88	0,219	2200	46	2,16
4,88	0,215	3350	60	2,47
4,88	0,212	4420	73	2,63
4,88	0,207	5620	83	2,86
4,93	0,206	6710	91	3,07
5,88	0,270	1110	23	2,20
5,88	0,265	2250	39	2,61
5,88	0,260	3460	56	2,75
5,88	0,256	4450	75	2,58
5,88	0,250	5710	78	3,12
5,90	0,249	6610	93	3,00
6,87	0,320	1110	18	2,83
6,87	0,314	2350	40	2,69
6,88	0,309	3420	51	2,99
6,88	0,303	4520	66	3,04
6,88	0,298	5560	83	2,91
6,93	0,295	6760	93	3,10
7,86	0,378	1130	19	2,85
7,87	0,371	2300	39	2,80
7,87	0,364	3450	50	3,18
7,88	0,358	4420	69	2,91
7,88	0,351	5660	86	2,94
7,90	0,348	6630	105	2,77

TABLE C.5

PHOSPHORIC ACID - IRON DISTRIBUTION

10% LA-1, 20% decanol in kerosene. ^{59}Fe tracer. Phosphoric acid concentrations found by calculation.

Column headings: A - $[H_3PO_4]_{aq}$ (M)
B - $[H_3PO_4]_{org}$ (M)
C - $[Fe^{3+}]_{aq}$ (ppm)
D - $[Fe^{3+}]_{org}$ (ppm)
E - Selectivity for PO_4^{3-} over Fe^{3+}

A	B	C	D	E
0,79	0,224	930	196	1,34
0,79	0,222	1970	303	1,83
0,80	0,221	3060	411	2,06
0,80	0,219	4040	469	2,36
0,80	0,218	5020	549	2,50
0,85	0,220	6160	634	2,51
1,77	0,273	1040	97	1,65
1,77	0,271	2110	174	1,86
1,78	0,269	3260	225	2,19
1,78	0,267	4340	279	2,33
1,78	0,266	5360	305	2,62
1,83	0,267	6490	358	2,65
2,75	0,328	1060	75	1,69
2,75	0,325	2170	126	2,04
2,76	0,323	3310	171	2,27
2,76	0,321	4350	215	2,35
2,76	0,319	5460	240	2,63
2,81	0,319	6510	235	3,15

Table continued overleaf.

TABLE C.5 continued

For column headings, see page C.6.

A	B	C	D	E
3,76	0,388	1100	55	2,07
3,76	0,385	2240	102	2,26
3,77	0,383	3340	128	2,65
3,77	0,380	4510	163	2,79
3,77	0,377	5530	184	3,00
3,81	0,378	6681	211	3,14
4,73	0,464	1120	52	2,10
4,73	0,460	2250	82	2,68
4,74	0,457	3360	112	2,89
4,74	0,454	4480	142	3,02
4,74	0,450	5660	182	2,95
4,78	0,450	6730	191	3,31
5,73	0,551	1120	41	2,62
5,73	0,547	2300	82	2,69
5,73	0,543	3460	107	3,07
5,74	0,539	4550	127	3,37
5,74	0,535	5620	153	3,42
5,78	0,536	6720	165	3,78
6,72	0,656	1110	35	3,08
6,72	0,651	2290	71	3,14
6,73	0,647	3450	107	3,11
6,73	0,642	4570	121	3,61
6,73	0,637	5700	136	3,95
6,77	0,637	6880	171	3,78
7,70	0,783	1160	34	3,43
7,70	0,777	2320	71	3,32
7,71	0,771	3510	104	3,38
7,71	0,766	4640	132	3,50
7,71	0,760	5770	165	3,44
7,74	0,759	6960	180	3,79

TABLE C.6

SULPHURIC ACID DISTRIBUTION

5% LA-1, 10% decanol and 10% LA-1, 20% decanol in kerosene. ^{35}S tracer.

% LA-1	$[H_2SO_4]_{aq}$ (M)	$[H_2SO_4]_{org}$ (M)
5	0,95	0,091
5	1,93	0,102
5	2,86	0,114
5	3,80	0,123
5	4,80	0,137
5	5,74	0,167
5	6,54	0,214
5	7,54	0,292
10	0,85	0,151
10	1,85	0,190
10	2,85	0,204
10	3,78	0,219
10	4,68	0,245
10	5,64	0,306
10	6,36	0,368

TABLE C.7

PHOSPHORIC ACID - SULPHURIC ACID DISTRIBUTION

5% LA-1, 10% decanol in kerosene. ^{32}P and ^{35}S tracers. Aqueous phosphoric acid concentrations found by calculation.

Column headings:
A - $[H_3PO_4]_{aq}$ (M)
B - $[H_3PO_4]_{org}$ (M)
C - $[H_2SO_4]_{aq}$ (M)
D - $[H_2SO_4]_{org}$ (M)
E - Selectivity for SO_4^{2-} over PO_4^{3-}

A	B	C	D	E
2,93	0,085	0,0054	0,0260	165,7
2,96	0,058	0,0208	0,0423	103,8
2,97	0,041	0,0593	0,0534	64,8
2,97	0,039	0,105	0,0565	41,5
2,98	0,033	0,181	0,0613	30,5
2,98	0,032	0,260	0,0630	22,3
4,91	0,156	0,0100	0,0214	67,3
4,94	0,120	0,0304	0,0328	44,6
4,96	0,090	0,0657	0,0472	39,4
4,96	0,086	0,108	0,0540	28,9
4,98	0,065	0,184	0,0598	24,9
4,98	0,064	0,259	0,0645	19,3
5,92	0,190	0,0131	0,0184	43,7
5,94	0,159	0,0322	0,0311	36,0
5,95	0,124	0,0698	0,0433	29,7
5,96	0,114	0,112	0,0497	23,2
5,97	0,092	0,186	0,0573	19,9
5,97	0,090	0,262	0,0621	15,7

Table continued overleaf.

TABLE C.7 continued

For column headings, see page C.9.

A	B	C	D	E
6,91	0,252	0,0155	0,0160	28,4
6,93	0,210	0,0359	0,0276	25,3
6,94	0,168	0,0731	0,0401	22,8
6,95	0,150	0,115	0,0473	19,1
6,95	0,140	0,188	0,0565	14,9
6,96	0,122	0,262	0,0626	13,7
7,90	0,316	0,0172	0,0145	21,1
7,91	0,278	0,0382	0,0254	18,9
7,92	0,246	0,0762	0,0373	15,8
7,94	0,210	0,118	0,0450	14,5
7,95	0,181	0,189	0,0560	13,0
7,95	0,167	0,264	0,0613	11,0

TABLE C.8

PHOSPHORIC ACID - SULPHURIC ACID DISTRIBUTION

10% LA-1, 20% decanol in kerosene. ^{32}P and ^{35}S tracers. Aqueous phosphoric acid concentrations found by calculation.

Column headings:
A - $[H_3PO_4]_{aq}$ (M)
B - $[H_3PO_4]_{org}$ (M)
C - $[H_2SO_4]_{aq}$ (M)
D - $[H_2SO_4]_{org}$ (M)
E - Selectivity for SO_4^{2-} over PO_4^{3-}

A	B	C	D	E
2,81	0,257	0,0017	0,0291	190,3
2,85	0,196	0,0063	0,0559	130,0
2,90	0,142	0,0272	0,0846	63,7
2,92	0,113	0,0607	0,0999	42,6
2,94	0,095	0,129	0,113	27,2
2,94	0,087	0,201	0,122	20,5
4,78	0,391	0,0052	0,0255	59,8
4,82	0,331	0,0142	0,0479	49,4
4,85	0,270	0,0382	0,0735	34,6
4,88	0,229	0,0696	0,0910	27,9
4,90	0,196	0,134	0,109	20,3
4,91	0,179	0,202	0,121	16,5
5,77	0,474	0,0073	0,0235	39,1
5,82	0,402	0,0186	0,0436	33,9
5,86	0,348	0,0430	0,0688	26,9
5,88	0,298	0,0746	0,0863	22,8
5,89	0,262	0,137	0,106	17,4
5,90	0,238	0,207	0,118	14,1

Table continued overleaf.

TABLE C.8 continued

For column headings, see page C.11.

A	B	C	D	E
6,77	0,575	0,0094	0,0215	26,8
6,80	0,504	0,0224	0,0400	24,1
6,85	0,423	0,0475	0,0644	21,9
6,86	0,410	0,0813	0,0798	16,4
6,89	0,341	0,143	0,101	14,3
6,90	0,331	0,208	0,117	11,7
7,74	0,717	0,0113	0,0198	18,9
7,78	0,642	0,0252	0,0373	18,0
7,81	0,576	0,0532	0,0592	15,1
7,84	0,518	0,0851	0,0765	13,6
7,86	0,475	0,145	0,0991	11,3
7,88	0,421	0,212	0,114	10,1

TABLE C.9

PHOSPHORIC ACID - SULPHURIC ACID - IRON DISTRIBUTION

5% LA-1, 10% decanol in kerosene. ^{32}P and ^{35}S tracers, and ^{59}Fe in a separate test. Aqueous phosphoric acid concentrations found by calculation.

Column headings: A - $[H_3PO_4]_{aq}$ (M)
B - $[H_3PO_4]_{org}$ (M)
C - $[H_2SO_4]_{aq}$ (M)
D - $[H_2SO_4]_{org}$ (M)
E - $[Fe^{3+}]_{aq}$ (ppm)
F - $[Fe^{3+}]_{org}$ (ppm)
G - Selectivity for SO_4^{2-} over PO_4^{3-}
H - Selectivity for PO_4^{3-} over Fe^{3+}

A	B	C	D	E	F	G	H
4,96	0,085	0,113	0,0483	1020	3,3	24,8	5,3
4,96	0,085	0,113	0,0488	2020	5,1	25,2	6,8
4,96	0,086	0,115	0,0464	2980	7,0	23,3	7,3
4,96	0,079	0,115	0,0468	4030	8,4	25,7	7,6
4,96	0,077	0,115	0,0469	5020	10,0	26,2	7,8
4,96	0,078	0,116	0,0457	5970	11,0	24,9	8,6
7,97	0,135	0,113	0,0491	1010	5,9	25,7	3,0
7,97	0,133	0,114	0,0482	2010	11,2	25,4	3,0
7,97	0,126	0,115	0,0473	2990	16,0	26,2	2,9
7,98	0,122	0,115	0,0468	4070	20,5	26,6	3,0
7,97	0,124	0,116	0,0465	5000	24,3	25,8	3,2
7,98	0,117	0,117	0,0449	6120	27,7	26,1	3,2

Table continued overleaf.

TABLE C.9 continued

For column headings, see page C.13.

A	B	C	D	E	F	G	H
4,94	0,112	0,266	0,0585	1020	2,1	9,7	11,0
4,94	0,115	0,264	0,0603	1980	3,0	9,8	15,3
4,94	0,108	0,265	0,0591	2940	4,2	10,2	15,3
4,94	0,105	0,266	0,0583	4080	5,0	10,3	17,3
4,94	0,103	0,266	0,0583	5030	5,7	10,5	18,4
4,94	0,108	0,266	0,0587	6040	6,3	10,2	20,9
7,95	0,183	0,266	0,0596	1010	4,1	9,7	5,7
7,95	0,185	0,267	0,0591	1960	7,7	9,6	5,9
7,95	0,189	0,267	0,0594	2970	11,0	9,4	6,4
7,95	0,183	0,270	0,0565	4030	14,0	9,1	6,6
7,95	0,176	0,269	0,0573	5070	17,2	9,6	6,5
7,95	0,168	0,268	0,0578	6020	19,9	10,2	6,4

TABLE C.10

PHOSPHORIC ACID - SULPHURIC ACID - IRON DISTRIBUTION

10% LA-1, 20% decanol in kerosene. ^{32}P and ^{35}S tracers, and ^{59}Fe in a separate test. Aqueous phosphoric acid concentrations found by calculation.

Column headings: A - $[H_3PO_4]_{aq}$ (M)
B - $[H_3PO_4]_{org}$ (M)
C - $[H_2SO_4]_{aq}$ (M)
D - $[H_2SO_4]_{org}$ (M)
E - $[Fe^{3+}]_{aq}$ (ppm)
F - $[Fe^{3+}]_{org}$ (ppm)
G - Selectivity for SO_4^{2-} over PO_4^{3-}
H - Selectivity for PO_4^{3-} over Fe^{3+}

A	B	C	D	E	F	G	H
4,88	0,238	0,0762	0,0847	1020	9,1	22,8	5,4
4,88	0,226	0,0761	0,0847	2040	15,5	24,0	6,1
4,88	0,230	0,0769	0,0841	3040	20,4	23,2	7,0
4,89	0,222	0,0773	0,0836	4050	25,2	23,8	7,3
4,89	0,217	0,0781	0,0829	4980	29,9	23,9	7,4
4,89	0,202	0,0794	0,0817	5990	31,9	24,9	7,8
7,91	0,374	0,0737	0,0869	1030	15,2	24,9	3,2
7,91	0,372	0,0760	0,0849	2040	27,7	23,7	3,5
7,91	0,357	0,0753	0,0855	3040	39,7	25,2	3,5
7,91	0,346	0,0760	0,0848	4100	50,1	25,5	3,6
7,91	0,332	0,0768	0,0841	5100	59,1	26,0	3,6
7,91	0,339	0,0797	0,0815	6060	69,1	23,9	3,8

Table continued overleaf.

TABLE C.10 continued

For column headings, see page C.15.

A	B	C	D	E	F	G	H
4,85	0,281	0,217	0,108	1010	5,6	8,6	10,5
4,86	0,269	0,213	0,112	1990	8,1	9,5	13,6
4,86	0,271	0,213	0,112	3020	11,0	9,4	15,3
4,86	0,267	0,217	0,109	4110	13,4	9,1	16,9
4,86	0,265	0,215	0,110	5090	15,2	9,5	18,2
4,86	0,261	0,217	0,108	6090	17,1	9,3	19,1
7,88	0,434	0,217	0,110	1020	10,3	9,2	5,5
7,88	0,445	0,216	0,111	2000	18,8	9,1	6,0
7,89	0,425	0,221	0,107	3040	26,6	9,0	6,2
7,88	0,433	0,216	0,111	4120	37,8	9,3	6,0
7,89	0,431	0,220	0,107	5140	42,0	8,9	6,7
7,89	0,413	0,218	0,109	6120	48,0	9,5	6,7

TABLE C.11

WATER TAKEUP BY ORGANIC PHASE

5% LA-1, 10% decanol in kerosene. Pure aqueous solutions of phosphoric acid used.

Column headings:
A - $[H_3PO_4]_{aq}$ (M)
B - $[H_3PO_4]_{org}$ (M)
C - Specific gravity of organic phase
D - % organic volume increase
E - $[H_2O]_{org}$ (M)
F - Molar ratio $H_2O:H_3PO_4$ in organic phase

A	B	C	D	E	F
0,90	0,108	0,8053	1,32	0,416	3,85
1,86	0,133	0,8063	1,37	0,356	2,68
2,84	0,156	0,8080	1,53	0,392	2,51
3,82	0,185	0,8101	1,96	0,533	2,88
5,82	0,272	0,8151	2,56	0,595	2,19
7,83	0,382	0,8219	3,35	0,701	1,84

Original organic phase density = 0,7976 g l^{-1}

TABLE C.12

CURVE FITTING OF IRON DISTRIBUTION DATA

Coefficients of polynomials used to fit the data in Tables C.4 and C.5 are given here. Refer to equation 3.2 with m=5, n=4. Acid molarities are first divided by 10 and parts per million Fe^{3+} by 10000 before the data is fitted, and so the coefficients below apply to these modified concentration units.

5% LA-1		10% LA-1	
Subscripts i,j	coeff. a_{ij}	subscripts i,j	coeff. a_{ij}
1,1	1659,28	1,1	3187,33
1,2	-2319,61	1,2	-4660,82
1,3	1249,15	1,3	3933,95
2,1	-743,021	2,1	-1642,26
2,2	680,725	2,2	1619,81
		2,3	-1459,47
2,4	-209,634		
3,1	150,488	3,1	399,345
3,2	-79,4864	3,2	-138,170
		3,3	127,556
4,1	-13,3616	4,1	-48,6445
4,4	1,72425		
5,1	0,42048	5,1	2,38767
5,2	0,33993		

TABLE C.13

CURVE FITTING OF IRON DISTRIBUTION DATA

5% LA-1, 10% decanol in kerosene. Data taken from Table C.4 Predicted organic Fe^{3+} concentrations given for round number aqueous concentrations.

Column headings: A - $[H_3PO_4]_{aq}$ (M)
B - $[H_3PO_4]_{org}$ (M)
C - $[Fe^{3+}]_{aq}$ (ppm)
D - $[Fe^{3+}]_{org}$ (ppm) (predicted by fit)
E - Selectivity for PO_4^{3-} over Fe^{3+} .

A	B	C	D	E
1	0,111	1000	89	1,24
1	0,109	2000	152	1,44
1	0,107	3000	194	1,66
1	0,106	4000	221	1,92
1	0,104	5000	241	2,16
1	0,102	6000	257	2,38
2	0,133	1000	56	1,19
2	0,131	2000	94	1,40
2	0,129	3000	119	1,63
2	0,127	4000	136	1,86
2	0,125	5000	151	2,07
2	0,123	6000	165	2,24
3	0,158	1000	37	1,41
3	0,155	2000	62	1,67
3	0,153	3000	80	1,92
3	0,150	4000	94	2,13
3	0,148	5000	107	2,29
3	0,145	6000	122	2,39

Table continued overleaf.

TABLE C.13 continued

For column headings, see page C.19.

A	B	C	D	E
4	0,189	1000	28	1,68
4	0,186	2000	47	1,98
4	0,183	3000	62	2,22
4	0,180	4000	75	2,39
4	0,177	5000	89	2,49
4	0,174	6000	103	2,55
5	0,229	1000	24	1,90
5	0,225	2000	41	2,21
5	0,222	3000	55	2,44
5	0,218	4000	68	2,58
5	0,215	5000	81	2,65
5	0,211	6000	93	2,73
6	0,277	1000	22	2,06
6	0,272	2000	38	2,40
6	0,268	3000	51	2,64
6	0,264	4000	63	2,78
6	0,259	5000	76	2,86
6	0,255	6000	85	2,99
7	0,329	1000	21	2,27
7	0,324	2000	35	2,64
7	0,319	3000	47	2,89
7	0,314	4000	60	3,00
7	0,308	5000	72	3,04
7	0,303	6000	84	3,11
8	0,386	1000	18	2,65
8	0,380	2000	31	3,02
8	0,374	3000	44	3,16
8	0,368	4000	60	3,09
8	0,362	5000	78	2,90
8	0,356	6000	99	2,70

Standard deviation of a single prediction = 4,3

TABLE C.14

CURVE FITTING OF IRON DISTRIBUTION DATA

10% LA-1, 20% decanol in kerosene. Data taken from Table C.5. Predicted organic Fe^{3+} concentrations given for round number aqueous concentrations.

Column headings:

A - $[H_3PO_4]_{aq}$ (M)
B - $[H_3PO_4]_{org}$ (M)
C - $[Fe^{3+}]_{aq}$ (ppm)
D - $[Fe^{3+}]_{org}$ (ppm) (predicted by fit)
E - Selectivity for PO_4^{3-} over Fe^{3+}

A	B	C	D	E
1	0,235	1000	161	1,46
1	0,233	2000	273	1,70
1	0,232	3000	354	1,96
1	0,230	4000	417	2,21
1	0,228	5000	480	2,38
1	0,227	6000	557	2,45
2	0,286	1000	97	1,48
2	0,284	2000	163	1,74
2	0,283	3000	208	2,03
2	0,281	4000	242	2,32
2	0,279	5000	272	2,56
2	0,277	6000	308	2,69
3	0,345	1000	64	1,80
3	0,342	2000	111	2,06
3	0,340	3000	145	2,34
3	0,338	4000	172	2,63
3	0,336	5000	194	2,88
3	0,334	6000	217	3,08

Table continued overleaf.

TABLE C.14 continued

For column headings, see page C.21.

A	B	C	D	E
4	0,413	1000	47	2,20
4	0,410	2000	87	2,36
4	0,407	3000	120	2,54
4	0,405	4000	148	2,73
4	0,402	5000	172	2,92
4	0,399	6000	192	3,12
5	0,488	1000	37	2,65
5	0,485	2000	72	2,68
5	0,482	3000	105	2,74
5	0,479	4000	135	2,84
5	0,475	5000	160	2,97
5	0,472	6000	179	3,16
6	0,581	1000	30	3,18
6	0,577	2000	61	3,15
6	0,574	3000	91	3,17
6	0,570	4000	118	3,23
6	0,566	5000	141	3,35
6	0,563	6000	159	3,54
7	0,695	1000	30	3,33
7	0,690	2000	58	3,42
7	0,686	3000	83	3,54
7	0,682	4000	106	3,67
7	0,677	5000	127	3,82
7	0,672	6000	144	4,00
8	0,825	1000	43	2,39
8	0,819	2000	78	2,63
8	0,814	3000	107	2,86
8	0,809	4000	132	3,06
8	0,803	5000	157	3,19
8	0,798	6000	184	3,26

Standard deviation of a single prediction = 8,8

TABLE C.15

CURVE FITTING OF PHOSPHORIC ACID - SULPHURIC ACID DISTRIBUTION

Refer to the simple extended BET treatment in Section 4.7.1. Only the 5% LA-1 data of Table C.7 was fitted, together with the phosphate only distribution of Table C.2 (no Fe^{3+} present).

Computed parameters:
p_{AO} = 13,057
p_{BO} = 765000,0
c_A = 16,043
c_B = 1761,6
v_{Am} = 0,1928

where A refers to H_3PO_4 and B to H_2SO_4.

Column headings:
A - $[H_3PO_4]_{aq}$ (M)
B - $[H_2SO_4]_{aq}$ (M)
C - $[H_3PO_4]_{org}$ (M) (measured)
D - $[H_3PO_4]_{org}$ (M) (predicted by fit)
E - Percentage error of predicted value

A	B	C	D	E
0,90	0,0000	0,098	0,089	-9,3
1,89	0,0000	0,121	0,139	14,4
2,89	0,0000	0,161	0,174	8,2
3,88	0,0000	0,193	0,205	6,5
4,87	0,0000	0,232	0,235	1,7
5,87	0,0000	0,270	0,268	-0,7
6,86	0,0000	0,325	0,306	-6,0
7,85	0,0000	0,397	0,350	-12,0

Table continued overleaf.

TABLE C.15 continued

For column headings, see page C.23.

A	B	C	D	E
2,93	0,0054	0,085	0,120	40,5
2,96	0,0208	0,058	0,079	35,2
2,97	0,0593	0,041	0,059	42,4
2,97	0,105	0,039	0,053	36,4
2,98	0,181	0,033	0,049	48,8
2,98	0,260	0,032	0,048	47,3
4,91	0,0100	0,156	0,164	4,9
4,94	0,0304	0,120	0,126	5,2
4,96	0,0657	0,090	0,108	19,6
4,96	0,108	0,086	0,100	16,6
4,98	0,184	0,065	0,095	46,5
4,98	0,259	0,064	0,093	44,6
5,92	0,0131	0,190	0,190	0,1
5,94	0,0322	0,159	0,158	-0,8
5,95	0,0698	0,124	0,138	10,8
5,96	0,112	0,114	0,130	14,4
5,97	0,186	0,092	0,124	34,8
5,97	0,262	0,090	0,122	34,9
6,91	0,0155	0,252	0,223	-11,2
6,93	0,0359	0,210	0,193	-8,3
6,94	0,0731	0,168	0,174	3,6
6,95	0,115	0,150	0,165	10,2
6,95	0,188	0,140	0,159	13,8
6,96	0,262	0,122	0,156	28,3
7,90	0,0172	0,316	0,267	-15,6
7,91	0,0382	0,278	0,236	-15,0
7,92	0,0762	0,246	0,217	-11,7
7,94	0,118	0,210	0,209	-0,4
7,95	0,189	0,181	0,202	11,9
7,95	0,264	0,167	0,199	19,0

Standard deviation of a single prediction = 0,023.

TABLE C.16

CURVE FITTING OF PHOSPHORIC ACID - SULPHURIC ACID DISTRIBUTION

Refer to the extended BET treatment in Section 4.7.2. Below are given the parameters for the three fits attempted, namely 5% and 10% LA-1, both without Fe^{3+} (see Tables C.7 and C.8), and 5% LA-1 with Fe^{3+} (see Table C.9). In each case, the phosphate distribution with no sulphate present has been included in the fit (see Tables C.2 and C.3). The units of q are kcal (g mole)$^{-1}$.

parameter	5% LA-1	10% LA-1	5% LA-1 with Fe^{3+}
p_{AO}	12,265	12,451	15,184
p_{BO}	6,3204	5,6152	40,679
v_{Am}	0,15067	0,31384	0,20481
q_A	7,5637	7,5632	7,5606
q_B	14,097	14,250	14,471
q_{AA}	6,0238	5,8676	6,2660
q_{BB}	9,6729	9,8409	1,0687
q_{AB}	5,4123	5,4968	5,4993
q_{BA}	9,7388	7,5941	5,3880

TABLE C.17

CURVE FITTING OF PHOSPHORIC ACID - SULPHURIC ACID DISTRIBUTION

Fit for 5% LA-1 with no Fe^{3+} present. Parameters given in Table C.16.

Column headings:
A - $[H_3PO_4]_{aq}$ (M)
B - $[H_2SO_4]_{aq}$ (M)
C - $[H_3PO_4]_{org}$ (M) (measured)
D - $[H_3PO_4]_{org}$ (M) (predicted by fit)
E - Percentage error of predicted value

A	B	C	D	E
0,90	0,0000	0,098	0,084	-14,0
1,89	0,0000	0,121	0,127	4,8
2,89	0,0000	0,161	0,159	-1,1
3,88	0,0000	0,193	0,190	-1,2
4,87	0,0000	0,232	0,225	-2,9
5,87	0,0000	0,270	0,268	-1,0
6,86	0,0000	0,325	0,323	-0,5
7,85	0,0000	0,397	0,402	1,2
2,93	0,0054	0,085	0,118	38,6
2,96	0,0208	0,058	0,074	27,1
2,97	0,0593	0,041	0,045	10,0
2,97	0,105	0,039	0,035	-8,5
2,98	0,181	0,033	0,029	-12,3
2,98	0,260	0,032	0,026	-19,2
4,91	0,0100	0,156	0,164	5,4
4,94	0,0304	0,120	0,117	-1,8
4,96	0,0657	0,090	0,089	-1,6
4,96	0,108	0,086	0,075	-13,0
4,98	0,184	0,065	0,064	-1,2
4,98	0,259	0,064	0,059	-8,1

Table continued overleaf.

TABLE C.17 continued

For column headings, see page C.26.

A	B	C	D	E
5,92	0,0131	0,190	0,197	3,9
5,94	0,0322	0,159	0,154	-3,1
5,95	0,0698	0,124	0,120	-3,2
5,96	0,112	0,114	0,105	-7,9
5,97	0,186	0,092	0,092	-0,3
5,97	0,262	0,090	0,085	-5,5
6,91	0,0155	0,252	0,245	-2,5
6,93	0,0359	0,210	0,201	-4,5
6,94	0,0731	0,168	0,165	-1,2
6,95	0,115	0,150	0,148	-1,6
6,95	0,188	0,140	0,132	-5,6
6,96	0,262	0,122	0,124	1,6
7,90	0,0172	0,316	0,319	1,2
7,91	0,0382	0,278	0,272	-2,1
7,92	0,0762	0,246	0,233	-5,2
7,94	0,118	0,210	0,213	1,7
7,95	0,189	0,181	0,195	7,7
7,95	0,264	0,167	0,184	9,8

Standard deviation of a single prediction = 0,009.

TABLE C.18

CURVE FITTING OF PHOSPHORIC ACID - SULPHURIC ACID DISTRIBUTION

Fit for 10% LA-1 with no Fe^{3+} present. Parameters given in Table C.16.

Column headings: A - $[H_3PO_4]_{aq}$ (M)
B - $[H_2SO_4]_{aq}$ (M)
C - $[H_3PO_4]_{org}$ (M) (measured)
D - $[H_3PO_4]_{org}$ (M) (predicted by fit)
E - Percentage error of predicted value

A	B	C	D	E
0,79	0,0000	0,225	0,183	-18,5
1,77	0,0000	0,272	0,273	0,5
2,75	0,0000	0,337	0,336	0,0
3,75	0,0000	0,396	0,397	0,3
4,73	0,0000	0,467	0,464	-0,6
5,73	0,0000	0,549	0,546	-0,5
6,71	0,0000	0,663	0,650	-2,0
7,69	0,0000	0,786	0,793	0,9
2,81	0,0017	0,257	0,310	20,7
2,85	0,0063	0,196	0,256	30,8
2,90	0,0272	0,142	0,159	12,1
2,92	0,0607	0,113	0,114	1,3
2,94	0,129	0,095	0,087	-7,6
2,94	0,201	0,087	0,077	-11,7
4,78	0,0052	0,391	0,403	3,1
4,82	0,0142	0,331	0,338	2,4
4,85	0,0382	0,270	0,258	-4,4
4,88	0,0696	0,229	0,216	-5,4
4,90	0,134	0,196	0,182	-7,4
4,91	0,202	0,179	0,166	-7,1

Table continued overleaf.

TABLE C.18 continued

For column headings, see page C.28.

A	B	C	D	E
5,77	0,0073	0,474	0,470	-0,9
5,82	0,0186	0,402	0,404	0,3
5,86	0,0430	0,348	0,332	-4,8
5,88	0,0746	0,298	0,289	-2,9
5,89	0,137	0,262	0,252	-3,8
5,90	0,207	0,238	0,233	-1,9
6,77	0,0094	0,575	0,566	-1,7
6,80	0,0224	0,504	0,497	-1,4
6,85	0,0475	0,423	0,430	1,7
6,86	0,0813	0,410	0,384	-6,3
6,89	0,143	0,341	0,348	2,1
6,90	0,208	0,331	0,328	-0,7
7,74	0,0113	0,717	0,702	-2,1
7,78	0,0252	0,642	0,637	-0,8
7,81	0,0532	0,576	0,565	-1,9
7,84	0,0851	0,518	0,526	1,4
7,86	0,145	0,475	0,486	2,4
7,88	0,212	0,421	0,465	10,6

Standard deviation of a single prediction = 0,019.

TABLE C.19

CURVE FITTING OF PHOSPHORIC ACID - SULPHURIC ACID DISTRIBUTION

Fit for 5% LA-1 with Fe^{3+} present. Parameters given in Table C.16.

Column headings: A - $[H_3PO_4]_{aq}$ (M)
B - $[H_2SO_4]_{aq}$ (M)
C - $[Fe^{3+}]_{aq}$ (ppm)
D - $[H_3PO_4]_{org}$ (M) (measured)
E - $[H_3PO_4]_{org}$ (M) (predicted by fit)
F - Percentage error of predicted value

A	B	C	D	E	F
0,90	0,0000	0	0,098	0,079	-19,7
1,89	0,0000	0	0,121	0,132	8,3
2,89	0,0000	0	0,161	0,172	6,7
3,88	0,0000	0	0,193	0,208	8,0
3,88	0,0000	0	0,232	0,208	-10,2
5,87	0,0000	0	0,270	0,284	5,1
6,86	0,0000	0	0,325	0,329	1,4
7,85	0,0000	0	0,397	0,384	-3,3
4,96	0,113	1020	0,085	0,082	-4,5
4,96	0,113	2020	0,085	0,081	-4,1
4,96	0,115	2980	0,086	0,082	-4,2
4,96	0,115	4030	0,079	0,082	3,9
4,96	0,115	5020	0,077	0,082	5,8
4,96	0,116	5970	0,078	0,082	5,0

N.B. The figure in column A, fifth row, was incorrectly given to the computer as 3,88, whereas it should be 4,87. However, this mistake would not appreciably affect the rest of the fit.

Table continued overleaf.

TABLE C.19 continued

For column headings, see page C.30.

A	B	C	D	E	F
7,97	0,113	1010	0,135	0,141	4,8
7,97	0,114	2010	0,133	0,142	6,9
7,97	0,115	2990	0,126	0,142	13,1
7,98	0,115	4070	0,122	0,142	16,7
7,97	0,116	5000	0,124	0,142	14,3
7,98	0,117	6120	0,117	0,143	22,1
4,94	0,226	1020	0,112	0,100	-10,9
4,94	0,264	1980	0,115	0,104	-9,5
4,94	0,265	2940	0,108	0,104	-4,2
4,94	0,266	4080	0,105	0,104	-0,8
4,94	0,266	5030	0,103	0,104	0,7
4,94	0,266	6040	0,108	0,104	-3,5
7,95	0,266	1010	0,183	0,169	-7,2
7,95	0,267	1960	0,185	0,169	-8,2
7,95	0,267	2970	0,189	0,169	-10,2
7,95	0,270	4030	0,183	0,170	-7,5
7,95	0,269	5070	0,176	0,170	-3,8
7,95	0,268	6020	0,168	0,169	0,8

N.B. The figure in column B, seventh row, was incorrectly given to the computer as 0,226, whereas it should be 0,266.

Standard deviation of a single prediction = 0,013.