AN INVESTIGATION OF CATION - EXCHANGE IN AQUEOUS PYRIDINE

by

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PREFACE

The research which is the subject of this thesis was carried out between June, 1962, and January, 1968, both in the Chemistry Department of the University of Cape Town and in the Chemistry Division of the Port Elizabeth Technical College. The work is original and has not been submitted to any other University.

I should like to express my appreciation to Professor E. C. Leisegang and Dr. R. Arnold, who supervised the work at different times, for their advice and assistance; and express my thanks to Dr. S. C. Churms for her generous help and guidance.

I am deeply indebted to my wife for her patience and encouragement as well as for her hard work in typing the rough draft and stencils.

Finally, I would like to thank those friends and colleagues who helped in any way to realize this ambition.

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ERRATA

PREFACE: I wish to acknowledge the financial support provided by the South African Council for Scientific and Industrial Research and to thank them for their support.

This thesis presents a comparative investigation of the ion-exchange behaviour of a typical carboxylic acid resin, Amberlite IRC 50, and a typical sulphonic acid resin Zeo-Karb 225, in aqueous and aqueous pyridine solutions of the alkaline earth metal cations.

The ion-exchange phenomena investigated included; swelling, preferential sorption of solvent and selectivity variations with loading, degree of neutralization of the resin, solvent composition and choice of solution phase anion. The chromatographic separation of the alkaline earth metals using aqueous pyridine eluants was also investigated.

The solvent composition was found to exert a considerable effect on all the aspects of ion-exchange investigated. The swelling and sorption results are explained by examining the difference in solvent structure in the resin and solution phases.

The selectivity behaviour of the resins was examined theoretically in terms of various mechanistic models. The results obtained showed big selectivity changes with variation in solvent composition. These observations substantiated the theoretical predictions. The most important factor causing the selectivity variations is thought to be ion-solvent interaction. The usual correlation between swelling and selectivity was not observed.

The selectivity results obtained, indicated the possibility of an improved method for separating the alkaline earth metals by ion-exchange chromatography. This possibility was examined experimentally

but the desired result was not obtained. The problem was investigated further and a suggestion for further research along these lines is made.

The results obtained in this work demonstrate the important part played by the solvent in ion-exchange phenomena.

B. M. Ilsley.

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1. INTRODUCTION

1.1. OBJECTIVE

Most previous work in the field of cation-exchange selectivity has been concerned with:-

(a) Sulphonic acid resins.
(b) Monovalent cations.
(c) Aqueous solutions.

The work on carboxylic acid resins has, with the exception of that of Marshall and Garcia [1], been confined to monovalent cations.

The exchange properties of divalent ions have been investigated by certain authors [2, 3] using sulphonic acid resins. In most cases however the reference ion used was the hydrogen ion. Since it is extremely difficult to use the hydrogen ion as a reference on weak acid resins, this work on sulphonic acid resins cannot easily be compared with that on carboxylic acid resins.

Several studies have been made in solvents other than water. These have been confined mainly to neutral solvents such as acetone, ethanol and methanol. Macintosh [4, 5] investigated the behaviour of the alkali metals on both carboxylic and sulphonic acid resins in a basic solvent, monoethanolamine. The study of exchange on weak acid resins in basic solvents is interesting because of the levelling action of the solvent, which causes both strong and weak acid resins to be fully ionized. Aqueous monoethanolamine is, however, an unsatisfactory solvent for the alkaline earths. Pyridine was therefore chosen as solvent, since it has a fairly high basic strength (K_b = 8.85 at 25°C)[6] and is an excellent solvent for the alkaline earth perchlorates. A further advantage is that pyridine combines a high dipole moment (2.2 Debye)[7] with a low dielectric constant, 12.3 [8]. The fact that the dipole moment is similar to that of water enables a distinction to be made between the effect of this property and that of dielectric constant on cation-exchange phenomena.

Thus, as so little is known of the ion exchange behaviour of divalent ions, particularly on carboxylic acid resins, and to the knowledge of the author cation-exchange phenomena in aqueous pyridine have never before been investigated, the objective of this thesis is:-

> To investigate the ion-exchange behaviour of the cations magnesium, calcium, strontium and barium on both Zeo-Karb 225 (a sulphonic acid resin) and Amberlite IRC 50 (a carboxylic acid resin) using a pyridine/water solvent of varying composition.

1.2. THE SCOPE OF THE WORK

The aspects of the ion-exchange behaviour of the resins which have been investigated are :-

1. The weight-swelling of the two ion-exchange resins, in single ionic forms, in pyridine/water mixtures of varying composition.
2. Sorption of solvent by the two resins, in single ionic forms, from pyridine/water mixtures of varying composition.
3. Determination of the selectivity coefficients of barium, strontium and calcium relative to magnesium:
    - (a) At various loadings (see page 17), with water as solvent, for Amberlite IRC 50.
    - (b) At various values of α (degree of neutralization of the resin) for Amberlite IRC 50 with water as solvent.
    - (c) At various solvent compositions for Amberlite IRC 50 and Zeo-Karb 225.
4. The effect of the choice of anion on the selectivity of Amberlite IRC 50 and Zeo-Karb 225 for the ions studied.
5. The possibility of an improved chromatographic separation of the alkaline earth metals using pyridine/water as solvent.

Since the research was confined to two resins the introduction and review which follow deal only with cation-exchange on sulphonic and carboxylic acid resins in bead form. Anion-exchange and other types of cation-exchange materials are not considered.

1.3. CATION - EXCHANGE RESINS

A cation-exchange resin is a typical gel consisting of a matrix, which is an irregular, macromolecular, three-dimensional framework of hydrocarbon chains, and, attached to the matrix, anionic groups, such as $-SO_3^-$, in the case of Zeo-Karb 225, and $-COO^-$, in the case of IRC 50.

Linear hydrocarbon macromolecules with anionic groups attached e.g. polystyrene sulphonic acid, are soluble in water. Ion-exchange resins, however, are made insoluble by the introduction of cross-links, which interconnect the various hydrocarbon chains. An ion-exchange resin bead is therefore practically one single macromolecule. Its dissolution would require breaking of carbon-carbon bonds and the resins therefore do not dissolve in solvents by which they are not destroyed. The matrix is, however, elastic and can be expanded, the process being known as swelling.

To maintain electroneutrality in the resin beads mobile cations, called counterions, are present and these are associated with the resin anions to differing degrees. Cation-exchange resins are therefore cross-linked polyelectrolytes.

The spatial structure of the cation-exchange resins is such that they are inherently heterogeneous in character. The homogeneous gel model assumes that the resin phase can be treated as a concentrated aqueous solution, in which the anions are immobilized by a polymer network. Goldring[9], however, considers that this model has many shortcomings and states that there are apparently regions in every ion-exchange resin that are highly cross-linked, and others where the polymer may be so lightly cross-linked that locally its properties approach that of a linear polymer. This means that the charge density and concentration of exchange groups will vary from region to region. This approach was given support by the work of Reichenberg and McCauley[10] on selectivity of resins of various degrees of cross-linking and that of Glueckauf et al [11, 12, 13, 14] on the rate of diffusion of co-ions out of ion-exchange membranes. According to Reichenberg [15] the most direct evidence for the non-uniformity of the properties of exchange sites and its effect on selectivity is afforded by the results of a study of two identical resin samples of the same specific capacity. The method used to sulphonate the resin samples was such that if the resins were homogeneous they would be identical in all respects, but if they were heterogeneous they would differ in that the sulphonate groups would be situated preferentially in regions of lower localized cross-linking in one resin and be randomly distributed with respect to cross-linking in the other. The selectivity properties of the two resins were in fact markedly different, thus confirming the assumption that the resins were originally heterogeneous in structure. This phenomenon greatly complicates any theoretical prediction of the effect of ionic composition on the magnitude of selectivity. However, if the selectivity coefficients are averaged over the exchanger as a whole the effect is not serious. Furthermore, with resins of low cross-linking, such as those used in the present work, much of the ion-exchange behaviour can be explained by extensions of the theories of polyelectrolyte solutions, as has been done by Katchalsky[16] and Rice and Nagasawa[17]. Structural heterogeneity has therefore not been considered as a factor in the present work.

The preparation of cation-exchange resins will not be reviewed as it has been extensively dealt with by Helfferich[18] and has, in any case, no bearing on the present work.

Since a cation-exchange resin is insoluble when it is in contact with a solution of an electrolyte it forms a distinct physical phase which is known as the resin phase. As explained previously cations within the resin phase which are associated with the resin anions are known as counter-ions. A certain amount of electrolyte may be taken up by the resin from solution without being replaced by another species of solute. The cations so taken up are known as sorbed cations, and the anions taken up in equivalent amount are known as co-ions.

Before equilibrium between the resin phase and a solution phase is considered, one further property of ion-exchange resins must be dealt with, i.e. swelling. Swelling occurs when the elastic hydrocarbon matrix is caused to expand, enabling the resin beads to sorb additional solvent. The factors which lead to swelling are:

1. The solvation tendency of the fixed ionic groups and counter-ions[19]. Ion-dipole interactions between these groups and the solvent cause solvent to be held in the resin phase. Ions which have large solvated volumes will tend to cause more

swelling than ions with small solvated volumes. The nature of the solvent will obviously affect ion-solvent interactions.

2. The osmotic pressure difference between resin and solution phases[19] will also affect the degree of swelling. The resin phase can be considered to be a highly concentrated solution of ions relative to the dilute external phase. Solvent will therefore tend to move from the solution phase into the resin phase.

3. The electrostatic repulsions between neighbouring fixed ionic groups and between charged resin chains[20] will tend to cause the resin matrix to expand. Sorption of solvent then occurs in order to fill the additional space so created. The nature of the solvent affects the strength of these repulsions.

The magnitude of all three of these expanding forces decreases as swelling progresses. The solvation tendency diminishes as the solvation shells of the ions near completion, the osmotic pressure difference decreases as the resin phase becomes more dilute and the electrostatic repulsions decrease as the fixed groups and resin chains move further apart. These expanding forces are opposed by the cross-linking of the resin matrix; the greater the degree of cross-linking of the resin the greater the force required to cause the resin to swell. Therefore, other factors being equal, a highly cross-linked resin will swell less than a resin having a low degree of cross-linking. Irrespective of the degree of cross-linking, the resistance of the resin matrix to expansion increases as the swelling increases.

Therefore, as a resin swells, the three forces giving rise to swelling decrease, and the resistance of the resin matrix to swelling increases. Swelling equilibrium will be attained when the magnitude of these opposing forces is equal.

In the present work the weight-swelling of the two resins has been measured under various conditions. Weight-swelling is defined as the weight in grams, of solvent taken up, per gram of dry hydrogen form resin.

1.4. THE MEANING OF SELECTIVITY AND THE SIGNIFICANCE OF SELECTIVITY COEFFICIENTS

When a cation exchange resin is in contact with a solution of an electrolyte the mobile cations present on the exchanger (counterions) can exchange with cations in the solution phase. The amounts of ions exchanged are stoichiometrically equivalent. The exchange reaction may be represented in general terms by the equation:

$$qR_pA^{p+} + pB^{q+} = pR_qB^{q+} + qA^{p+} \qquad (1\text{-}1)$$

where R is the resin anion.

A is the counterion.

B is a cation originally in the solution phase.

p is the valency of cation A.

q is the valency of cation B.

The two cations will, in general, not be held equally strongly by the exchanger. Thus if an exchanger is in contact with a solution of an electrolyte and if, after equilibrium between the two phases has been reached, the solution phase contains the two exchangeable cations in equivalent amounts then, in general, the amounts of these cations in the resin phase will not be equal; i.e. one of the two cations will be preferred to the other.

1.4.1. The Practical Selectivity Coefficient

The practical selectivity coefficient, or separation factor, for the exchange reaction (1-1) written above is defined by:

$$k_A^B = \frac{\bar{m}_B \; m_A}{\bar{m}_A \; m_B} \qquad (1\text{-}2)$$

where $\bar{m}_B$ = molal concentration of cation B in the resin phase.
$\bar{m}_A$ = molal concentration of cation A in the resin phase.
m_A = molal concentration of cation A in the solution phase.
m_B = molal concentration of cation B in the solution phase.

Since the separation factor is the quotient of the concentration ratios of the two counterions its numerical value is not affected by the choice of concentration units.

1.4.2. The Selectivity Coefficient K_A^B

Instead of the practical selectivity coefficient the selectivity coefficient K_A^B can be used to describe the equilibrium.

This is defined by:

$$K_A^B = \frac{\bar{m}_B^{\,p} \; m_A^{\,q}}{\bar{m}_A^{\,q} \; m_B^{\,p}} \qquad (1\text{-}3)$$

In this work both cations are divalent so that equation (1-3) becomes:

$$K_A^B = \frac{\bar{m}_B^{\,2} \; m_A^{\,2}}{\bar{m}_A^{\,2} \; m_B^{\,2}}$$

$$\therefore \quad K_A^B = \left(\frac{\bar{m}_B \; m_A}{\bar{m}_A \; m_B}\right)^2 \qquad (1\text{-}4)$$

and from equation (1-2)

$$K_A^B = (k_A^B)^2 \qquad (1\text{-}5)$$

The selectivity coefficient can therefore be obtained by squaring the practical selectivity coefficient if both ions are divalent.

It should be clearly understood that, although the numerical value of the selectivity coefficient is not in this case affected by the choice of concentration units, as it is when the valences of the exchanging ions are not the same, the consequence of the fact that the exchange does not involve monovalent ions only is that the practical selectivity coefficient is no longer numerically equal to the selectivity coefficient. Confusion tends to arise in the minds of some authors on this point. The selectivities given in this thesis are all reported as practical selectivity coefficients.

If the selectivity coefficient (K_A^B) is not unity it indicates a difference in the relative preference of the solution and resin phases for the two competing ions. This preference reflects the relative effect of the two components on the thermodynamic properties of each phase. These effects are summarized in the term activity, which is a measure of escaping tendency: the higher the activity of a component in solution the greater its escaping tendency. Thus the preference of the solution phase for the two counterions A and B (relative to a standard state in which no preference exists) is the inverse of the ratio of their activities, $\frac{a_B}{a_A}$

1.4.3. The Corrected Selectivity Coefficient $K'_{B/A}$

The selectivity coefficient represents the resultant of all interactions, in both the resin phase and the solution phase, that give rise to selectivity. A quantity $K'_{B/A}$, called a corrected selectivity coefficient, reflects the preference of the exchanger phase only. In this case the selectivity coefficient is corrected for solution phase preferences.

In the case where the resin phase shows no preference $K'_{B/A} = 1$ and if at equilibrium the exchanger contains more of cation B than cation A this can only be attributed to solution phase activities.

$$\therefore \qquad \frac{\bar{m}_B}{\bar{m}_A} = \frac{a_B}{a_A}$$

and from equation (1-4)

$$K_A^B = \left(\frac{a_B \quad m_A}{a_A \quad m_B}\right)^2$$

In the general case where $K'_{B/A}$ is not unity the effect of resin selectivity must be reflected in K_A^B

$$\therefore \qquad K_A^B = K'_{B/A}\left(\frac{a_B \quad m_A}{a_A \quad m_B}\right)^2$$

From equation (1-4)

$$\left(\frac{\bar{m}_B \quad m_A}{\bar{m}_A \quad m_B}\right)^2 = K'_{B/A}\left(\frac{a_B \quad m_A}{a_A \quad m_B}\right)^2$$

$$K'_{B/A} = \left(\frac{\bar{m}_B \quad a_A}{\bar{m}_A \quad a_B}\right)^2 \qquad (1\text{-}6)$$

and since

$$a_A = f_A \quad m_A$$

$$a_B = f_B \quad m_B$$

where f_A, f_B are the activity coefficients of A and B in the solution phase,

$$K'_{B/A} = \left(\frac{\bar{m}_B \quad m_A \quad f_A}{\bar{m}_A \quad m_B \quad f_B}\right)^2 \qquad (1\text{-}7)$$

From equations (1-4) and (1-7) it can be seen that in dilute solution, where if it is not true that $f_A = f_B = 1$ then certainly with similar cations $\frac{f_A}{f_B} = 1$,

$$K'_{B/A} = K_A^B$$

and from equation (1-5)

$$K'_{B/A} = (k_A^B)^2 \qquad (1\text{-}8)$$

This result is used in the calculation of the thermodynamic equilibrium constant K_{aA}^{B} (see page 15)

It is important to note that $K'_{B/A}$ has a constant value only if the ratio of the amounts of the counterions (in either phase) is kept constant, since $K'_{B/A}$ is not an equilibrium constant or selectivity constant but a selectivity coefficient. Therefore $K'_{B/A}$ has a precise meaning only if the ratio of the amounts of the counterions in either the resin phase or the solution phase is also stated. Since $K'_{B/A}$ is a measure of selectivity in the resin phase only the counterion ratio ratio in the resin phase is generally used. The usual practice is to state not the ratio $\frac{\bar{m}_B}{\bar{m}_A}$ but $\bar{X}_A$, the equivalent fraction of A ions in the resin phase. This value $\bar{X}_A$ is often referred to as the <u>loading</u>.

Combining equations (1-7) and (1-4) gives:

$$K'_{B/A} = K_A^B \left(\frac{f_A}{f_B}\right)^2 \qquad (1\text{-}9)$$

Thus K_A^B may be corrected for the selectivity arising from interactions in the solution phase by the introduction of the factor $\left(\frac{f_A}{f_B}\right)^2$. The use of $K'_{B/A}$ therefore eliminates the effect of selectivity due to solution phase activity. The introduction of an analogous factor $\left(\frac{\bar{f}_B}{\bar{f}_A}\right)^2$, where $\bar{f}_B$ and $\bar{f}_A$ are activity coefficients in the resin phase, eliminates the effect of selectivity arising from this phase as well. By this process all selectivity effects are eliminated and the quantity on the left hand side of the equation (1-10) below must therefore be unity.

$$\left(\frac{\bar{m}_B}{\bar{m}_A}\,\frac{m_A}{m_B}\,\frac{\bar{f}_B}{\bar{f}_A}\,\frac{f_A}{f_B}\right)^2 = 1 \qquad (1\text{-}10)$$

or

$$\left(\frac{\bar{m}_B}{\bar{m}_A}\,\frac{m_A}{m_B}\,\frac{f_A}{f_B}\right)^2 \left(\frac{\bar{f}_B}{\bar{f}_A}\right)^2 = 1$$

Substituting equation (1-7) gives

$$K'_{B/A}\left(\frac{\bar{f}_B}{\bar{f}_A}\right)^2 = 1$$

$$\therefore \qquad K'_{B/A} = \left(\frac{\bar{f}_A}{\bar{f}_B}\right)^2 \qquad (1\text{-}11)$$

Hence the corrected selectivity coefficient is nothing more than the square of the ratio of the activity coefficients of the two cations in the resin phase.

This statement is, however, valid only if the activity coefficients in both phases are defined in such a way as to make them exactly analogous. For this reason the relationship described in equation (1-11) cannot be tested experimentally, because there is no independent way of evaluating $\frac{\bar{f}_A}{\bar{f}_B}$ without arbitrary conventions or extrathermodynamic assumptions.

1.4.4. Thermodynamic Selectivity Constant K_{aA}^{B}

A number of authors [21] define K_{aA}^{B} as follows:

$$K_{aA}^{B} = \frac{\bar{m}_B^{\,p} \; m_A^{\,q} \; \bar{f}_B^{\,p} \; f_A^{\,q}}{\bar{m}_A^{\,q} \; m_B^{\,p} \; \bar{f}_A^{\,q} \; f_B^{\,p}}$$

This in the case of divalent ions would be:

$$K_{aA}^{B} = \left(\frac{\bar{m}_B \; m_A \; \bar{f}_B \; f_A}{\bar{m}_A \; m_B \; \bar{f}_A \; f_B}\right)^2 \qquad (1\text{-}12)$$

As before the problem in determining K_{aA}^{B} is that the ratio $\frac{\bar{f}_B}{\bar{f}_A}$ cannot be evaluated. By making the assumption that if the resin is entirely in the B form ($\bar{X}_B = 1$) then $\bar{f}_B$ is unity, if entirely in the A form ($\bar{X}_A = 1$) $\bar{f}_A$ is unity, certain authors [22, 23, 24, 25] showed that the application of the Gibbs - Duhem equation gave:

$$\ln K_{aA}^{B} = \int_0^1 \ln K'_{B/A} \, d\bar{X}_B \qquad (1\text{-}13)$$

Reichenberg [26] points out that since $K'_{B/A}$ expresses interactions in the resin phase only, so too must K_{aA}^{B}, despite the fact that according to equation (1-12) it is symmetrical with respect to both phases. He states that this paradox arises from the different nature of the standard states chosen for defining f_A and f_B on the one hand and $\bar{f}_A$ and $\bar{f}_B$ on the other.

Where it is useful to express the selectivity of an exchanger by a single meaningful value, K_{aA}^{B} can be determined from measurements of $K'_{B/A}$ by applying equation (1-13). This may be done accurately by making a large number of measurements of values of $K'_{B/A}$ at values of $\bar{X}_B$ varying from nearly zero to nearly unity, or by applying the approximation

$$K_{aA}^{B} = (K'_{B/A}) \text{ at } \bar{X}_B = 0.5 \qquad (1\text{-}14)$$

In this case K_{aA}^{B} can be obtained by interpolation after only a few values of $K'_{B/A}$ have been measured.

The thermodynamic selectivity constant is related to the standard free-energy change of the exchange reaction(1-1) by the equation:

$$\Delta G^{\circ} = - RT \ln K_{aA}^{B} \qquad (1\text{-}15)$$

where ΔG° is the standard free-energy change involved in the transfer of 1 mole of B from an infinite amount of solution in the standard state to 1 mole of exchanger initially completely in the A form and the transfer back to the solution of 1 mole of A. R is the universal gas constant and T the absolute temperature.

1.4.5. Quantities Used For Correlating Selectivity Coefficients

As stated previously (see page 5) selectivity coefficients are averages made over a resin sample, and should be correlated with quantities which are also averaged over a similar resin sample. Quantities commonly used for this purpose are swelling, degree of neutralization of the resin (α) and loading.

Swelling has been discussed previously (see page 6) and is used to correlate the data presented in chapter three.

The degree of neutralization of the resin (α) is given by the fraction of the exchange sites able to taking part in an exchange process i.e.

$$\alpha = \frac{\text{Available exchange sites}}{\text{Total exchange sites}}$$

The resin sites which are "not available" are sites which are covalently bonded to the counter-ion and hence do not take any significant part in ion-exchange. In the present work covalent bonding occurs only when the weak acid resin Amberlite IRC 50 is in the hydrogen form. The carboxylate groups are covalently bonded to hydrogen ions and remain inert with respect to ion-exchange provided the pH of the solution is below 7. In this way both the charge on the resin chains and the field strength of the carboxylate groups is reduced. Most measurements of selectivity coefficients have been made at $\alpha = 1$. Selectivity coefficients measured at lower values of α show marked and significant changes, e.g. Gregor et al.[27] found that the sequence of the selectivity coefficients of the alkali metals on Amberlite IRC 50 reversed below $\alpha = 0.2$. Selectivity coefficients are correlated with α in chapter four.

The "loading" or ionic composition of the resin is given by the mole fraction of the exchange sites which are in one ionic form. For example, if two cations A and B are present on the resin and 60%

of the exchange sites are in the A form the ionic composition of the resin is represented as

$$\bar{X}_A = 0.6$$

The significance of the correlation of selectivity coefficient with loading has been fully discussed previously (see page 16). The experimental data are correlated with loading in chapter four.

In the present work selectivity coefficients are also correlated with the composition of the solvent in both the solution phase and the resin phase. If, for example, the mole fraction of pyridine present in the pyridine/water mixture in the resin phase was 0.6, the situation would be represented by

$$\bar{X}_{\text{pyridine}} = 0.6$$

and in the solution phase

$$X_{\text{pyridine}} = 0.6$$

Selectivity coefficients are correlated with solvent composition in chapter four.

1.5. THEORETICAL APPROACHES TO CATION - EXCHANGE SELECTIVITY

1.5.1. A Thermodynamic or Mechanistic Approach?

The numerous attempts that have been made to resolve the problem of the selective behaviour of ion-exchange materials may be classified into two broad categories. In those in the first category rigorous thermodynamic treatment, that requires no model and no assumptions with respect to the mechanism of the phenomenon, is employed. As a result little is learnt about the phenomenon itself. Furthermore the equations developed in these approaches have a limited usefulness for predictive purposes, since making the observations necessary to predict the results is usually more difficult than the direct measurement of the selectivity coefficients. In the second category various models are introduced which attempt to correlate particular aspects of ion-exchange behaviour. A good deal of information about the ion-exchange process evolves as a result, but with the loss of thermodynamic rigour. Provided the information obtained is used to provide qualitative explanations the loss of thermodynamic rigour is not a serious defect. This type of approach is sometimes known as the mechanistic approach.

Even in the simplest cases understanding of the factors and mechanisms underlying ion-exchange selectivity is imperfect. Formal thermodynamic treatments can only be applied to simple systems such as mono-monovalent exchange in dilute aqueous solution on strong acid resins.

The complexity of the systems in the present work, which involve divalent ions, mixed aqueous and non-aqueous solvents and studies on both sulphonic and carboxylic acid resins, mitigates against the successful or useful employment of a thermodynamic approach.

For this reason the approach employed in accounting for the selectivities observed falls into the second category. An attempt will be made to explain the selectivity behaviour in terms of one or other of the models postulated in the literature. It should, however, be borne in mind that extending the use of these models, which were developed for simple systems, to a complex system increases the risk of making assumptions which are in fact not valid. The conclusions drawn from this work should therefore be regarded as purely qualitative.

1.5.2. Gregor's Model

Gregor postulated a model [28, 29] in which the exchanger is regarded as consisting of two parts, an un-crosslinked polyelectrolyte with solvent, and the cross-linking. In his earliest application of this model Gregor assumed that the system behaved ideally except for solvation. Selectivity was attributed primarily to the difference in partial molar volume of the counterions in the exchanger. From these postulates a mathematical expression can be derived.

$$RT \ln K'_{B/A} = \pi (\bar{V}_A - \bar{V}_B)$$

where $\bar{V}_A$, $\bar{V}_B$ are the hydrated volumes of the counterions in the exchanger, π the elastic counterpressure caused by the stretching of the cross-linking and $K'_{B/A}$ the corrected selectivity coefficient (see page 11).

According to this theory, equilibrium is reached when the elastic counterpressure is equal to the residual osmotic pressure.

Gregor's theory offers a simple mechanistic explanation of the swelling and equilibrium properties of ion-exchangers and has been fully discussed in the literature [30]. On the basis of this theory certain deductions may be made:-

1. The counterion with the smallest hydrated volume will be most preferred by the resin, i.e. in the present work the affinity sequence should be:-

Ba > Sr > Ca > Mg

2. An affinity reversal (change in sign of ln $K'_{B/A}$) must be accompanied by a change in the hydrated volumes of the counterions i.e. if originally $\bar{V}_A > \bar{V}_B$ then after affinity reversal $\bar{V}_B > \bar{V}_A$.

3. If $\bar{V}_A > \bar{V}_B$ then as $\bar{X}_B$ increases the resin contracts and π decreases. Provided this is not also accompanied by a change in $\bar{V}_A - \bar{V}_B$, the increase in $\bar{X}_B$ should therefore lead to a decrease in ln $K'_{B/A}$.

Although the model provides a simple mechanistic explanation it is not adequate in accounting for all observed ion-exchange phenomena. This model is, for example, particularly inadequate in explaining the results obtained in the present work. Furthermore it has been demonstrated that for exchanges involving the alkali cations and halide anions the pressure-volume term is small, and does not dominate the value of $K'_{B/A}$, so that resin elasticity is not the dominant cause of selectivity [31, 32].

In systems where selectivity could not be explained on the basis of swelling-pressure and ionic size alone Gregor and co-workers [33] postulated ion-pair formation. Their distinction between free solvent and solvation shells, and between associated and free counterions was, however, arbitrary, so that the employment of this approach led to a drastic loss of thermodynamic rigour. Gregor's theory was used by Glueckauf[31] in its more general form, with an additional term containing the ratio of the activity coefficients of the counterions in the exchanger phase, and using unhydrated ions as the reference components. A similar approach has been used by other authors,[34 - 39] but none of these approaches, although more rigorous thermodynamically, contributes materially to the mechanistic understanding of selectivity.

Marinsky[40] uses the Gregor model in its original form, i.e. with hydrated ionic species. To facilitate his analysis he confines his discussion to those systems in which one of the two counterions is present in trace amount and deals only with the alkali metals in dilute solution on a sulphonic acid resin. His starting point is the general form of the equation obtained from the Gregor model i.e.

$$\ln K_A^B = \ln \frac{\bar{f}_A^{\,+}}{\bar{f}_B^{\,+}} + \ln \frac{f_B^{\,+}}{f_A^{\,+}} + \frac{\pi}{RT}\left(\bar{V}_A - \bar{V}_B\right)$$

where $\bar{f}_A^{\,+}$, $\bar{f}_B^{\,+}$ = activity coefficients in resin phase

$f_A^{\,+}$, $f_B^{\,+}$ = activity coefficients in solution phase

$\bar{V}_A$, $\bar{V}_B$ = partial molar volumes in resin phase

π = swelling pressure

He has evaluated the first term using the method of Feitelson[41], who employed the Fuoss - Katchalsky - Lifson polyelectrolyte theory, as adapted by Gregor and Kagawa[42] to counterions of different sizes, to calculate the interaction between a particular ion and a polyelectrolyte gel whose thermodynamic properties were completely determined by another ion. The distance of closest approach used in this calculation was estimated by Marinsky from hydration parameters obtained from measurements, on an essentially unrestrained ion exchanger, of the variation with monomer molality of the osmotic coefficient of a macro-ion.

The value of the second term is easily obtained by using the published value of the mean activity coefficients of pure electrolytes at the ionic strengths employed in the selectivity experiment. Ion-ion interaction can be neglected in calculating this term because of the dilute solutions used.

The third term, the so-called "pressure-volume" term, can be calculated in a much less arbitrary manner than was employed by Gregor. The volume assignments are made by using the hydration parameters referred to above, volumes being calculated from the bare ion radius plus a volume of 30 A^3 for each molecule of bound water. The internal pressure π at each situation can be deduced from the osmotic behaviour of each ionic form of the essentially unrestrained exchanger.

The value of this approach for the prediction of ion-exchange selectivity as a function of the cross-linking of the exchanger when one of the two counterions is present in trace amount is demonstrated by Marinsky[40]. He calculates values of the selectivity for K^+ and Cs^+ (Cs^+ in trace quantity) of Bio-Rad A G - 50 - W at various DVB contents and compares these with experimentally measured data. Agreement between experimentally determined and calculated values is excellent. He further substantiates his theory by comparing experimental and calculated values for the distribution of pairs of counterions between this resin and its linear polyelectrolyte analogue, polystyrene sulphonate. Once again excellent agreement is obtained and he therefore concludes that this treatment provides a good deal of insight into the ion-exchange phenomenon.

Marinsky appears, therefore, to have developed the most successful of the treatments of ion-exchange based on the Gregor model. The basic theory is similar to other treatments, but the three contributing terms are more accurately evaluated in the Marinsky treatment.

1.5.3. The Theory Of Eisenman

The theory of Eisenman [43, 44] differs from those based on the Gregor model in a number of respects, but particularly in two:-

1. Hydration of ions is recognized (as in other theories) to be important, but it is considered in terms of its energetics rather than its effect on ionic size.

2. Electrostatic interactions are regarded as the primary cause of affinity reversals.

According to Eisenman's theory these two factors can be employed to predict almost quantitatively the order in which affinity reversals will occur within a family of ions. In considering the ion-exchange process in which a monovalent cation (1) is taken from the bulk of a dilute solution and brought into contact with a fixed group, while simultaneously the counterion (2) is removed from the fixed group and returned to the bulk of the dilute solution, Eisenman distinguishes between two types of interaction energy, which correspond to the factors listed above. These are:-

(1) The free energies required to remove from, or rearrange around, the fixed grouping and the counterion as many water molecules as are necessary to permit the contact (or close approach) of these two ions. Such free energies will be closely related to the standard free energies of hydration of the fixed group and counterion. If these free energies are ΔG_A (for the fixed group) and ΔG_1 for sorption of cation (1), and $-\Delta G_A$ and $-\Delta G_2$, respectively, for desorption of cation (2), the change in the free energy of the system will be $\Delta G_1 - \Delta G_2$.

(2) The electrostatic interaction between the ion and the fixed group. For simplicity Eisenman treats both the counterion and the fixed grouping as nonpolarizable point charges, each at the centre of an incompressible sphere. If the fixed grouping has a radius r_A and cations (1) and (2)

have ionic radii (not hydrated radii) r_1 and r_2, the change in the free energy of the system when ion (1) replaces ion (2) is given by:-

$$\frac{e^2}{r_A + r_2} - \frac{e^2}{r_A + r_1}$$

where e is the electronic charge expressed in suitable units.

The overall change in the free energy of the system for the ion exchange process is therefore:-

$$\Delta G^o_{1/2} = \left(\frac{e^2}{r_A + r_2} - \frac{e^2}{r_A + r_1}\right) - (\Delta G_2 - \Delta G_1)$$

and since

$$\Delta G^o_{1/2} = - RT \ln K_{a\ 1/2}$$

determining the value of $\Delta G^o_{1/2}$ can lead to predictions of thermodynamic equilibrium constants.

The argument may be pursued qualitatively from this point by comparing the exchange of potassium (1) and sodium (2) on both sulphonic and carboxylic acid resins.

Relative to the carboxylate grouping, the sulphonate grouping is large (r_A is large). Eisenman describes this as the case of a fixed grouping of low field strength. Regardless of the counterions involved

$$\frac{e^2}{r_A + r_2} - \frac{e^2}{r_A + r_1}$$

will be small and $\Delta G^{o}_{1/2}$ will be determined mainly by the term $-(\Delta G_2 - \Delta G_1)$ which, as explained above, is related to the difference of the standard free energies of hydration of the counterions. For the counterions potassium (1) and sodium (2) ΔG_1 is smaller than ΔG_2 and hence $\Delta G^{o}_{1/2}$ will be negative and $K_{1/2}$ will be greater than one, i.e. potassium will be preferred to sodium.

This argument leads to the "normal" affinity sequence for the alkali metals, i.e. Cs > K > Na > Li.

In contrast to this, exchange on the carboxylate group, where r_A is fairly small, will be markedly different. In this case, where the fixed grouping has a high field strength, the term

$$\frac{e^2}{r_A + r_2} - \frac{e^2}{r_A + r_1}$$

will now be more important than the term $(\Delta G_2 - \Delta G_1)$, and since r_2 is smaller than r_1 the electrostatic term will be positive. If $\Delta G_{1/2}$ is positive, $K_{1/2}$ will be less than one and sodium will be preferred to potassium.

The argument can be made quantitative by making the assumption that $(\Delta G_2 - \Delta G_1)$ is equal to, or proportional to, the difference in the standard free energies of hydration of the two counterions. Known values of the standard free energy of hydration of various salts with a common anion may then be used without any assignment of this total free energy between cation and anion. Such values are given in tables of thermochemical data and in some textbooks of physical chemistry [45, 46]. Assigned values for cationic radii[47] can then be used to calculate the theoretical consequences of varying r_A. The accuracy of the resulting predictions of selectivity reversals indicates that Eisenman's theory is basically sound. It does, however, require some modification, since the sequences found experimentally for carboxylate resins do not agree with predictions.

Ling [48, 49] introduced an approach basically similar to Eisenman's but adapted it to make it particularly suitable in the case of protein molecules in biological systems. Ling's model emphasized the carboxylate group and, using values for the polarizability of this group up to 2.0 A^3, he calculated the affinity sequences to be expected at various values of the effective field strength of the fixed grouping. The sequences he predicted were identical to those predicted by Eisenman from his simpler model.

1.5.4. Reichenberg's Model

Reichenberg [50] applies Eisenman's theory directly to the alkali metal cations. Using the two interaction energies considered by Eisenman, i.e. hydration and coulombic, he obtains the same affinity sequences as were predicted by Eisenman.

At this point he introduces a refinement along the lines proposed by Ling. He assumes an ion to be a point charge situated on a spherical polarizable particle. A new kind of interaction then arises - that between an ion and the dipole induced in a second ion by its field. Reichenberg points out that this interaction is proportional to the polarizability of the second ion and inversely proportional to the fourth power of the distance between the centres of the two ions (as an approximation) using a value of 4.0 A^3 for the polarizability of the carboxylate grouping with known values for the cation polarizability, he obtained some [51], but not all, of the affinity sequences found experimentally for carboxylate resins of high capacity. The polarizability of 4.0 A^3 is a value for the whole carboxylate grouping, whereas Ling's maximum value of 2.0 A^3 is based primarily on a consideration of the ionized oxygen atom of this grouping.

Reichenberg has further modified the Eisenman model by taking into account the fact that anionic groupings like the sulphonate or carboxylate grouping consist of a number of atoms, so that it is only an approximation to regard them as single point charges. They should in fact be treated as a system of point charges, although at present very little is known about their charge distribution[52]. The general effect of such a system is discussed by Reichenberg [53] who arrives at the conclusion that the effect of a multi-point-charge distribution is to contribute terms to the interaction energy which are roughly inversely proportional to the third power of the distance of separation. This reinforces the effect of the induced polarization interactions and hence the tendency for the resin to show affinity sequences which are the reverse of the "normal" sequence is increased, as well as the tendency for the reversals to commence with counterions of small rather than large size.

If the combined effect of induced polarization and multi-point-charge interactions is sufficiently large, the affinity reversal sequences obtained will be similar to those found experimentally with carboxylate resins.

Reichenberg [50] also points out that the overlapping of the fields of fixed groupings probably has a significant effect. This is indicated by the fact that reversals are promoted by increases in the degree of cross-linking and the specific capacity, also in the case of carboxylate resins, by increase in the degree of ionization of the resin. All these facters tend to reduce the average steric separation of the ionized fixed groups. This increased overlapping of the fields of these groups is thought to increase the electrostatic interaction energy, while not affecting the "dehydration" energy to the same extent.

Finally Reichenberg [50] deals with the effect of swelling on selectivity. He advances the theory that a significant fraction of the counterions undergo some degree of stripping [54], even when the "normal" selectivity sequence is observed, and takes the view that only ions which, as a result of this stripping, touch (or nearly touch) the fixed groupings make a significant contribution to the over-all selectivity. If the resin is highly swollen there will for each fixed group be a relatively large volume of solvent in which the counterion will be found. The larger this volume the smaller the proportion of counterions that will at any instant be touching (or nearly touching) the fixed groupings. Under these conditions the effect of swelling would be to reduce the interactions giving rise to selectivity.

In summary, then, Reichenberg's model is basically similar to the model of Eisenman and Ling, but seeks to take into account, quantitatively, the effect of interaction polarization and, qualitatively, the effects of multi-point-charge interactions, the overlapping of the fields of fixed groupings and swelling.

1.5.5. Selectivity As Competitive Solvation Of The Ions

A different approach to the problem of accounting for selectivity phenomena has been employed by Chu, Whitney and Diamond[55, 56, 57, 58]. Ion exchange selectivity is treated as a competition among the resin ions, coions and water molecules for "solvating" the counterions in the two phases. The argument is restricted to the behaviour of a variety of tracer ions with respect to a single macro-electrolyte and for the purpose of explaining the present work it is necessary to consider only these authors analysis of the dilute external solution case [58].

For their purposes they define a dilute solution as one in which anion-cation interactions are negligible and the water activity remains unity. The only effects which must be corrected therefore, are ion-water interactions, water structure, and resin ion-counterion interactions.

The basic difference between this and other models is that other models tend to emphasize a particular aspect of the resin phase, whereas Whitney and Diamond consider the ion-exchange process to be a distribution between two aqueous phases: the dilute external solution phase and the concentrated electrolyte resin phase. The distributional effects are considered to arise from the differences between the two phases which are:-

1. The matrix-fixed ion is relatively immobile, though the matrix itself can swell when in contact with an external solution to an extent dependent on its degree of cross-linking.
2. There is less unbound or "free" water per ion in the resin phase, and electrostatic interactions are stronger there than in the dilute external solution (the effective dielectric constant of the resin phase is lower).
3. The "free" water that remains in the resin phase has less structure, i.e. on the average a water molecule is hydrogen-bonded to fewer other water molecules than in a dilute aqueous solution.

The first difference is the special feature emphasized by the model basing selectivity on the pressure-volume effect; this has been shown to be inadequate.

The second difference is the special feature emphasized by models invoking electrostatic interactions between counterions and resin anions as the basis of selectivity.

Chu, Whitney and Diamond believe that the electrostatic ion-pairing of the counterions and resin anions does influence selectivity, especially in the case of weak-acid and weak-base resins, but they consider the effects on the ion-water and water-water interactions of the difference in water structure between the resin and dilute external phases to be a major factor in ion-exchange selectivity, particularly for strong-base and strong-acid resins.

Before examining the contention by these authors that selectivity results from a competitive solvation of ions, consideration should be given to the interactions they consider important in establishing which phase will preferentially solvate the ion. These interactions are water-water, ion-water, ion-ion and ion-resin matrix.

Water-water interactions, resulting from the tendency of water molecules at room temperature to form a highly hydrogen-bonded network with relatively strong intermolecular forces, influence ion exchange selectivity in two ways. Large ions which do not hydrate easily can cause a tightening of the water structure, so that water tends to reject an ion of this type. In the resin phase this effect is not evident to the same extent, since the structure of the water has been disturbed by the hydrocarbon matrix, which confines the internal phase to small spatial volumes in which the average water molecule is not bound to as many other water molecules as is the case in the external phase. Thus the resin phase has a smaller tendency than the dilute external phase to reject large, poorly hydrated molecules. Water structure also influences selectivity in that ion-pairing can result from large, poorly hydrated ions being forced together to minimize their disturbance of the water structure.

The other interactions listed above, ion-water, ion-ion and ion-resin matrix, have been discussed previously and will not be reviewed again at this point.

Chu, Whitney and Diamond now define solvation as including any mechanism which disperses the charge on the ion and lowers its free energy. From this starting point they deduce that those interactions which lead to the greatest overall lowering of free energy will take place, hence the ion will be "solvated" in that phase in which the favoured interaction is more likely to occur. The argument is similar to that of Eisenman in that they approach the problem in terms of energetics, but they use the term "solvation" to include interactions with both solvent and resin anion.

When these arguments are applied to the selectivity of the alkaline earth metals in dilute solution on strong acid resins, the conclusion can be drawn that the need for solvation can generally be satisfied through ion hydration, i.e. water will be preferred to the resin anion in the competition for solvation of the cation. The aqueous phase will therefore be strongly selective towards those ions with small crystallographic radii, which thus preferentially enter the dilute external phase, forcing the larger ions into the more poorly solvating resin phase. The selectivity order [59] will therefore be Mg < Ca < Sr < Ba, which is confirmed in the present work. This assumes that with the sulphonic acid resins the difference in hydration in the two phases plays the dominant role in determining selectivity, which is in agreement with Eisenman's model. The change in selectivity with specific capacity or cross-linking is considered to be merely a result of the accompanying dilution or concentration of resin phase.

The cation is assumed by these authors to retain its primary hydration shell in the resin phase. In support of this Diamond and Whitney [60] quote Boyd and Soldano [61], who found that the chromium ion exists in the resin phase (Sulphonic acid resin) with all six waters of hydration intact. When a strongly hydrated cation bonds with the resin anion there must therefore be a bridge consisting of at least one water molecule between the two ions, removing the possibility of a contact type ion pair in the resin phase. This argument differs markedly from that of Reichenberg (see page 30) who believes that a significant fraction of the counterions actually undergo some degree of stripping, even with sulphonic resins.

In the case of exchange on weak acid resins, specific cation-resin anion interactions are considered to play an important role. An increase in the complexing ability of the resin anion should tend to draw the smaller cation into the resin phase more strongly and eventually lead to an affinity reversal.

1.5.6. A Summary Of The Mechanistic Models Accounting For Ion-Exchange Phenomena.

Of the various models discussed, three may be considered to offer a reasonable explanation of ion-exchange phenomena. These are:-

1. Marinsky's treatment of the Gregor model.
2. Reichenberg's model.
3. The model of Chu, Whitney and Diamond.

Marinsky uses the Gregor model in its original form but is able to evaluate the term containing the ratio of the resin phase activities and the pressure-volume term more accurately than previous workers. In dealing with pressure-volume effects he considers hydration in terms of volumes, and not in terms of energetics.

Reichenberg follows the line of thinking of Eisenman and Ling. He considers selectivity in terms of the energetics of hydration and of coulombic interaction between the ions. He believes that partial stripping occurs when cations interact with resin anions (even in the case of strong acid resins).

Chu, Whitney and Diamond deal with selectivity as a competitive solvation of the ions, emphasizing the importance of solvent structure and solvation. They define solvation very broadly to include interaction between the cation and the resin anion and discuss it in terms of energetics. They consider that virtually no stripping (certainly of the primary hydration shell) of the hydrated cations occurs.

1.6. CATION - EXCHANGE IN NON - AQUEOUS AND MIXED SOLVENTS

Water is by no means the only solvent which allows ion-exchange to take place. There are other solvents in which electrolytes can dissolve and dissociate and in which most of the common ion-exchangers are stable. Such solvents are formamide, anhydrous ammonia, ethylene glycol, methanol, ethanol, acetone, monoethanolamine, pyridine and acetic acid.

Ion exchange equilibria in non-aqueous and mixed solvents have been studied by many investigators [62]. Both ion-exchange and swelling equilibria are strongly affected by the nature of the solvent.

An additional factor is introduced in considering ion-exchange in mixed solvents in that the solvent composition of resin phase and solution phase may differ if one of the solvent components is selectively sorbed by the resin. This aspect has been studied in the present work.

The importance of non-aqueous solvents is that they can enhance or reverse the selectivities of ion-exchange resins and permit a closer investigation of the role of the solvent in the ion-exchange process.

Non-aqueous solvents may differ from water in three important respects: dielectric constant, dipole moment and solvent structure.

With the exception of formamide the dielectric constants of the non-aqueous solvents listed above are lower than that of water, and for the purpose of this discussion it is necessary only to discuss the effect of introducing a solvent phase of lower dielectric constant.

The most obvious result of lowering the dielectric constant is to increase the interactions between ions of opposite charges, so that ion-pair formation and association are favoured. Thus interactions between the resin anions and the counterions, and between the cations and anions in the solution phase, will be stronger. For this reason the choice of anion is a good deal more important where non-aqueous solvents are used than when water is the solvent. To minimize solution phase effects it is desirable to choose an anion which will associate as little as possible with the cations. It was for this reason that the perchlorate anion was selected for the present work. A theoretical justification for this choice is given later (see page 119) when the effect of the various anions in pyridine solutions is discussed.

A decrease in dielectric constant may also affect solvation, by increasing the strength of ion solvent dipole interactions. The swelling of the resin may also be affected, but in a somewhat different way. An initial increase in swelling will result from the increased force of repulsion between ionized resin groups and between charged resin chains. The swelling will reach a maximum value and then decrease as the degree of ionization of the resin groups decreases due to increased resin anion and counterion interaction. This effect is fully discussed later (see page 70).

A particularly important result of lowering the dielectric constant is its influence on the selectivity of the resin, which will be affected by both the increased ion-pair formation and the changes in swelling.

The rate of ion-exchange in systems with organic solvents of low dielectric constant is nearly always considerably lower than in comparable aqueous systems [63, 64, 65, 66, 67]. Particular care must therefore be taken to ensure that equilibrium is in fact attained when selectivity measurements are made with organic solvents.

The second difference between non-aqueous solvents and water is usually a difference in dipole moment. The solvent with the higher dipole moment will tend to interact more strongly with the ions, which will affect both the swelling and the selectivity of the resins. This effect is discussed later, but is not critical in the present work, since the dipole moments of water and pyridine are similar (see page 70).

The effect of solvent structure is particularly important when ion-exchange is considered as a competitive solvation of ions by the two phases. This aspect is considered for the particular case in question, i.e. for pyridine, at a later stage (see page 106).

2. EXPERIMENTAL METHODS

2.1. MATERIALS

2.1.1. RESINS

Three resins were used in this work. The properties of two, Amberlite IRC 50 and Zeo-Karb 225 (SRC 5), were investigated, while the third resin, Zeo-Karb 225 (SRC 15), was used in the chromatographic separation of the alkaline earth metals.

AMBERLITE IRC 50

This resin, produced by the Rohm and Haas Company of Philadelphia, U.S.A., is a carboxylic acid cation exchange resin, consisting of polymethacrylic acid polymers crosslinked with approximately 2-6% divinylbenzene [1, 68, 69]. It is supplied as beads in the hydrogen form.

Before use the resin was screened and conditioned. Sufficient resin was processed initially to enable all subsequent experimental work to be performed on samples from this one batch. The screening was carried out on nylon sieves with plastic rims, the 22-36 mesh fraction being collected. Conditioning was carried out in the following manner:- The resin was allowed to stand for a few hours in 4% sodium hydroxide solution, with occasional stirring, and then transferred to a large column, where it was back-washed with de-ionized water. The flow rate during back-washing was sufficient to fluidize the resin and carry over any small resin chips inadvertently retained during screening. The resin was then conditioned on the column by elution with 0.1 N hydrochloric acid, 4% sodium hydroxide solution and acid again, in that order, with thorough back-washing between each treatment. After a final washing with de-ionized water containing a few drops of hydrochloric acid per litre, the resin was removed from the column, air dried, and stored in a sealed polythene container. This resin was stored and weighed out in the hydrogen form, as this form is not easily hydrolysed and provides a convenient basis for reference.

In certain experiments the resin was required to be in the magnesium form. A supply of resin in this form was obtained by converting some of the hydrogen form resin to the Mg form as described on page 52). The Mg form resin was air dried and stored in a sealed polythene container.

ZEO - KARB 225 (SRC 5)

This resin, produced by the Permutit Company of London, is a sulphonic acid cation exchange resin, consisting of sulphonated polystyrene polymers crosslinked with 2% divinylbenzene [70]. It is supplied as beads in the sodium form, 14-52 mesh.

Before use the resin was conditioned, sufficient resin being processed initially to enable all subsequent experimental work to be performed on samples from this one batch. The resin was back-washed in a large column, as in the case of the Amberlite IRC 50, and conditioned by alternate elution with 1 N hydrochloric acid and 4% sodium hydroxide solution, the final elution being carried out with the sodium hydroxide solution. After being washed with de-ionized water containing a few drops of sodium hydroxide per litre, the resin was removed from the column, air dried, and stored in a sealed polythene container. Some of this sodium form resin was converted to the magnesium form by elution with a threefold excess of 1 N magnesium perchlorate on a large column; the resin was then washed with a very dilute solution of magnesium perchlorate, air dried and stored in a sealed polythene container.

This resin was stored and weighed out in both the sodium form and the magnesium form, separately, as both these forms are stable and both were required in experimental procedures.

ZEO -KARB 225 (SRC 15)

This resin is similar to the Zeo-Karb 225 (SRC 5) except that it contains 8% divinylbenzene and is supplied as 100 - 200 mesh beads[70], in the sodium form. It is more suitable for chromatographic separations on account of its small particle size. This resin was conditioned in the same way as the Zeo-Karb 225 (SRC 5), the conditioning being carried out in the chromatographic columns in which it was to be used.

2.1.2. CHEMICALS, SOLVENTS AND SOLUTIONS.

All chemicals used in this work were Analytical Reagent (A.R.) grade. Two solvents were used, water and pyridine. All water used in this work was purified by distillation followed by passage through a mixed bed resin, Amberlite MB-1, analytical grade. The pyridine was Analytical Reagent (A.R.) grade, supplied by Protea Laboratory Services of Johannesburg, South Africa.

The solutions used were made directly from the salts, with the exception of the calcium, strontium and barium perchlorate solutions, which were prepared by neutralizing aliquots of dilute perchloric acid with excess of the solid carbonate salt. The neutral solutions were warmed and stirred, to expel carbon dioxide and ensure complete reaction, and then excess solid was removed by filtration. The solid was washed with de-ionized water, the washings added to the filtrates, and, after cooling, the solutions were made up to a standard volume. The perchlorate solutions used in all experiments were 0.05 M.

2.2. RESIN DRYING

Resins were dried by heating for 24 hours at 105° C. Both Zeo-Karb 225 [71, 72] and Amberlite IRC 50 [73] are believed to be stable at temperatures up to 120° C, although Kitchener [72] states that polymethacrylic acid resins show a slow loss of weight at 120° C, which may be due to either the removal of the last traces of water or decomposition. However when the H form IRC 50 was heated for a further 48 hours at 105° C it showed no further detectable weight change. This method was therefore adopted for the determination of the moisture content of the air dry resins used in the selectivity experiments. Samples of resin used in moisture content determinations were not used subsequently in other experiments in case their properties had been affected in any way. When a set of resin samples was weighed out for an experiment, the first and last samples were reserved for moisture determinations.

In cases where the amount of solvent remaining on the resin had to be determined extremely accurately, as, for example, in the swelling and sorption experiments, the resin was dried in a vacuum oven, at 105°C and 2 mm Hg, for 24 hours. A further loss in weight of up to 5% occurs on heating at reduced pressure.

2.3. ANALYTICAL METHODS

2.3.1. Determination Of Alkaline Earth Cations

The alkaline earth cations were determined by titration with standard EDTA solution, the Mg and Ca by direct titration, the Sr and Ba by adding excess EDTA and back-titrating with standard Mg solution. In all cases only a single cationic species was present, a previous separation having been carried out where necessary. It was thus never necessary to determine, for example, Mg in the presence of Ca. The indicator used in all titrations was Solochrome Black, and the titrations were, as usual, carried out in the presence of an ammonia/ammonium chloride buffer (pH = 10.0).

The determination of Mg concentration was carried out by diluting the solution containing the Mg to approximately 0.01 M (with respect to Mg), adding 2 ml of buffer per 100 ml of solution and a little solid indicator, and titrating with standard 0.05 M EDTA until just before the end point. The solution was then warmed to about 40° C [74] and the titration was continued until the end point, indicated by a change in the colour of the solution from red to blue, was reached.

The Ca concentration was determined as described above for Mg except that near the end point 0.30 ml of standard Mg solution was added to improve the end point; the final titration volume was corrected accordingly.

The Sr and Ba concentrations were estimated by adding excess standard EDTA solution and then back-titrating with a standard Mg solution, using the method described for the determination of Mg (the colour change in this case is blue to red). Sharp end points were obtained in the Mg, Ca and Sr titrations under these conditions, while the end point of the Ba titration was fairly sharp. Indicators which permit the direct titration of Ba against EDTA are available, but in the separation of the barium ions from the others by an ion exchange method (see later) the Ba was eluted from the column with excess EDTA, so that a back-titration of the EDTA was necessary in any event.

The EDTA was standardized against two primary standards:

1. By titration against dry calcium carbonate. The solid calcium carbonate was dried at 105°C for 3 hours and dissolved in a slight excess of 0.1 N hydrochloric acid. The solution was gently boiled to expel carbon dioxide, the pH adjusted to 10.0 by addition of an ammonia/ammonium chloride buffer and the titration carried out as in the case of the Ca determinations described above.
2. By titration against dry zinc oxide. The zinc oxide was dried for 3 hours at 105°C and dissolved in a slight

excess of 0.1 N hydrochloric acid. The solution was diluted with water and a few drops of xylenol orange indicator added. Sufficient solid hexamethylene tetramine, which acts as a buffer, was added, to produce a wine red colour. The solution was then titrated with the EDTA solution to the end point at which the indicator turns yellow.

The results obtained by these two methods were not significantly different.

The accuracy of the Ca and Ba determinations was checked by assaying aliquots of a bulk solution of Ca and Ba perchlorate by independent methods as well as by the standard method given above using EDTA. The Ca was determined by precipitation as the oxalate and titration against standard permanganate solution, and the Ba was determined by precipitation as the sulphate. The results are given in Table 1 below. The results shown for the independent assays are both the mean of three determinations carried out by an independent analyst. The results shown for the EDTA titrations are both the mean of a set of ten titrations.

Table 1. ACCURACY OF EDTA TITRATION OF ALKALINE EARTH METALS COMPARED WITH INDEPENDENT ASSAYS.

Ion determined	Molarity determined by EDTA	Molarity determined by independent method
Ca	0.1231	0.1230
Ba	0.1251	0.1253

These results given in Table 1. show that the accuracy of the EDTA titrations is well within the limits of experimental error and they also confirm the accuracy of the method of standardization used for the EDTA.

The precision of the volumetric methods was also determined, by performing a set of ten titrations in each case. The results are given in Table 2 below.

Table 2. PRECISION OF EDTA TITRATIONS OF ALKALINE EARTH METALS.

Ion titrated	% Standard Deviation
Mg	Less than 0.1
Ca	Less than 0.1
Sr	0.2
Ba	0.3

The results given in table 2. show that the precision of the EDTA titrations is such that this analytical method is adequate for the purposes of the present work.

2.3.2. Separation Of A Mixture Of Mg, Ca And Ba By Ion Exchange Chromatography.

The method of separation was based on that proposed by Honda [75] for the separation of Mg, Ca, Sr and Ba in solution. On investigation it was found that Honda's method did not give a good separation of Ca from Sr or of Sr from Ba. A modified form of the method could however be used for the separation of Mg, Ca and Ba from a mixture of all three ions, and for the separation of the pairs Mg/Ca, Mg/Sr and Mg/Ba. The ions were separated by elution chromatography using a chromatographic column 1.1 cm in diameter, packed with the sulphonic acid resin Zeo-Karb 225 (SRC 15), analytical grade, to a height of 20 cm. The resin, initially in the Na form, was converted to the ammonium form by elution with 1.0 N ammonium acetate. The column was then washed with water and the solution containing Mg, Ca and Ba passed through it. The cations were all held on the column and each was subsequently eluted under different conditions. The Mg was eluted with approximately 80 ml of 1.0 N ammonium acetate, then the Ca with about 50 ml of 1.5 N ammonium acetate, and finally the Ba, which required a 50% excess of 0.05 M EDTA, buffered to a pH of 10.0, the EDTA was subsequently washed through the column with water. The flow rates were in all cases between 12 and 18 ml per hour.

The separated fractions of Mg, Ca and Ba were then analysed as described in 2.3.1. It was necessary, however, to adjust the pH of the Ba fraction to 10.0 by adding ammonia solution, since some of the ammonia in the solution escaped while the buffered EDTA was being collected, and the pH consequently fell.

The recovery of each ion individually from the column was checked by passing a known quantity of a standard solution of the ion through the column, eluting and titrating the eluate. In each case the recovery was found to be 100%, within the limits of titration error.

The accuracy and precision of this method of separation of Mg, Ca and Ba from a solution containing all three ions was then determined. The volumes of EDTA equivalent to 25.0 ml aliquots of solutions containing only Mg, Ca and Ba, respectively were determined by the standard methods. 25.0 ml aliquots of each of these solutions were then well mixed, and the mixture absorbed on the resin column and separated as described above. The separated fractions were titrated with EDTA and the volumes of EDTA required to titrate each cation were compared with those required before mixing and separation. The results are given in Table 3 below. Each represents the mean of the results obtained in eight separations, identical volumes of the same solutions being used in each separation and analysis.

Table 3. ACCURACY OF METHOD OF SEPARATION.

Ion Determined	Before mixing and Separation ml EDTA	After mixing and Separation ml EDTA
Mg	17.40	17.28
Ca	17.25	17.16
Ba	23.6	23.9

It would appear that the very small amounts of Ca and Mg not eluted in the Ca and Mg fractions are recovered together with the Ba on elution with excess EDTA. The Ba titrations are only given to one decimal place since the end point of this titration is only fairly sharp. The precision of the method of separation, as calculated from the deviation of the titration results from the mean of the values obtained, rather than from the theoretically correct value, is given below in Table 4.

Table 4. PRECISION OF METHOD OF SEPARATION.

Ion determined	% Standard Deviation
Mg	0.3
Ca	0.2
Ba	0.6

The precision of the method of separation naturally includes the precision of the EDTA titrations.

The analytical method used in the separation and determination of the alkaline earth metals in solution therefore appears to be satisfactory for the purpose of selectivity determinations and capacity measurements. It must be emphasized, however, that considerable experience is necessary in performing the EDTA titrations. The sets of titrations and separations to establish the accuracy and precision of the method were carried out only after considerable familiarization with the techniques required.

2.4. CAPACITY DETERMINATIONS.

Amberlite IRC 50

It was necessary to determine the exchange capacity of this resin to enable the value of α to be calculated in later work, as well as to check the results obtained in selectivity experiments. The capacity of the resin for the ions H^+, Mg^{2+}, Ca^{2+} and Ba^{2+} was determined by the following method. Five samples of the resin in the hydrogen form, were weighed out. Two were reserved for moisture determinations, while each of the remaining three was treated as follows. The resin was transferred to a small exchange column (diameter 1.0 cm, maximum height of resin bed 10 cm) and converted to the Na form by elution with a 300% excess of 4% sodium hydroxide solution over a period of 24 hours (the exchange sites must be converted to the Na form since exchange with sites in the H-form is extremely slow in the case of carboxylic acid resins). The resin was then washed with de-ionized water by the following procedure. The exchange column was inserted into a rubber stopper fitting into a Buchner flask and sucked dry. The resin was then washed in the column with a small quantity of de-ionized water and again quickly sucked dry. The column was then removed from the Buchner, the bottom end placed in a beaker of de-ionized water, and the water sucked up to near the top of the column, so as to fluidize the resin bed and thoroughly wash the surface of the resin. The column was then quickly replaced in the Buchner and sucked dry, and finally the resin was once again washed in the column with a small quantity of de-ionized water and sucked dry. This method, which will hereafter be called the standard procedure, is believed to give the most thorough washing of the resin without risk of hydrolysis, since the total time of contact between the wash water and the resin does not exceed ten seconds.

The resin was now considered to be completely in the Na form with all excess sodium hydroxide removed. To determine the capacity of the resin for the alkaline earth cations a .05 M solution of the perchlorate of the appropriate ion was sucked up into the column, in order to exclude air bubbles, and a 200% excess of this solution was then passed through the column, rapidly at first and then progressively more slowly, so that the total volume took 24 hours to pass through the column. The resin was then washed with de-ionized water by the standard procedure, after which it was considered to be completely in the desired ionic form, with all excess of the ion removed. The alkaline earth cation was then eluted with 100% excess of N/4 hydrochloric acid, over a period of 4 hours, the cation determined in the eluate by titration with standard EDTA, and the total exchange capacity of the resin for this ion calculated from the titration results and the weight of the resin in the hydrogen form, corrected for the weight of moisture present. The capacity for H^+ was estimated by passing a known excess of standard N/10 hydrochloric acid through the resin in the Na form, washing the resin with de-ionized water, adding the washings to the eluate and titrating the excess acid in the eluate with standard N/10 sodium hydroxide. The results of these capacity determinations are given in Table 5 below.

Table 5. TOTAL EXCHANGE CAPACITY OF IRC 50.

Ion	Total exchange capacity in m.eq/gm dry H form resin
H	10.87
Mg	10.91
Ca	10.92
Ba	10.8

Since the precision of the analytical method for Ba is lower than that found in the other cases (see page 50) the capacity for Ba is given to a lower degree of accuracy. As expected, in the presence of the non-complexing perchlorate anion the capacities for the different alkaline earth cations were the same (within the limits of experimental error). The capacity for H^+ also agreed with the values obtained for the alkaline earths, within experimental error.

Zeo-Karb 225

As reported above the exchange capacity of Amberlite IRC 50 was determined for the H^+, Mg^{2+}, Ca^{2+} and Ba^{2+} ions. The reason for this was to ascertain whether the resin showed a different capacity for these different ions. It was considered possible that the capacity for H^+ might differ from that for the alkaline earths, as a result of a solution phase reaction of the type:

$$Mg^{2+} + X^- \rightarrow Mg\,X^+$$

where X^- is the anion present in the solution phase.

The results shown above indicate that this reaction does not occur when the anion in the solution phase is the perchlorate ion.

In view of these experimental findings it was considered sufficient to determine the exchange capacity of Zeo-Karb 225 for one of these ions only. The exchange capacity was determined for Mg, since a bulk supply of air dry resin in the Mg form was available. The method used in this determination was to elute a sample of the Mg form resin, approximately 0.7 gm, with a 50% excess of buffered EDTA solution. The excess EDTA in the eluate was then determined by titration with a standard Mg solution, as described in the case of the Ba determinations (see page 45). The capacity of the resin was found by this means to be 4.75 m.eq./g dry H form resin.

2.5. SELECTIVITY DETERMINATIONS

When selectivity measurements are made the usual practice is to maintain a constant "loading", i.e. a constant proportion of the two exchanging ions in the resin phase (see page 17), since selectivity varies with loading. In the present work this procedure was not followed for two reasons:-

(i) The change in selectivity coefficient with loading is small when compared with the changes in selectivity coefficient caused by other effects investigated.

(ii) From the practical aspect it is important to know how effectively the resins are able preferentially to select ions from a solution of constant composition.

Two basic methods were used to determine selectivities, batch methods and column methods. Though selectivity is usually determined by a batch method, column methods were used in the present work for the following reasons:

(i) In cases where the preferential uptake of ions from a solution phase of constant composition must be measured, a column method is the only feasible procedure.

(ii) In the experiments carried out to determine the change of selectivity with α, the desired value of α was reached by eluting the resin with a buffer solution. It was then more convenient to complete the experiment without removing the resin sample from the column.

On checking it was found that the values of selectivities determined by column methods did not differ significantly from those obtained by batch methods.

2.5.1. Column Methods

For reasons of practical convenience column methods of equilibration were used in all the work concerned with aqueous solutions and measurement of changes in selectivity with loading and with change in α. The glass columns used for these experiments had a diameter of 1.0 cm and the resin bed which was supported by a sintered glass disc, could have a height of up to 10 cm. The flow rate through the column was controlled by plastic taps fitted to the bottom of the column, and a constant head of liquid was maintained above the resin by a "chicken feeder" device. The column equilibration was executed as follows. An appropriate amount of the resin was weighed out and converted to the Na form if necessary. The resin was then washed by the standard procedure. Known volumes of solutions of the perchlorates of the ions under investigation were well mixed, so that the resulting solution contained at least a 200% excess of exchangeable cations, and this solution was passed through the column, rapidly at first and then progressively more slowly, the total contact time being 48 hours.

Since the resin was eluted with an eluant of constant composition, the concentration of the two cations in the solution phase at equilibrium was therefore known. To determine the selectivity coefficient it was therefore only necessary to determine the ratio of the concentrations of these ions in the resin phase. This was done by washing the resin with de-ionized water, by the standard procedure, to remove adhering solution phase and eluting the two ions from the resin, with 100% excess of N/4 hydrochloric acid in the case of Amberlite IRC 50 and 1 N sodium chloride in the case of Zeo-Karb 225. The two ions in the eluate were then separated by ion-exchange chromatography and determined by titration with EDTA, as described previously, and the selectivity coefficient was calculated.

Loading was varied by varying the ratio of the volumes of the perchlorate solutions of the two ions (and hence the concentrations of these ions).

Where the variation of selectivity coefficient with α (mole fraction of resin sites not in hydrogen form) was determined the composition of the solution phase was kept constant, equal concentrations of the two ions under investigation being present. The resin was converted to a desired value of α by the following procedure: after conversion to the Na form, the resin was washed by the standard procedure, and then eluted with a sodium acetate/acetic acid buffer. Depending on the ratio of H^+ to Na^+ and on the concentrations of these ions in the buffer solution, a definite fraction of the resin sites revert to the hydrogen form and the resin therefore assumes a definite value of α. (It is not possible to relate the value of α to the pH of the buffer used, as the concentration of Na^+ is also a factor). The resin can then be equilibrated with two alkaline earth cations as before. It was found that the α value changed only very slightly during equilibration in the selectivity experiments, since effectively only sites in the Na form exchange with the alkaline earth metal ions; with the carboxylic acid resin used in these experiments exchange involving sites in the hydrogen form takes place at an extremely slow rate. The actual value of α is calculated from the total exchange capacity of the resin used and that fraction of the resin occupied by the alkaline earth cation, as calculated from the EDTA titrations of the eluate.

The uptake of Mg, Ca and Ba from a solution containing an equal concentration of each cation was also determined, the three ions being eluted in separate fractions and determined as described in section 2.3.2.

2.5.2. Batch Methods.

Batch methods of equilibration were used in the selectivity determinations involving pyridine/water solvents, which involved both Amberlite IRC 50 and Zeo-Karb 225, the same method being used in both cases.

An appropriate amount of Mg form resin was weighed out (approximate weights of air-dry resins: Amberlite IRC 50 1 g, Zeo-Karb 225 0.7 g) into a 100 ml conical flask. 10.0 ml of an aqueous perchlorate solution of the alkaline earth metal under investigation was then pipetted into the flask, followed by a definite volume of pure pyridine, in order to achieve the desired solution phase composition. The flask was sealed and shaken for 48 hours. The contents of the flask were then transferred to a small exchange column fitted into a clean Buchner flask, and the solution phase was separated from the resin phase. The resin remaining in the column was washed once rapidly with a small amount of water and sucked dry. The solution in the Buchner flask (washings plus original solution phase) was then analysed for Mg and the other alkaline earth metal present after separation of these two ions by ion exchange chromatography. The resin in the exchange column was then eluted and the concentration of the alkaline earth metals determined, after separation. The eluant used was 1 N sodium chloride for Zeo-Karb 225 and N/4 hydrochloric acid for Amberlite IRC 50.

2.6. DETERMINATION OF WEIGHT - SWELLING AND SOLVENT DISTRIBUTION BETWEEN RESIN PHASE AND SOLVENT PHASE.

One experiment was designed to measure both the weight-swelling and the distribution of pyridine and water between the resin and solution phases. This experiment was carried out with both Zeo-Karb 225 and Amberlite IRC 50, at a number of different solvent compositions on five different forms of the resins, viz. the H, Mg, Ca, Sr and Ba forms; the resins were converted to these forms as described in section 2.4.

2.6.1. Weight-swelling Experiments

The weight-swelling was determined by the centrifugation method of Conway, Green and Reichenberg [76]. The resin was allowed to swell in the solvent for seven days. A few drops of wetting agent

(0.2% sodium oleyl sulphate) were then added to the solvent and the resin was immediately transferred to a filter tube fitted with a sintered glass filter, the open end being covered with a rubber cap to prevent evaporation. The filter tube was fitted into a centrifuge tube and the excess solvent was removed by centrifuging at 300 g for 15 minutes. The resin was then transferred to a tared weighing bottle with a ground glass stopper and weighed, to obtain its swollen weight, after which it was dried, first in an oven at 105°C, and then in a vacuum oven at 105°C and 2 mm Hg, and weighed again, to obtain the weight of dry resin. The weight-swelling, in g solvent sorbed per g dry H form resin was then calculated.

The accuracy of any weight-swelling determination is difficult to assess, since the measured value of the weight-swelling varies considerably with the method of determination. The weight of solvent held on the resin when the centrifugation method is used will depend on the speed of centrifugation among other variables. The values obtained for the weight-swelling in g/g dry H form resin of the H form of Amberlite IRC 50 by various methods are given below:-

Polarimetric [77]	0.86
Centrifugation [76]	1.01
Centrifugation [78]	1.42
Centrifugation (This work)	0.97

The value of weight-swelling determinations would therefore appear to lie in obtaining precise rather than accurate, results which can be used for purposes of comparison. The precision of the weight-swelling determinations was tested by measuring the weight-swelling of several samples of Amberlite IRC 50 under the same conditions, precautions being taken to ensure that the experimental procedures were the same in every case. The following results were obtained:-

TABLE 6. WEIGHT - SWELLING OF AMBERLITE IRC 50

Form of Resin	Expt. 1	Expt. 2	Expt. 3	Mean.
	g/g dry H form resin	g/g dry H form resin	g/g dry H form resin	g/g dry H form resin
H	0.97	0.97	0.97	0.97
Mg	1.94	1.97	1.97	1.96
Ca	1.69	1.67	1.67	1.68
Sr	1.47	1.47	1.49	1.48
Ba	1.17	1.16	1.18	1.17

From these results it is apparent that the precision of the method used is high. This must be attributed to the fact that the experimental conditions were exactly the same in each case. The weight-swelling data obtained in the combined weight-swelling and sorption experiments can therefore be used with confidence for qualitative comparisons between various forms of the resins, even though the accuracy of each result as an absolute measure of weight-swelling is doubtful.

2.6.2. Combined Weight-Swelling and Solvent Sorption Determinations

Five 1 g samples of air dry resin (known moisture content) were weighed into small, tall form weighing bottles with ground glass stoppers, and to each was added 4 ml of solvent, the composition varying from one to another. For example, to the five samples of Amberlite IRC 50 in the Mg form were added:-

Sample	ml H_2O	ml Pyridine	Total ml
IRC Mg 1	4	0	4
IRC Mg 2	3	1	4
IRC Mg 3	2	2	4
IRC Mg 4	1	3	4
IRC Mg 5	0	4	4

The volumes of solvent added must be small in order to increase the accuracy with which the composition of the solvent in both resin phase and solution phase can be determined (see appendix 2).

The weighing bottles were tightly stoppered and allowed to stand for seven days, with periodic shaking. The composition of the solvent phase was then determined by sampling the supernatant liquid with a dropper tube and determining the refractive index of this liquid on an Abbe refractometer. The solvent composition was read from a calibration curve previously prepared (see fig. 1). The error in determining the solvent composition by this method is much less than the errors involved in the weight-swelling measurements. The weight-swelling was then determined by the method described in 6.1. above. From the weight of dry resin, the total weight of solvent sorbed, the original moisture content of the resin and the composition of the solution phase, the composition of the solvent in the resin phase was calculated (see appendix 1). p 135

The accuracy and precision of the weight-swelling as determined in the combined experiments are subject to the comments made in 2.6.1. above. The value obtained for the composition of the solvent in the solution phase is very accurate, since it is determined directly from the calibration curve of refractive index versus composition. From this curve it is estimated that the composition of the solvent in the solution phase can be obtained within ± 0.2% of the correct value, with a high degree of confidence. The composition of the solvent in the resin phase can not be estimated as accurately, since it depends on all three measurements made. A determination of the maximum probable error (see appendix 2) of one of these experiments reveals that a maximum probable error of 7% can be expected in determining the composition of the solvent in the resin phase. In the example given in appendix 2 the value obtained for resin phase solvent composition was 15% pyridine. The true value for the solvent composition is therefore within 7% of 15%, i.e. 15% ± 1% pyridine. For the purposes of qualitative comparison

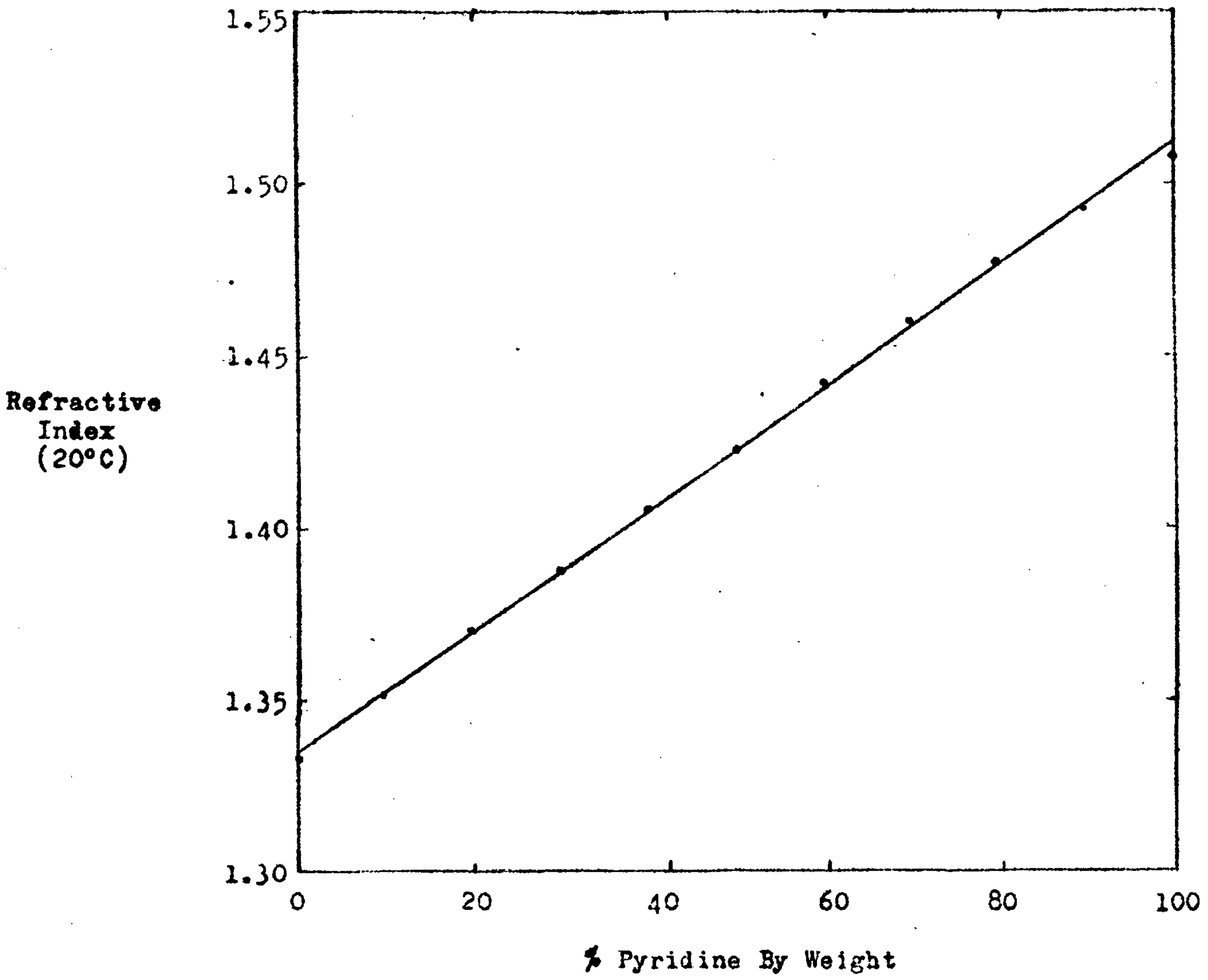

FIG. 1. CALIBRATION CURVE. VARIATION OF REFRACTIVE INDEX WITH SOLVENT COMPOSITION.

this order of accuracy is acceptable. The precision of the combined determinations was not determined.

2.7. ATTAINMENT OF EQUILIBRIUM

One of the obvious precautions which must be observed in any ion exchange experiment is to ensure that equilibrium has in fact been attained. Particular care was given to this aspect of the experimental work since carboxylic acid resins, when in the H form, can take inordinately long to reach equilibrium. This has been attributed [76] to the low degree of dissociation in these resins, which gives rise to low concentration gradients in the resin phase and hence slow rates of diffusion in the resin bead. Fortunately all the selectivity experiments were performed on the salt forms of Amberlite IRC 50 and Zeo-Karb 225, both of which exchange at a comparatively rapid rate [79, 80]. Equilibrium is usually attained in less than 2 hours. In all experiments in the present work 48 hours was allowed for attainment of equilibrium. This was considered to be more than adequate.

Further justification for the belief that equilibrium was attained in the various types of experiment is given below.

Capacity Experiments

The capacity of the various forms of Amberlite IRC 50 was found to be virtually the same, despite the fact that the capacity of the H form and that of the various salt forms was determined by somewhat different methods. This leads to the conclusion that equilibrium had been attained in all cases.

Selectivity Determinations

Certain of the practical selectivity coefficients were determined by both batch methods and column methods, both methods yielding identical results, within the limits of experimental error. Secondly, equilibrium was approached from two directions in certain batch experiments, identical results being obtained whatever the initial form of the resin.

Kinetic Experiments

Some approximate kinetic measurements were made (see chapter 5). These measurements were made for ammonium/magnesium exchange on both Amberlite IRC 50 and Zeo-Karb 225, both resins being originally in the magnesium form. In both cases the amount of exchange after 1 minute was 95% of that obtained after 48 hours.

For all the reasons given above the period of 48 hours allowed in this work for equilibrium to be reached is considered adequate.

3. WEIGHT SWELLING AND SORPTION CHARACTERISTICS OF RESINS IN WATER/PYRIDINE SOLUTIONS

3.1. SWELLING

3.1.1. Experimental Results

The results of the weight swelling determinations carried out on both Amberlite IRC 50 and Zeo-Karb 225 in solvents of different water/pyridine composition are given in Appendix III, Tables 7 - 16, and represented graphically in Figs. 2 (74. and 3. p77

The weight swelling has been calculated as grams of solvent per gram of dry H form resin, so that the swelling of the various ionic forms could be compared. The weight swelling was calculated in this way rather than as millimoles solvent per milli equivalent of resin, since the primary effect of swelling on selectivity is its influence on the pressure - volume term. The densities of the two solvents are virtually the same, so that volume swelling and consequent expansion or contraction effects are better deduced from weight swelling calculated in grams than in millimoles.

3.1.2. Effect Of Composition Of Solvent On Swelling Of Resin In Various Single Ionic Forms.

The experimental method, in which the resin in a single ionic form was equilibrated with a solvent containing no ions, produces the following consequences which should be clearly borne in mind in interpreting the results of the swelling determinations:

1. Only one type of cation is present.
2. Virtually all the cations are in the resin phase.
3. The only anions present are resin anions, which are fixed.

These facts simplify the task of interpreting the data, since the ionic composition of the external phase remains constant and hence this phase does not affect the resin swelling to any marked degree. Swelling is influenced primarily by changes in the composition of the solvent sorbed by the resin; for this reason the weight swelling is plotted against the composition of the solvent in the resin phase, not that in the solution phase. The conclusions drawn from these determinations can therefore be applied to resin phase interactions and separated from the effect of ionic interactions and ion-solvent interactions in the solution phase. This is useful in interpreting selectivity data where it is sometimes uncertain whether selectivity effects must be attributed to resin phase effects or competitive solvation between resin and solution phase.

As explained previously (see page 6) the swelling of an ion-exchange resin is caused by three factors:-

1. The solvation tendency of the fixed ionic groups and counter ions.
2. The osmotic pressure difference between the resin phase and the solution phase.
3. The electrostatic repulsion between neighbouring fixed

ionic groups and between charged resin chains.

Swelling equilibrium is achieved when these forces are balanced by the elastic tendency of the expanded resin matrix to contract.

Introducing a non-aqueous component, in this case pyridine, into the solvent affects the swelling of the resin considerably. The effect of increasing the concentration of pyridine in the solvent on the three factors listed above should be examined, bearing in mind that the dipole moments of water (1.84 Debye) [81] and pyridine (2.2 Debye) [7] are similar, but that the dielectric constants are very different (water 79, pyridine 12.3) [8].

The first factor, solvation, depends on the degree of ion-solvent interaction which increases with increased dipole moment and decreased dielectric constant. It is therefore reasonable to expect increased solvation of ions in the resin phase, and a consequent increase in swelling, as the percentage of pyridine in the resin phase increases.

The effect of the change of solvent composition on the second and third factors is governed largely by the change in dielectric constant, since these effects are most influenced by ion-ion interactions, which increase markedly as the dielectric constant decreases. It is assumed that although dielectric saturation will reduce the bulk dielectric constant in the resin, the effect of substituting pyridine molecules for water molecules will still be to reduce the effective dielectric constant in the resin. The direct effect of this lowering of dielectric constant will be an increase in ion-pair formation [82, 83] in the resin phase.

The second factor, osmotic pressure difference, will be affected insofar as increased ion-pair formation will decrease the number of osmotically active ions in the resin phase and hence swelling will tend to be reduced [84].

The third factor, electrostatic repulsion, will be reduced by an increase in ion-pair formation between resin anions and counter ions. The charges on the resin chains, fixed ionic groups and counter ions will be reduced, resulting in a decrease in swelling [85, 86]. The effect of increased ion-pair formation is, however, counteracted by the increase in the strength of electrostatic repulsion when the dielectric constant is lowered [87], provided the charges are not completely neutralized by association with counter ions.

This effect is evident in the swelling of strong-acid resins (particularly in the H form) in aqueous alcohols [18, 19], where the dipole moments of the solvents are similar (water 1.84 Debye, methanol 1.68 Debye, ethanol 1.70 Debye), but the dielectric constants are different (water 79, methanol 32 and ethanol 26). The swelling increases initially as the bulk dielectric constant decreases, but passes through a maximum and thereafter falls again reaching a value in the pure alcohol which is lower than that in pure water [88, 89]. This phenomenon may be explained as follows. Initially the increase in electrostatic repulsion due to decrease in dielectric constant exceeds, the decrease due to reduction of the fixed charges resulting from ion-pair formation. This net increase in electrostatic repulsion causes the initial increase in swelling with decreasing dielectric constant. As the dielectric constant is lowered still further the ion-pairing becomes so extensive that this becomes the dominant factor. A net decrease in electrostatic repulsion results, causing the swelling to decrease as the dielectric constant falls, the reverse of the initial trend.

A similar effect could be anticipated with pyridine and therefore the third factor, electrostatic repulsion, could well tend to cause swelling to increase as pyridine is added initially, but to decrease subsequently as further amounts of pyridine are added.

The swelling results must therefore be interpreted with some care, in view of the fact that opposing effects are present.

In order to summarize the arguments presented and to facilitate their application to the experimental results, they are presented below in tabular form:-

Factor	Direct effect of increasing % Pyridine	Effect on Swelling of increasing % Pyridine
1. Solvation	Solvation increased	Swelling increased
2. Osmotic pressure difference	Ion-pairing increases hence number of osmotically active groups decreases.	Swelling decreased
3. Electrostatic repulsion	Repulsive force between charges of a given magnitude increases but magnitude of charges is decreased by ion pairing.	Swelling increases initially and then decreases to less than original value

A further complication occurs in connection with the weight-swelling of the H forms of the two resins. Since pyridine is basic (pK_b = 8.85 at 25°C) [6] and will therefore react with the H^+ ion to produce the pyridinium ion, a further cationic exchange species is produced. The reaction

$$R^-H^+ + \text{Pyridine} \rightarrow R^- \text{Pyridinium}^+$$

should go virtually to completion with the strong sulphonic acid resin Zeo-Karb 225. The carboxylate grouping, however, has approximately the same basic strength as the pyridine molecule (pK_b of acetate ion = 9.2 at 25°C) [6], pyridine being probably a slightly stronger base than the ionized form of Amberlite IRC 50. In this case a certain percentage of the exchange sites will remain in the hydrogen form. This percentage will decrease as the concentration of pyridine in the resin phase is increased.

0.7 to 0.8 g of the resins were used in each swelling experiment. The lowest pyridine content occurred when 1 ml of pyridine and 3 ml water were added to these resin samples. The amounts of pyridine required to neutralize the H present in the samples of Zeo-Karb 225 and Amberlite IRC 50 would be approximately 0.3 ml and 0.6 ml respectively. Since both H form resins show a strong preference for pyridine at low pyridine concentrations (see Figs. 4 and 5), it may be assumed that particularly in the case of Zeo-Karb 225, it was in fact the weight-swelling of the pyridinium form of the resin, not the H form, which was determined in the present work.

3.1.3. Swelling Of Amberlite IRC 50

The discussion will first devolve on the variation in swelling of each ionic form as the % pyridine in the resin phase increases, and secondly the swelling of the various forms will be compared. The results under discussion are given in tables 7 - 12 and in fig 2.

The weight-swelling of the H form of Amberlite IRC 50 shows a significant increase with % pyridine, which flattens out at very high pyridine concentrations. This may be explained as follows. Initially the exchange sites are in the H form and are associated to an extent approaching covalent bonding. The addition of pyridine, a slightly stronger proton acceptor than the resin anion, causes the carboxylic acid group to ionize. The H^+ ions released form pyridinium ions with the pyridine molecules, and these ions become the counter-ions in place of H^+ with a resulting decrease in association with the resin anions. In this particular case there is therefore an initial decrease in ion-pairing as the percentage of pyridine in the resin is increased. A significant increase in swelling should result, since all three factors discussed previously (see page 71) now tend to act in the same direction, i.e. to increase the swelling. This tendency should be arrested once virtually all the sites have been converted to the pyridinium form. The swelling in fact reaches a maximum value when there is approximately 80% pyridine in the resin phase, and then decreases slightly. This explanation is also consistent with the swelling behaviour observed for the H form of Zeo-Karb 225 (discussed later).

The swelling behaviour of the Mg, Ca, Sr and Ba forms of Amberlite

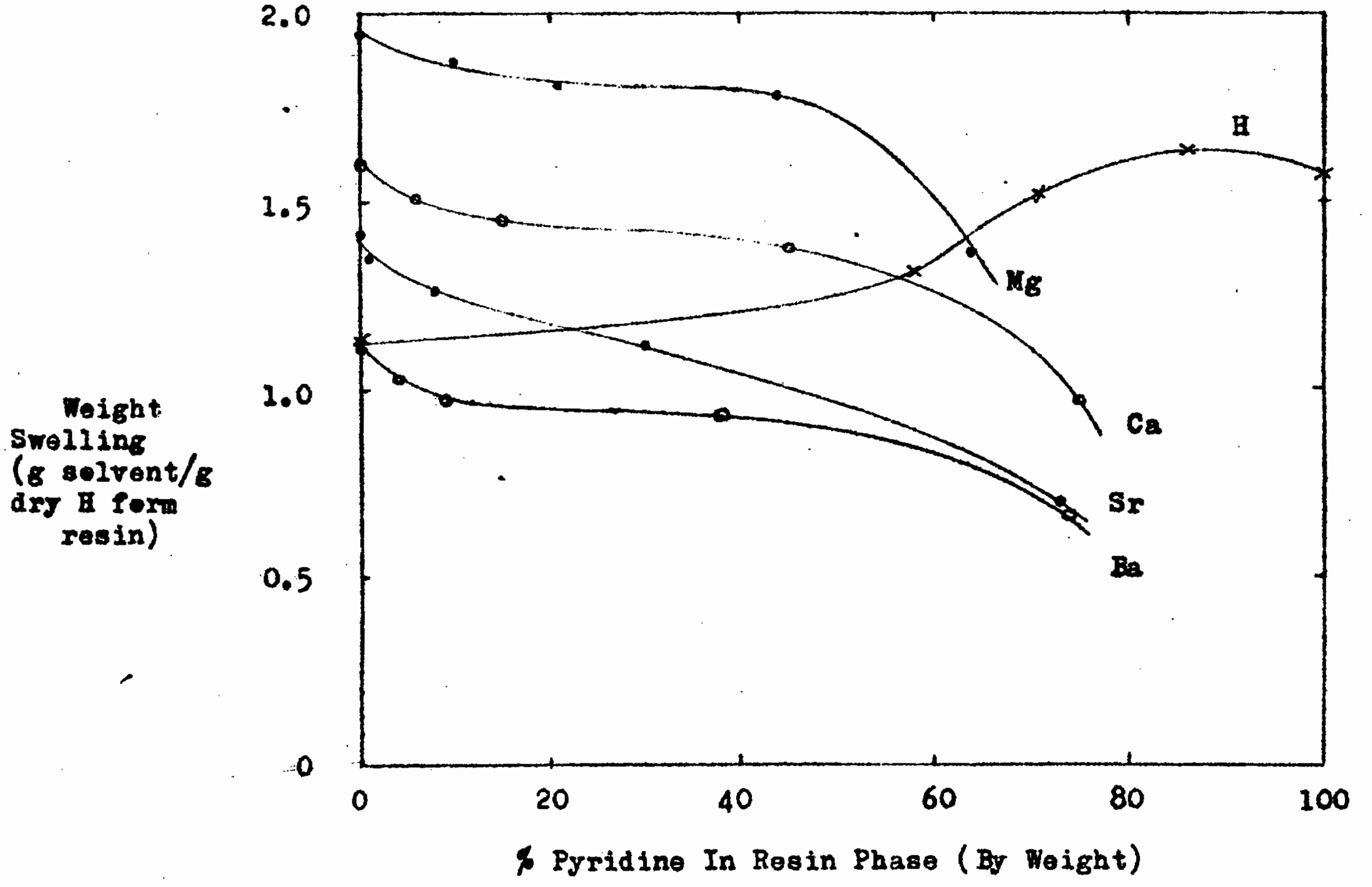

FIG. 2. WEIGHT SWELLING OF AMBERLITE IRC 50 IN VARIOUS SINGLE IONIC FORMS.

IRC 50 is very similar in all cases. In each case the swelling decreases continuously as the % pyridine in the resin phase increases, the rate of decrease being fairly high at low and high % pyridine, but small for intermediate values.

These results indicate that factors (2) and (3) outweigh factor (1) in this case. This is logical, since a degree of interaction exists between the cations and the carboxylate anions, even in pure water; since the carboxylate anion is more polarizable than the sulphonate anion, ion-ion interactions are likely to be stronger in this case than with sulphonate resins. The decrease in dielectric constant thus causes a more rapid initial increase in ion-pairing than in the case of sulphonate resins with the consequence that effect (2), which is solely influenced by ion-pairing, and effect (3), in which the influence of ion-pairing is now greater than that of increased repulsive force per unit charge, predominate over effect (1) over the full range of solvent composition. The maximum observed with sulphonate resins in aqueous alcohols is not found in this case.

The swelling sequence at low % pyridine is:-

$$Mg > Ca > Sr > Ba = H$$

The swelling sequence at high % pyridine is:-

$$\text{Pyridinium} > Mg > Ca > Sr > Ba.$$

The order of decreasing swelling shown above is also the order of decreasing solvated radius. This is to be expected since a small solvated radius leads to a small solvated volume (factor 1); as well as an increase in ion-pair formation between cation and resin-anion. which will also decrease swelling (factors 2 and 3).

3.1.4. Swelling Of Zeo-Karb 225

As in 3.1.3. the variation in swelling of each ionic form will be discussed, followed by a comparison of the swelling of the various forms of the resin. The results under discussion are given in tables 12 - 16, and in fig. 3.

In considering the weight swelling of the H form of Zeo-Karb 225 it should be borne in mind that in all the pyridine solutions in which the swelling was measured the resin was not, in fact, in the H form but completely in the pyridinium form. In this respect this resin differs from Amberlite IRC 50, where the resin was partially in the H form and partially in the pyridinium form. It is therefore not surprising that the swelling behaviour of the H form of the two resins differs. From fig. 3 it can be seen that the weight swelling of the H (pyridinium) form of Zeo-Karb 225 does not vary much with solvent composition; a very slight increase with increasing % pyridine is observed.

It would appear that in this case either the three factors giving rise to weight swelling vary very little with solvent composition or opposing effects balance one another over the full range. The former explanation seems more likely. It is reasonable to expect little ion-pairing between the large solvated pyridinium ion and the sulphonate

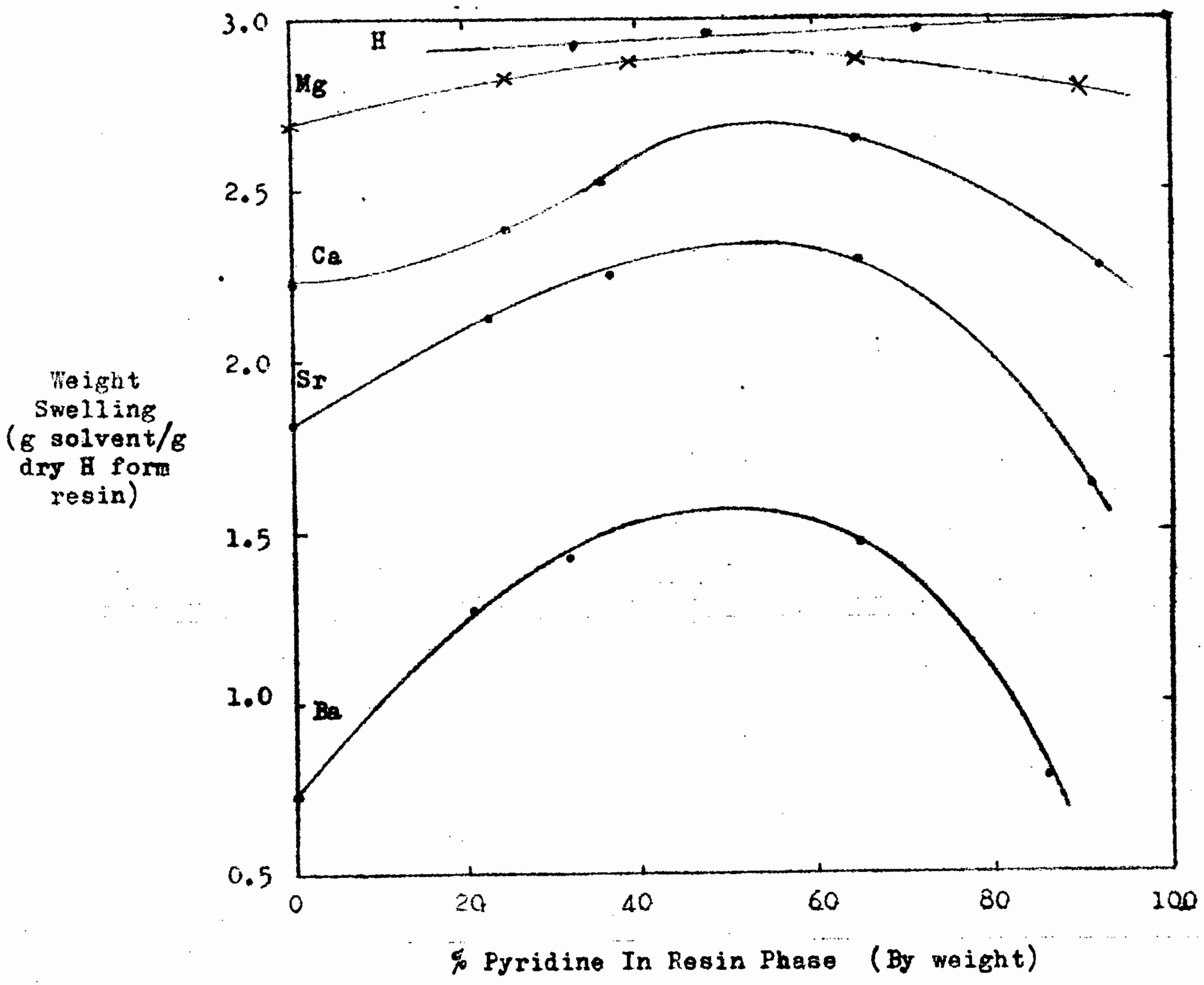

FIG. 3. WEIGHT SWELLING OF ZEO - KARB 225 IN VARIOUS SINGLE IONIC FORMS.

anion. If this does occur at high pyridine concentration the degree of ion-pairing will be small and the resultant decrease in swelling will be offset by the other factors, which will tend to increase swelling.

The swelling of the Mg, Ca, Sr and Ba forms shows a maximum at intermediate solvent compositions. This behaviour is typical of strong acid resins in a solvent system where the two components have similar dipole moments but different dielectric constants. The reasons for the maximum value have already been fully discussed (see page 70). The effect is not obtained with weak acid resins because a degree of association exists in these resins even in pure water.

The height of the maximum above the values of the swelling in pure water and pure pyridine for the various ionic forms of the sulphonic acid resin decreases in the order Ba > Sr > Ca > Mg. This is directly attributable to the factors which give rise to the maximum. The initial increase in the weight swelling is caused by the increased electrostatic repulsion arising from the decrease in dielectric constant, the repulsive force being inversely proportional to the square of the interionic distance. The resin in the Ba form is the least swollen, so that the interionic distance is the least in this case. The increase in repulsive force, and hence in swelling, as the dielectric constant is decreased is obviously greatest in this case. The decrease in swelling when the % pyridine in the resin phase exceeds 50% is attributed to ion-pairing. This effect will also be proportionately greater for the resin in which the interionic distance is smallest, i.e. the Ba form, and hence the decrease in swelling will be most marked for this ionic form. It is to be expected, therefore, that the Ba form will show the sharpest maximum and that the height of the maximum will decrease as the interionic distance in the resin increases.

The swelling sequence for the entire range of solvent composition is:-

Pyridinium > Mg > Ca > Sr > Ba

As with Amberlite IRC 50 the swelling decreases with decreasing size of the counter ion. No crossover of the swelling of the "H" form at high % pyridine occurs in this case as the resin is always completely in the pyridine form.

3.2. DISTRIBUTION OF PYRIDINE BETWEEN RESIN PHASE AND EXTERNAL PHASE

3.2.1. Experimental Results

The results of the sorption determinations carried out on both Amberlite IRC 50 and Zeo-Karb 225 in solvents of different water/pyridine composition are given in Appendix III, Tables 7 - 16, and represented graphically in Figs. 4 p80 and 5. 81

Since the solvent distribution is best represented as a ratio, it is calculated and plotted as:-

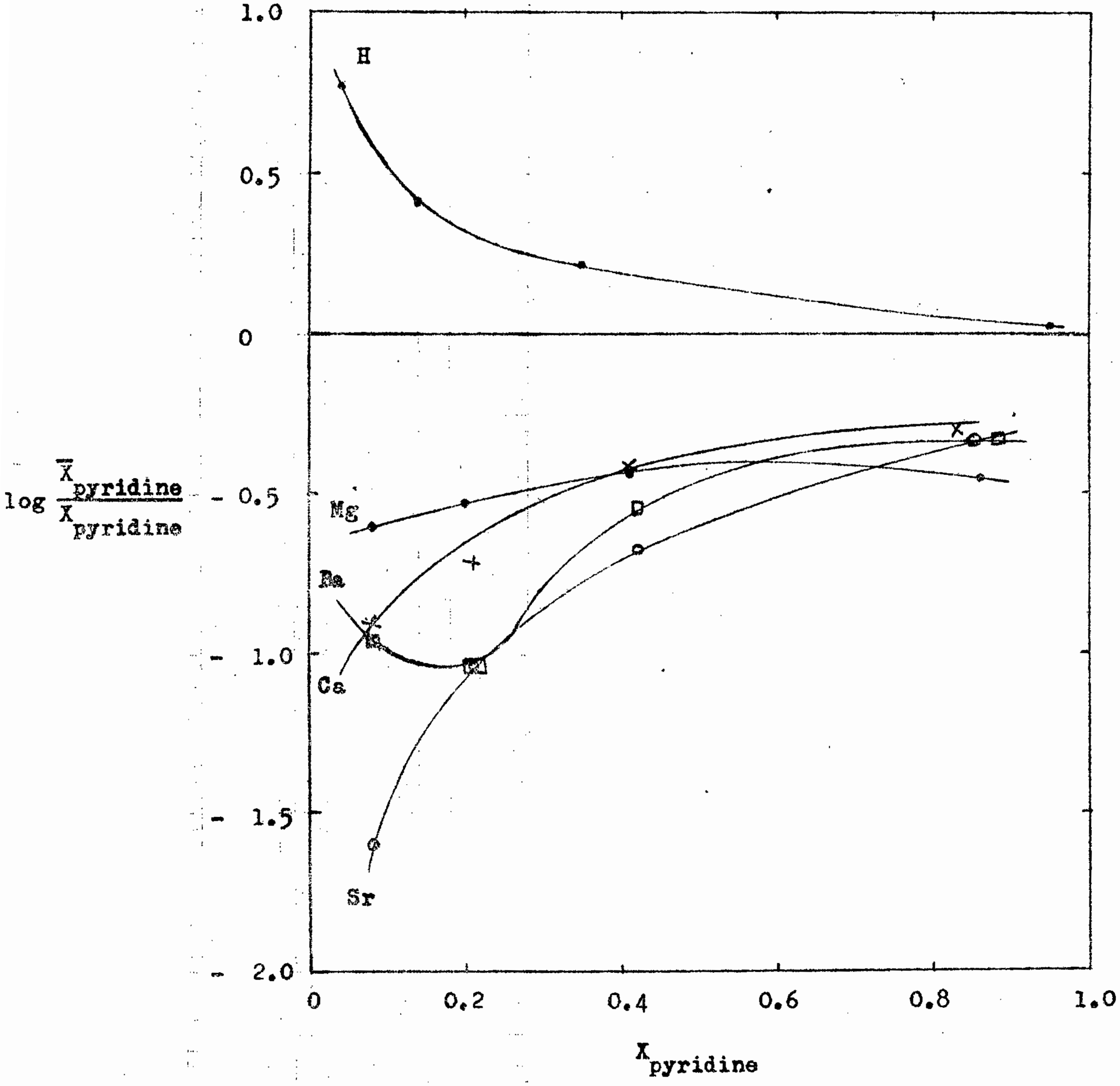

FIG. 4. DISTRIBUTION OF PYRIDINE BETWEEN RESIN PHASE AND SOLUTIO

PHASE AT VARIOUS SOLVENT COMPOSITIONS. AMBERLITE IRC 50

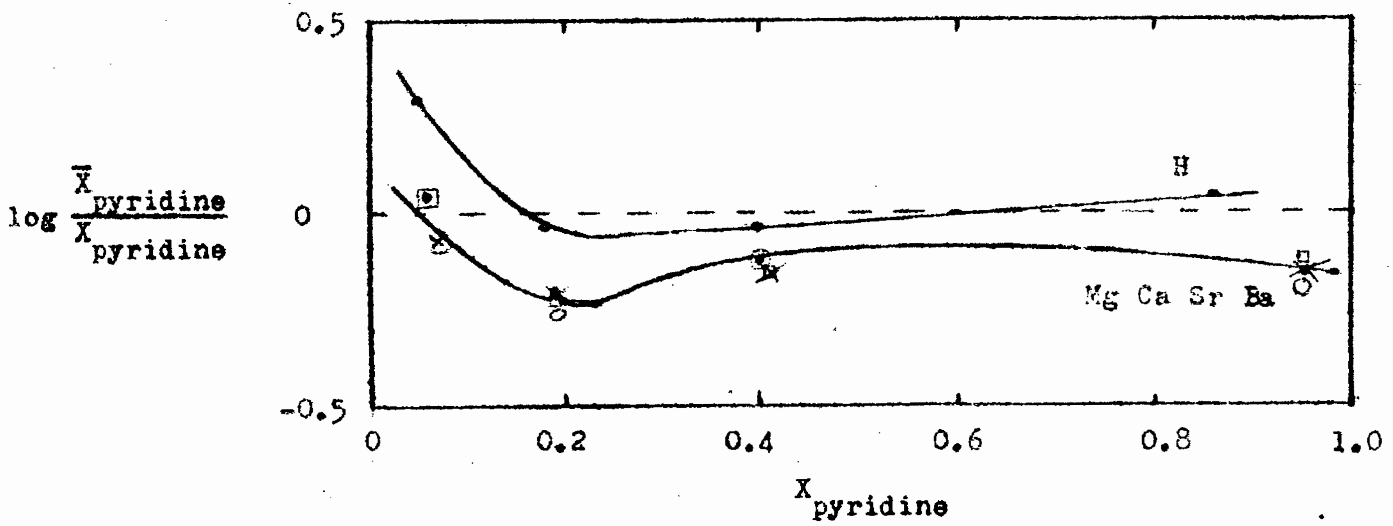

FIG. 5. DISTRIBUTION OF PYRIDINE BETWEEN RESIN PHASE AND SOLUTION PHASE AT VARIOUS SOLVENT COMPOSITIONS. ZEO - KARB 225.

$$\log \frac{\bar{X}_{\text{pyridine}}}{X_{\text{pyridine}}}$$

Where $\bar{X}_{\text{pyridine}}$ is the mole fraction of pyridine in the resin phase.

and X_{pyridine} is the mole fraction of pyridine in the solution phase.

This value is plotted against X_{pyridine} in Figs. 4 and 5.

3.2.2. Theoretical Considerations

From figs. 4 and 5 it can be seen that water is preferentially sorbed when the resins are in any salt form. This conforms with existing theories regarding solvent sorption from mixtures of water and organic liquids. Two explanations have been advanced for the preferential sorption of water: that water is sorbed in preference to the organic solvent because it is the more polar solvent and hence will preferentially solvate the ions in the resin phase [90, 91, 92], or that water is preferred since it has the smaller partial molar volume, so that pressure-volume effects will favour its selective sorption [93]. Since pyridine has a somewhat greater dipole moment than water (see page 69) the preferential sorption of water in this case must be attributed to its smaller partial molar volume rather than to greater solvating power. On the basis of this theory the prediction can be made that salt-resinate systems will in general selectively sorb water rather than pyridine.

We could further predict that Amberlite IRC 50, which has a slightly higher degree of cross-linking than the Zeo-Karb 225 used in the present work, will exert a greater swelling pressure in the resin phase and hence will have the stronger tendency to sorb the solvent with the smaller partial molar volume.

It is, however, somewhat debatable whether the effect of greater cross-linking satisfactorily accounts for both the very much greater preference for water shown by Amberlite IRC 50 compared with that shown by Zeo-Karb 225 in the present work, and the observed change in solvent distribution as the % pyridine increases. In these instances it is probably necessary to take into account solvent-solvent interactions. That these interactions do occur is evidenced by the fact that when pyridine is added to water heat is evolved, indicating that some type of bond formation has taken place.

The external phase initially contains only water (no cations were present), with the molecules associated through hydrogen bonding in the usual way. The resin phase, however, contains "free" water and "bound" water, the latter being those water molecules which are firmly attached to a resin anion or counterion by solvation forces. The proportion of bound water has been calculated to be of the order of 40% of the total water content of the resin in the case of Amberlite IRC 50 and approximately 17% in the case of Zeo-Karb 225 (see Appendix IV). p169 The percentages given above refer to water firmly bound in primary hydration shells. If the more loosely bound molecules of water in secondary hydration shells are included it is apparent that a considerable proportion of the water in the resin phase is firmly, or fairly firmly, bonded. Therefore when the pyridine bonds with the water in the external phase, which contains more "free" water, the total reduction in free energy is greater than that accompanying the bonding of pyridine with water in the resin phase. The distribution of pyridine between the two phases is therefore likely to favour the retention of the pyridine in the external phase. This effect should be more noticeable in the case of Amberlite IRC 50, where the resin contains less free water than does the Zeo-Karb 225. This theory would account for the fact that at low concentrations of pyridine in the external phase the Amberlite IRC 50 shows a very much greater preference for water than the Zeo-Karb 225.

3.2.3. Solvent Distribution Between Resin Phase And External Phase In Amberlite IRC 50

It is evident from Fig. 4 that with increasing % pyridine in the external phase the preference of the alkaline earth forms of Amberlite IRC 50 for water decreases. Since these ionic forms of the resin deswell as the % pyridine in the solvent increases (see fig. 2) p74, it is reasonable to expect that the consequent decrease in swelling pressure will contribute towards the observed decrease in preference for water, since the fact that water has the smaller partial molar volume becomes relatively less important. The solvent-solvent interaction effect should also lead to a decrease in the preference for water with increasing concentration of pyridine in the external phase for the following reasons. Firstly the deswelling occurs as a result of increased ion-pair formation, which will also have the effect of reducing hydration and hence the amount of bound water in the resin, thus making a greater percentage of free water available in the resin phase. Secondly, as the pyridine is preferentially retained by the external phase the % pyridine in this phase is always greater than that in the resin phase. The percentage of the water molecules bonding with pyridine will therefore be greater in the external phase than that in the resin phase, so that as the pyridine concentration increases the percentage of "free" water, and hence the amount of pyridine retained, will decrease relatively faster in the external phase.

The different salt forms of Amberlite IRC 50 show widely varying affinities for water at low % pyridine, where the order of affinity for water is Sr > Ca > Ba > Mg. At high % pyridine the affinity for water of the various forms does not differ significantly. This behaviour cannot be attributed to pressure-volume effects, which would tend to cause the most swollen form, i.e. the Mg form, with the highest swelling pressure, to show the greatest preference for water (the solvent with the smaller partial molar volume), whereas in fact the opposite is true, with the Mg form showing the least preference for water. The explanation must therefore lie in solvent-solvent interactions. In terms of the theory advanced in this thesis, which accounts for the preferential sorption of water by the resin in terms of the amounts of "free" water available in the resin and external phases, it is possible to explain the observed phenomena by postulating that, since there is no difference in the ionic composition of the external phase in the four cases, the proportion of free water present in the resin phase of the four salt forms at low % pyridine must lie in the order Mg > Ba > Ca > Sr. If this is in fact so the Mg and Ba forms, with the highest free water content, will show the greatest preference for pyridine followed in order of decreasing affinity for pyridine by the Ca and Sr forms of the resin. Calculation of the % free water from swelling data and hydration numbers (see Appendix lV)(149) provides excellent confirmation for these predictions. The % free water according to these calculations is in the order Ba > Mg > Ca > Sr. This may very well be the order of affinity for pyridine at % pyridine approaching zero. The fact that the magnitudes of and the differences in the affinity for pyridine of the various salt forms of the resin, can only be explained in terms of "free" water and solvent-solvent interactions, leads to the conclusion that these are the most important factors affecting the relative sorption of the two solvents by the resin and external phases.

The hydrogen form of Amberlite IRC 50, as expected, behaves completely differently to the salt forms; pyridine is in fact sorbed in preference to water over the full range of solvent composition, the affinity for pyridine being greatest at low % pyridine in the external phase. This behaviour can be explained in the same way as the swelling behaviour of the H form of Amberlite IRC 50 (see page 72), i.e. that pyridine, being basic in character, reacts with the hydrogen ion to form the pyridinium ion, which then becomes the counter ion. Under these circumstances the pyridine would obviously be preferentially sorbed by the resin phase. This tendency would be gradually reduced as the hydrogen ions on the resin react.

3.2.4. SOLVENT DISTRIBUTION BETWEEN ZEO - KARB 225 AND THE EXTERNAL PHASE

From fig. 5 it can be seen that at no stage does Zeo-Karb 225 show the very great preference for water exhibited by Amberlite IRC 50. This behaviour is consistent with the lower cross-linking and higher "free" water content of Zeo-Karb 225 (see page 84). The sorption characteristics are also different insofar as the distribution of solvent does not vary with solvent composition to the same extent as with Amberlite IRC 50 and the preference of the resin phase for pyridine passes through a minimum at approximately 20% (mole %) pyridine in the external phase. It is significant that this minimum value for pyridine sorption corresponds exactly with the maximum value for swelling, 45% (mass %) pyridine in the resin phase. i.e. the minimum affinity for pyridine occurs at maximum swelling. The same trend is shown by the results obtained with Amberlite IRC 50, where for a given ionic form the swelling tends to a maximum and pyridine sorption tends to a minimum at zero % pyridine in the external phase.

In the case of Amberlite IRC 50 the change in affinity for pyridine with increasing X_{pyridine} was attributed to a number of factors, including the deswelling of the resin, an increase in ion-pairing and the more rapid decrease in free water content of the resin phase. Since the sorption of the two solvents is in both cases related to swelling in the same way, the arguments employed, based on the factors listed above, to explain the shape of the pyridine sorption vs. solvent composition curve for Amberlite IRC 50 are thought to be valid for the same curve for Zeo-Karb 225. However swelling pressure effects are probably relatively more important than solvent-solvent interactions in this case since the "free" water content of Zeo-Karb 225 is much higher than that of Amberlite IRC 50. The minimum in affinity for pyridine at maximum swelling can be explained in terms of swelling pressure effects; at maximum swelling pressure the preference for the solvent of smaller partial molar volume (water) will be greatest. Differences in affinity for water among the various salt forms exist, but are very small. In general the order tends to be Ba > Sr > Ca > Mg. This order can be justified by the same argument employed previously in the case of Amberlite IRC 50, by referring to the "free" water contents of the various salt forms of Zeo-Karb 225 listed in Appendix lV. The free water content of the Ba form is lowest, and hence its tendency to sorb water rather than pyridine is highest. The very small differences in affinity for water among the various salt forms are attributable to the fact that the resin has a relatively high free water content in all the four salt forms studied.

The hydrogen form of Zeo-Karb 225 shows a preference for pyridine at low % pyridine which is directly attributable to the proton accepting power of the pyridine molecule. Since this is a strong acid resin the reaction proceeds to completion when less than 20% (mole %) pyridine is present in the external phase, so that the preference for pyridine drops rapidly to zero at this point. The resin is now in the pyridinium form and as with the Amberlite IRC 50 now shows little preference for either solvent.

4. ION EXCHANGE EQUILIBRIA IN WATER/ PYRIDINE SOLUTIONS

4.1. EXPERIMENTAL RESULTS

The results of the determinations of practical selectivity coefficients are given in tabular form in Appendix $\overline{\underline{V}}$ and represented graphically in figs. 6, 7, 8 and 9.

Four different types of data are presented:

(a) Selectivities of Amberlite IRC 50 for Ca, Sr and Ba relative to Mg at different loadings (Tables 17 - 19), Fig. 6.

(b) Selectivities of Amberlite IRC 50 for Ca, Sr and Ba relative to Mg at different values of α (Tables 20 - 22), fig. 7.

(c) Selectivities of both Amberlite IRC 50 and Zeo-Karb 225 for Ca, Sr and Ba relative to Mg at various solvent compositions (Tables 23 - 28), figs. 8 and 9.

(d) Miscellaneous determinations of the selectivity of Zeo-Karb 225 for Mg relative to NH_4 at different solvent compositions and that of the same resin for Sr relative to Mg with different anions at different solvent compositions (Tables 30 and 31).

4.2. EFFECT OF LOADING ON SELECTIVITY

The practical selectivity coefficient k_A^B determined in the equilibrium experiments may be assumed in dilute solution to be approximately equal to the corrected selectivity coefficient K'^B_A which

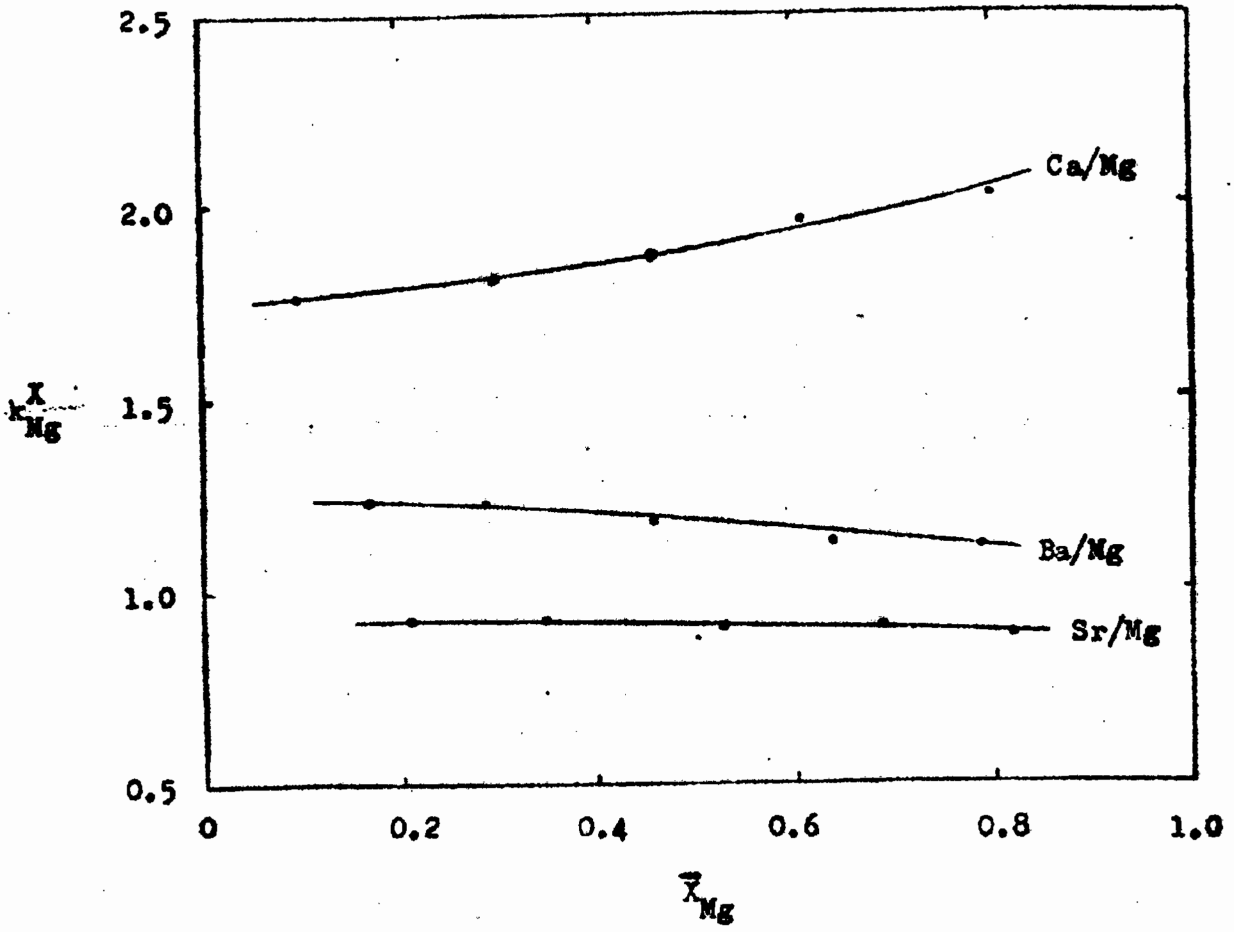

FIG. 6. PRACTICAL SELECTIVITY COEFFICIENT OF AMBERLITE IRC 50 FOR Ca, Sr AND Ba RELATIVE TO Mg AT VARIOUS LOADINGS.

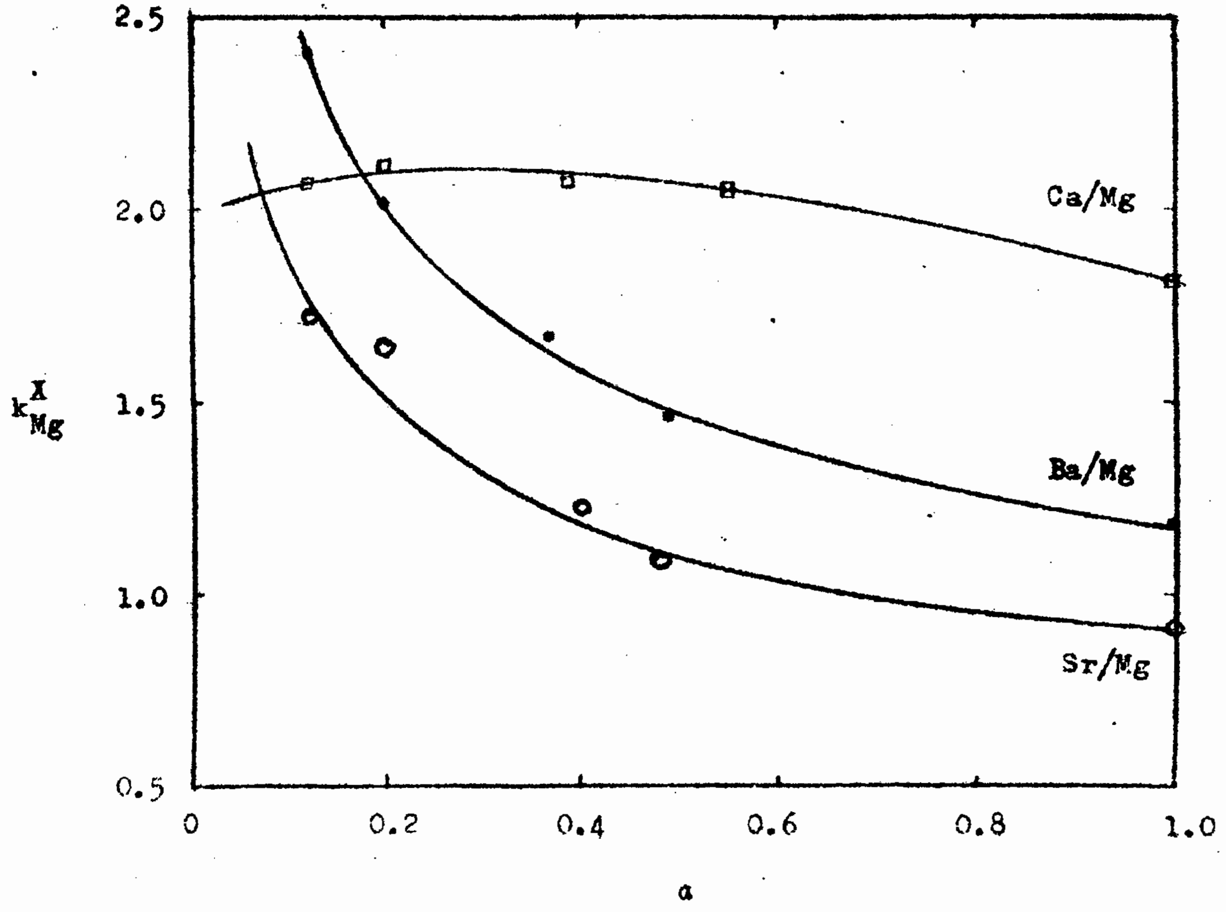

FIG. 7. PRACTICAL SELECTIVITY COEFFICIENT OF AMBERLITE IRC 50 FOR Ca, Sr and Ba RELATIVE TO Mg AT VARIOUS VALUES OF a.

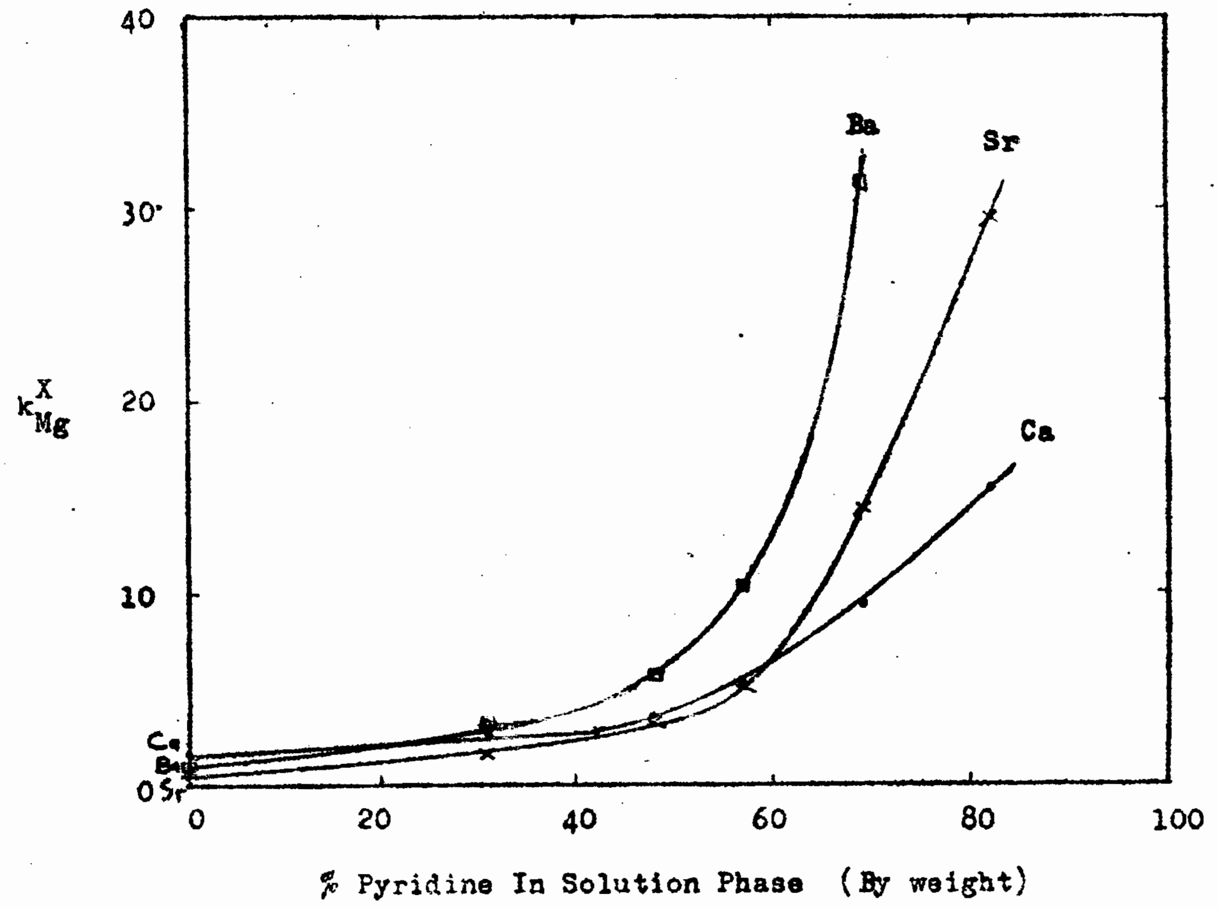

FIG. 8. PRACTICAL SELECTIVITY COEFFICIENT OF AMBERLITE IRC 50 FOR Ca, Sr and Ba RELATIVE TO Mg AT VARIOUS SOLUTION PHASE COMPOSITIONS

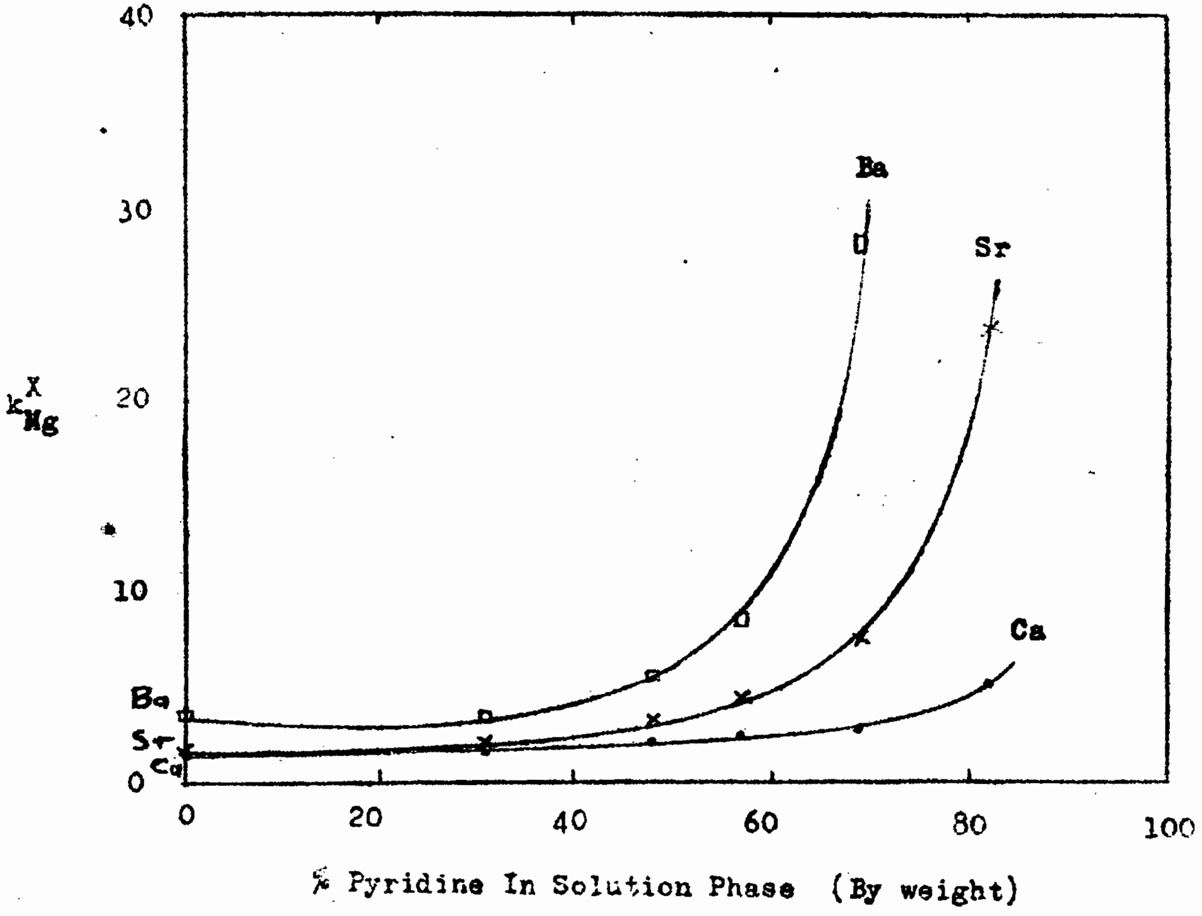

FIG. 9. PRACTICAL SELECTIVITY COEFFICIENT OF ZEO - KARB 225 FOR Ca, Sr AND Ba RELATIVE TO Mg AT VARIOUS SOLUTION PHASE COMPOSITIONS.

is a measure of the preference of the resin phase only. The corrected selectivity coefficient, if determined at a number of different loadings, can be used to estimate the thermodynamic equilibrium constant $K_{aB/A}$ which in turn is used to calculate the standard free energy of exchange of B for A (see page 16).

The measurement of the variation of k_A^B with ionic composition (loading) is important for this purpose, but the magnitude and causes of this variation are of less fundamental importance than the fact, magnitude and causes of selectivity itself. The resin phase activity coefficients which are defined to account for this variation are not analogous to solution phase activity coefficients and have significance in this connection only. One of the factors giving rise to this effect is considered to be the non-uniformity of exchange sites, so that one of the factors governing the value of the thermodynamic equilibrium constant $K_{aB/A}$ will be a distribution function expressing the magnitude of the non-uniformity. $K_{aB/A}$ is therefore a type of averaged selectivity for all sites. Unless the same type of average is made on the property (e.g. swelling) with which $K_{aB/A}$ is to be correlated, a precise correlation cannot be expected. Therefore extreme accuracy in the determination of $K_{aB/A}$ is not an advantage.

For this reason and also because preliminary work indicated a very small variation of k_A^B with loading, values of $K_{aB/A}$ were not determined in the present work. Further, the measured variations in k_A^B with α or solvent composition were very much greater than changes caused by varying the loading (see table 29). Since the results were to be used for qualitative comparison of resin affinity, no real advantage was therefore apparent in accurate by determining $K_{aB/A}$. k_B^A was therefore determined in each case at one loading only. In most cases this loading was similar for the various salt forms of the resin, thereby reducing any small error which may arise from this factor when this data is used for comparative purposes.

The small variation in k_B^A with loading is expected in resins of low cross-linking [94]. It is also to be expected that the system with the highest k_A^B will show the largest variation (see Table 29 below).

TABLE 29.

Percentage change in k_{Mg}^A for loading change from $\bar{X}_{Mg}$ 0.2 to $\bar{X}_{Mg}$ 0.8 on Amberlite IRC 50.

Exchanging cation A	k_{Mg}^A at $\bar{X}_{Mg} = 0.2$	k_{Mg}^A at $\bar{X}_{Mg} = 0.8$	% Change in k_{Mg}^A
Ca	1.80	2.03	13 %
Sr	0.93	0.90	3 %
Ba	1.24	1.11	11 %

From fig. 6 it can be seen that only the Mg/Ca system shows the normal trend, i.e. the preference for Ca increases as the value of $\bar{X}_{Mg}$ increases.

The change of k_A^B with $\bar{X}_B$ has been attributed to various causes.

Gregor [28, 29] explains this effect in terms of the hydrated volumes of the exchanging cations. These are in the order Mg > Ca > Sr > Ba. As $\overline{X}_{Mg}$ increases the resin becomes more swollen and the resulting increase in swelling pressure favours the uptake of the ion with the smaller hydrated volume. This theory correctly predicts the results obtained with the Mg/Ca system, but fails to explain the results obtained with the Mg/Sr and Mg/Ba systems.

This effect has also been explained in terms of the non-uniformity of the exchange sites [95], but this alternative does not offer a plausible explanation for the present results since the effect on the various salt forms of the same resin would be the same, so that the different trends observed are not explained. No explanation for this behaviour can be offered.

4.3. CHANGE IN PRACTICAL SELECTIVITY COEFFICIENTS k_{Mg}^{Ba}, k_{Mg}^{Sr} AND k_{Mg}^{Ca} WITH THE DEGREE OF IONIZATION (α) OF AMBERLITE IRC 50

The results of these determinations are given in Appendix V, Tables 20 - 22, and plotted in fig. 7. As α increases a series of affinity reversals occurs.

Range of α	Affinity sequence
0 - 0.1	Ba > Sr > Ca > Mg
0.1 - 0.2	Ba > Ca > Sr > Mg
0.2 - 0.6	Ca > Ba > Sr > Mg
0.6 - 1.0	Ca > Ba > Mg > Sr

At low α the resin exhibits the normal affinity sequence Ba > Sr > Ca > Mg, but as α increases the uptake of larger hydrated ions becomes more favoured and selectivity reversals occur in the order Ca > Sr, Ca > Ba and Mg > Sr.

These results will now be examined in terms of the three proposed models discussed in Chapter 1.

In considering the Marinsky model it is necessary to return to the basic Gregor equation (page 22). The second term, the ratio of the activity coefficients of the cations in the solution phase, will remain constant, since a constant solution phase composition was maintained in these experiments. The third term (the pressure-volume term) should change significantly with α, since the resin swells appreciably as α increases. The weight swelling of the different ionic forms of the resin at $\alpha = 1$ is in the order Mg > Ca > Sr > Ba = H, so that as the value of α increases, and the resin changes from the H form to a salt form, the swelling must increase and consequently the swelling pressure π increases. These increases will be greatest if the cations substituted for H are Mg/Ca, least if the cations are Mg/Ba. The effect of the pressure-volume term will therefore be to increase the tendency of the resin to take up the smaller hydrated cation as α increases. In fact, in all three cases, the resin shows a decreased tendency to take up the smaller hydrated cation as α increases. It must therefore be concluded that the pressure-volume term is dominant in determining the affinity of the resin for the alkaline earths only at very low values of α, and that at higher values of α the first term (the ratio of the activity coefficients of the cations in the resin phase) dominates the exchange. The observed change from the normal sequence must therefore be due to changes in this term resulting from interactions between the cations and the resin anions. Since the ratio $\frac{\bar{A}^+}{\bar{B}^+}$ must decrease significantly it must be assumed that the interaction between alkaline earth cation and resin anion is stronger in the case of magnesium than in the other cases. This conclusion is similar to that drawn by Gregor et al [27] in discussing the effect of α on the affinity of Amberlite IRC 50 for the alkali metals. These authors also observed affinity reversals, which they attribute primarily to cation-resin anion interaction. In this case, however, the affinity reversals were accompanied by reversals in the swelling sequence for the different ionic forms.

The conclusion drawn is that the interaction between the Mg ion and the carboxylate anion is greater than the interaction between the other alkaline earths and the carboxylate anion, when Amberlite IRC 50 is fully ionized. This conclusion has two consequences:

(1) At least partial stripping of the counterion must occur when interaction with the resin anion takes place, otherwise the Mg ion could not approach closer to the resin anion than the other alkaline earth cations (Mg has the smallest crystallographic radius but the largest solvated radius).

(2) The increased interaction and partial stripping should lead

> to a decrease in swelling since the solvation of the counterions has been reduced by stripping, the osmotic activity of the counterions and the resin anion has been reduced by the interaction and the electrostatic repulsion in the resin has been reduced by the reduction of electrostatic charge by the increased interaction.

The possibility of partial stripping would lend support to Reichenberg's model in preference to that of Chu, Whitney and Diamond.

The fact that the swelling of the Mg form of the fully ionized form of Amberlite IRC 50 is greater than that of the other alkaline earth forms is, however, a serious objection to the view that selectivity changes are caused by increased resin phase interaction. A more detailed investigation of this aspect should include the measurement of the changes in swelling with α of the various ionic forms of Amberlite IRC 50.

Further analysis of the results in terms of the Marinsky model reveals that the pressure-volume term, although outweighed by the resin phase activity term, should nevertheless make a significant contribution to the selectivity of the resin. The effect of the pressure-volume term, which opposes the effect of the resin activity term, should be greatest for the most swollen salt forms of the resin i.e. Mg/Ca > Mg/Sr > Mg/Ba. The negative slopes of the curves of practical selectivity coefficient against α should therefore lie in the order Mg/Ba > Mg/Sr > Mg/Ca. The observed order is in fact Mg/Ba = Mg/Sr > Mg/Ca, which is in reasonable agreement with these theoretical predictions.

Reichenberg's model gives a more direct and mechanistic explanation for this phenomenon. Reichenberg considers that the effect of increasing α is to reduce the average steric separation of the ionized fixed groups and hence to increase the overlapping of the fields of these groups. This overlapping is thought to increase the electrostatic interaction energy term while not affecting the dehydration energy term to the same extent (see page 25). This would tend to cause the reversal. In support of this Reichenberg points out that reversals are also promoted by increasing the degree of crosslinking and the specific capacity of the resin, both factors which cause the steric separation of the ionized fixed groups to be reduced.

Chu, Whitney and Diamond do not deal specifically with the phenomenon under discussion, but since they attribute the preference shown by weak acid resins for cations of small crystallographic radius to the fact that the resin anions have a greater solvating power than water, the selectivity reversals may be ascribed to increased electrostatic interaction energy resulting from overlapping of the fixed ionic groups. In this respect the models of Reichenberg and Chu, Whitney and Diamond are similar.

Measurements of the change of selectivity coefficient with α have been made on Amberlite IRC 50 by Gregor et al [27], using monovalent ions, and by Hanley [96], using trivalent ions. The results obtained by these investigators are similar to those obtained in the present work in that the affinities tend to revert to the normal sequence at low α.

4.4. THE EFFECT OF SOLVENT COMPOSITION ON THE PRACTICAL COEFFICIENTS OF THE ALKALINE EARTH METALS ON AMBERLITE IRC 50

The results of these determinations are given in appendix V, Tables 23 - 24, and plotted in fig. 8. As the % pyridine in the solution phase is increased the affinity of the resin for the smaller solvated ions increases. A series of affinity reversals occurs as indicated below:-

Solvent composition (% pyridine)	Affinity sequence
0 - 6	Ca > Ba > Mg > Sr
6 - 16	Ca > Ba > Sr > Mg
16 - 60	Ba > Ca > Sr > Mg
60 - 100	Ba > Sr > Ca > Mg

The normal affinity sequence Ba > Sr > Ca > Mg is exhibited at high % pyridine. As water is added affinity reversals occur in the order first Ca > Sr, then Ca > Ba and lastly Mg > Sr. The order in which these affinity reversals occur is exactly the same as that obtained by increasing the degree of ionization of the resin (see page 98). For this reason the exact sequence of the affinity reversals is considered to be significant. This aspect will be discussed further when the reason for the selectivity reversals has been examined.

A fact which seems surprising at first sight is that the selectivity reversals which appear when the solvent composition changes are not accompanied by corresponding changes in the swelling sequence of the various ionic forms of Amberlite IRC 50 (see previous Chapter).

This leads to the conclusion that the factors influencing swelling are not necessarily the same as those influencing selectivity.

Let us examine the consequences of the fact that, for example, the Ca form resin is more swollen than the Sr form over the full range of solvent composition but that a selectivity reversal occurs when there is about 10% pyridine in the resin phase (50% pyridine in the solution phase).

At 10% pyridine in the resin phase the swellings of the single ionic forms of the resin have changed somewhat from their values in pure water, but certainly very little relative to one another. As has been previously stated only resin phase interactions affect the swellings measured in the present work. Further, those effects which stem from ion-ion interactions in the resin phase affect the swelling of the alkaline earth forms of Amberlite IRC 50 to a greater extent than do solvation effects. It must be concluded therefore, that the ion-ion interactions between the resin anions and the various cations do not change much relative to one another as the solvent composition changes. To explain selectivity reversals it will therefore be necessary to examine solution phase effects, particularly ion-solvent interaction, rather than resin phase effects.

The Marinsky model does not provide an insight into the mechanism of this effect unless the resin phase activity coefficients and the swelling pressure are determined by the method outlined on page 22. This has not been done. It has also been shown (see page 100) that using the Marinsky model it is not possible to reconcile the swelling measurements obtained with Amberlite IRC 50 and the selectivity results at $\alpha = 1$.

In the earlier discussion of Reichenberg's model (see page 30), the reasons for the fact that cations do not exhibit the normal affinity sequence on Amberlite IRC 50 in water were fully dealt with. In summary it can be stated that with water as solvent the electrostatic interaction energy is greater than the free energy of hydration for a resin of this type, which has a fixed grouping of high field strength. This was reinforced by the effects of interaction polarization, multi-point-charge interactions and the overlapping of the fields of the fixed groupings. Reichenberg's model can be applied to the new situation with comparative simplicity, since the only changed factor is that the solvent now contains varying amounts of pyridine. The electrostatic interaction energy term should be unaffected by this change in solvent composition, since the crystallographic radii of the cations and the resin anion are used to calculate this term. As the change of solvent composition does not affect these radii, this term will remain constant. It should be emphasized, however, that the approach used in constructing this model necessitates the assumption that stripping or partial stripping of the cations occurs in the resin phase so that the fixed grouping and the counterion touch (or nearly touch) and therefore interact directly and not through a solvent bridge. If this assumption is in fact not valid then neither will be the argument that the electrostatic interaction energy term is unaffected by a change in solvent composition.

The hydration energy term, on the other hand, must of necessity be profoundly affected by change of solvent composition, as stated before pyridine should be a more effective solvating agent than water, in view of its somewhat higher dipole moment and lower dielectric constant. On addition of pyridine to the solvent, therefore, the free energy of solvation of the cations should become much greater than the value in water, with the result that this will become the predominant factor in determining the value of $\Delta G^{o}_{1/2}$

Consider, for example, the exchange process involving Sr/Mg and apply the Eisenman equation:-

$$\Delta G^{o}_{1/2} = \left(\frac{e^{2}}{r_{A} + r_{2}} - \frac{e^{2}}{r_{A} + r_{1}}\right) - (\Delta G_{2} - \Delta G_{1})$$

with magnesium as counterion (2) and strontium as counterion (1). As discussed previously (see page 27), in the case of Amberlite IRC 50, where the resin anion is the carboxylate grouping, r_{A} is fairly small; therefore in water as solvent, the first term (electrostatic interaction energy) is more important than the second (hydration energy). $\Delta G^{o}_{1/2}$ is positive and from the equation

$$\Delta G^{o}_{1/2} = - RT \ln K^{1}_{2}$$

it can be deduced that Mg (2) will be preferred to Sr (1). However if, as a result of the addition of pyridine to the solvent, the second term becomes more important than the first, $\Delta G^{o}_{1/2}$ will become negative and Sr (1) will be preferred to Mg (2). The series of selectivity reversals observed may therefore be predicted on the basis of Eisenman's theory, and the natural affinity sequence Ba > Sr > Ca > Mg may be expected when the % pyridine in the solvent is high. This reasoning could be confirmed by measurements of the solvation energies of the alkaline earth metals in water/pyridine mixtures.

Reichenberg's theory therefore provides a simple mechanistic explanation for the observed selectivity reversals.

When the data are examined in terms of the approach used by Chu, Whitney and Diamond three effects must be considered - solvent structure, ion-solvent interactions and resin anion/counterion interactions. Relatively more importance must be attached to the solvent structure than previously, since the structure of water, which is already extensively hydrogen bonded, is further tightened by the addition of pyridine (heat is given off when pyridine is added to water, indicating some degree of bond formation). The tendency of the solution phase to prefer cations of small crystallographic radius, which bond strongly with the solvent, will therefore be increased. The structure of solvent in the resin phase is disturbed by the hydrocarbon matrix and will not show this effect to the same extent. The effect of adding the pyridine would therefore be to increase the tendency of the solvent to force the larger cations, which do not interact as strongly with the solvent molecules, into the resin phase.

Ion-solvent and resin anion/counterion interactions are considered by these authors as a process of competitive solvation (solvation being very broadly defined - see page 34). The solvating power of the resin anions of the strong and weak acid resins and of water are believed to lie in the order carboxylate anion > water > sulphonate anion. A small cation will thus tend to remain in the solution phase if the resin is of the sulphonic acid type, since it is preferentially solvated by water molecules, but will tend to enter the resin phase if the resin is carboxylic, since it is now preferentially solvated by the resin anion. In both cases the total free energy reduction resulting from solvation is maximized.

The solvating power of pyridine is probably greater than that of the carboxylate anion, since its basic strength is greater (see page 72). This being so, the solvating power of the species competing for the cations would then lie in the order - pyridine > carboxylate anion > water > sulphonate anion, so that in a solvent of high % pyridine a small cation will always be preferentially solvated by the solution phase, irrespective of the nature of the resin anion.

Both the water structure effect and the competitive solvation effect should be increased considerably as a result of the preferential sorption of water by both resins in all the ionic forms involved in the equilibria studied, which causes the solvent in the solution phase to be richer in pyridine than that in the resin phase.

This model therefore accounts quite satisfactorily for the fact that with high % pyridine the normal affinity sequence is obtained and indicates that, as the % pyridine decreases, selectivity reversals may occur on carboxylic acid resins. The approach can never be as rigorous as Reichenberg's, however, in that quantitative determination of the solvation energy of cations by resin anions is difficult.

4.5. THE EFFECT OF SOLVENT COMPOSITION ON THE PRACTICAL SELECTIVITY COEFFICIENTS OF THE ALKALINE EARTH METALS ON ZEO - KARB 225

The results of these determinations are given in Appendix V, Tables 26 - 28, and plotted in fig. 9. As the % pyridine in the solution phase is increased the resin tends to show an increased preference for the smallest solvated ion. The normal affinity sequence Ba > Sr > Ca > Mg prevails over the full range of solvent composition, but the magnitude of the selectivity coefficients increases significantly as the % pyridine increases.

These results will be discussed only very briefly as the factors involved are in many respects identical with those arising in the case of Amberlite IRC 50.

In this case the selectivity sequence may be correlated with the swelling sequence of the various ionic forms, (see previous chapter); the swelling decreases as the affinity of the counter-ion for the resin increases. However the differences in swelling among the various forms do not account for the large relative increase in the selectivity values as the % pyridine is increased. For the reasons given on page 103, this leads once again to the conclusion that the explanation for the changes in selectivity lies in solution phase effects rather than in ion-ion interactions in the resin phase.

Because the resin phase activity coefficients and swelling pressures have not been evaluated, the results will not be discussed in terms of the Marinsky model.

The Reichenberg model can be applied as in the case of Amberlite IRC 50, with one significant difference. A sulphonic acid resin is considered to have a fixed grouping of low field strength (r_A is large). This means that the solvation energy term will be greater than the electrostatic interaction term and the cation with the higher free energy of solvation will remain preferentially in the solution phase. The normal affinity sequence should thus be obtained even with pure water as solvent. As pyridine is added the magnitude of the solvation energy term increases while, as explained previously (see pages 104 and 105), that of the electrostatic interaction term remains constant, so that the selectivity coefficients will increase further. The shapes of the curves obtained when the practical selectivity coefficients k_{Mg}^{Ba}, k_{Mg}^{Sr} and k_{Mg}^{Ca} are plotted against solvent composition are quite satisfactorily explained on this basis.

The model of Chu, Whitney and Diamond also provides an adequate explanation of these results. As in the case of Amberlite IRC 50 two effects must be examined; solvent structure and preferential solvation. The effect on the solvent structure of the addition of pyridine to the solvent will be exactly as discussed previously (see page 106), with the result that the tendency for the cation with the smaller crystallographic radius to remain in the solution phase will be increased. Preferential solvation, as pointed out previously (see page 107), depends on the relative solvating power of the competing species, which in this case will be in the order pyridine > water > sulphonate anion, so that the cations will always be preferentially solvated by the solution phase. The cation with the smallest crystallographic radius will be held most strongly in the solution phase and its preference for this phase will be increased on the addition of pyridine. Both these effects act in the same direction and will produce the normal affinity sequence, with an increase in selectivity coefficients as the % pyridine in the solvent is increased. The shapes of the curves obtained when the practical selectivity coefficients k_{Mg}^{Ba}, k_{Mg}^{Sr} and k_{Mg}^{Ca} are plotted against solvent composition can therefore also be satisfactorily explained on this basis.

4.6. EFFECT OF DIFFERENT ANIONS ON THE PRACTICAL SELECTIVITY COEFFICIENT k_{Mg}^{Sr} OF ZEO - KARB 225

4.6.1. Experimental Results

The practical selectivity coefficient k_{Mg}^{Sr} of Zeo-Karb 225 has been measured, in separate experiments, with perchlorate, chloride, nitrate and acetate as anions in the solution phase. The determinations were carried out both in water and in a solvent containing 69% by weight of pyridine at equilibrium. The results of these determinations are given below in Tables 30 and 31.

TABLE 30

Practical selectivity coefficient k_{Mg}^{Sr} for Zeo-Karb 225 in water with various anions in the solution phase.

Anion	$\bar{X}_{Mg}$	k_{Mg}^{Sr}
Perchlorate	0.45	1.81
Chloride	0.45	1.83
Acetate	0.52	1.35
Nitrate	0.56	1.21

The object of these experiments was to determine whether the anion has any significant effect on the exchange process at the dilutions employed, and to confirm that the perchlorate anion is in fact the optimum choice.

There is evidence in the literature [97] that divalent ions in the presence of certain anions form monovalent ions. A typical reaction is $Mg^{2+} + Cl^{-} \rightarrow MgCl^{+}$. This phenomenon is often referred to as partial complex formation. This effect cannot occur with monovalent cations, but when selectivity determinations are made with divalent cations significant errors can arise if the tendency to partial complex formation is different in the two cations under consideration. In fact the concentration of the anion in solution will then affect the values obtained for cation selectivities. Evidence for the existence of this effect has been provided by Gregor et al [97]. These workers observed a difference in the exchange capacity of Dowex 50 (a sulphonic acid resin) for Mg^{2+} and K^+, the apparent capacity being 5.23 m.eq. per g of H form resin in the case of Mg but only 4.90 m.eq. per g in that of K. To account for this it was pointed out that if some Mg^{2+} were actually going on to the resin as a monovalent ion of the type $MgCl^+$ or $MgOH^+$ the total amount of Mg taken up by the resin would be greater than expected.

TABLE 31.

Practical selectivity coefficient k_{Mg}^{Sr} for Zeo-Karb 225 in a pyridine/water mixture[X] with various anions in the solution phase

Anion	$\bar{X}_{Mg}$	k_{Mg}^{Sr}
Perchlorate	0.33	7.5
Chloride	0.33	5.8
Acetate	0.22	6.0
Nitrate	0.31	6.1

[X] 69% by weight of pyridine is present in the solvent at equilibrium.

Thus if Mg^{2+} and Ba^{2+} show different tendencies towards partial complex formation the selection of anion will certainly be a critical factor. The divergent results obtained by some previous workers are possibly due to this effect. The results given by Monge [98] for the selectivities of Amberlite IRC 50 for Mg, Ca, Sr and Ba are very different from those recorded in this thesis; it may therefore be significant that the anion used by Monge was chloride. Measurements of the selectivity of various resins for La^{3+}/Ce^{3+} also showed little reproducibility in the presence of chloride [99].

Difficulty was also encountered by Hanley [100] in measuring the selectivity coefficients on Amberlite IRC 50 of Lanthanum and trisethylenediaminecobalt (III). The problem is not fully discussed but would appear to stem from a combination of hydrolysis of the Amberlite IRC 50 and a reaction of the type $La^{3+} + OH^{-} \rightarrow LaOH^{2+}$, which takes place when hydroxyl ions are liberated following this hydrolysis.

In view of these problems the anion selected for the present work was the perchlorate anion, as it is reported [101] to have little or no tendency to form complex ions with Mg, Ca, Sr and Ba.

This contention is supported by the results of the capacity measurements (see page 53) performed in the present work. The capacity of Amberlite IRC 50 for H, Mg, Ca and Ba is the same, within the limits of experimental error. The conclusion can, therefore, be drawn that partial complex formation of the type $Mg^{2+} + ClO_4^{-} \rightarrow (MgClO_4)^{+}$ does not occur in aqueous solution. Furthermore the fact that no significant change in the resin capacity of either Zeo-Karb 225 or Amberlite IRC 50 occurred in the equilibrium experiments with a solvent containing a high % pyridine is evidence that this effect is also absent in these solvents.

Further support for the choice of perchlorate as anion is provided by the results given in Tables 30 and 31. It will be observed that, even in water as solvent, while the selectivity coefficients obtained with perchlorate and chloride as anion are similar, when the anion used is nitrate or acetate the selectivity coefficient is significantly lower (1.21 for nitrate as compared with 1.81 for perchlorate). In the pyridine/water solvent the selectivity coefficients obtained when chloride, acetate and nitrate are used as the anion are all significantly lower than that obtained with perchlorate as the anion.

The difference in the selectivity coefficients can only be ascribed to ion-pairing in the solution phase.

4.6.2. Ion Association In Aqueous and Mixed Solvents.

The most successful theoretical approach to this problem is that of Bjerrum [102]. This theory has been discussed at length by various authors [103, 104] and therefore the basic theory will not be reviewed in this thesis.

According to the Bjerrum theory there is for each electrolyte solvent system, a certain critical value of the distance of separation between oppositely charged ions within which such ions are associated into ion-pairs. This distance can be calculated from the formula:

$$q = \frac{|z_1 z_2| e^2}{2 \varepsilon kT}$$

where q = Bjerrum critical distance

$|z_1|$ = Algebraic value of cation valency

$|z_2|$ = Algebraic value of anion valency

ε = Dielectric constant

k = Boltzmann constant

T = Absolute temperature

e = Protonic charge

Substituting the appropriate values for a 2.1 electrolyte in water into the above equation gives:

$$q = \frac{2 \times 1 \times (4.8 \times 10^{-20})^2}{2 \times 78.3 \times 1.38 \times 10^{-16} \times 298 \times 10^{-8}}$$

$$= 7.1 \text{ Å}$$

With pyridine as solvent the value obtained is

$$q = \frac{2 \times 1 \times (4.8 \times 10^{-20})^2}{2 \times 12 \times 1.38 \times 10^{-16} \times 298 \times 10^{-8}}$$

$$= 46.7 \text{ Å}$$

Since the probability of oppositely charged ions approaching within 46.7 Å of each other greatly exceeds that of their approaching within 7.1 Å of each other, many more ion-pairs may be expected to form in pyridine than in water, provided the dilution of the ions is the same in both cases. This leads to the generalization that lowering the dielectric constant of the medium will increase ion-pairing.

The hydrated radii of ions can be deduced from a modification of the Stokes Law equation [105].

$$r = \frac{0.820 \, |z|}{\lambda^{o} \quad \eta^{o}} \left(\frac{r}{r_s} \right)$$

where

λ^{o} = Limiting ionic equivalent conductance (cm^{2} ohm^{-1} $equiv.^{-1}$)

η^{o} = Viscosity of solution at infinite dilution (poise)

$|z|$ = Algebraic value of valency of ion

r = Hydrated radius (Å) of ion

r_s = Stokes Law radius (Å) of ion = $\frac{0.820 \, |z|}{\lambda^{o} \quad \eta^{o}}$

$\left(\frac{r}{r_s} \right)$ = Stokes Law correction factor

Values calculated from this equation, of the hydrated radii of the cations studied in the present work are given below in Table 32; these values are taken from the literature [105].

TABLE 32. Estimates of the radii of hydrated cations

Cation	Crystallographic radius	Hydrated radius
	Å	Å
Mg	0.65	4.4
Ca	0.99	4.2
Sr	1.13	4.2
Ba	1.35	4.1

The hydrated radius of the perchlorate anion can be calculated similarly. For this ion in aqueous solution at 25°C

$$\lambda^{o} \eta^{o} = 60 \quad \text{(ref. 106)}$$

The value for η^{o} is in centipoises and must be converted to poises before it can be used in the Stokes Law equation. Thus

$$r_s = \frac{0.820 \times 1 \times 100}{60}$$

$$= 1.37 \text{ Å}$$

The appropriate Stokes Law correction factor may be found by extrapolation of the curve of the correction factor plotted against Stokes Law radius [107]. This gives a value of 1.9 for $\frac{r}{r_s}$ for perchlorate.

Thus

$$r = 1.37 \times 1.9$$

$$= 2.6 \text{ Å}$$

The theoretical distance of closest approach for two oppositely charged ions is given by the sum of their hydrated radii. The distances for the perchlorate anion and the alkaline earth cations, calculated from the hydrated radii determined above are given below in Table 33.

The value of the constant $\lambda^{o} \eta^{o}$ does not change much from one solvent to another [108], therefore it can be assumed that these calculated distances of closest approach will be very little changed in pyridine.

The argument may be pursued quantitatively from this point and the degree of association of the salts in both water and pyridine calculated. For the present purpose however, it is sufficient to point out that the distances of closest approach listed in Table 33 (± 7 Å), are very much less than the Bjerrum critical distance for a 2:1 electrolyte in pyridine (46.7 Å) but only just within the critical distance for such an electrolyte in water (7.1 Å). It is obvious, therefore, that very few ions will approach within the critical distance in water, but a considerably greater number will do so in pyridine.

It is therefore possible to demonstrate theoretically that the alkaline earth perchlorates will be virtually non-associated in water, but will be associated to varying degrees in pyridine.

The hydrated radius of the nitrate ion, calculated by the method given above, is 2.4 Å. This is less than the value for the perchlorate ion, so that closer distances of approach are possible between the nitrate ion and cations. This ion should therefore exhibit a slightly greater tendency towards ion-pair formation than the perchlorate anion.

4.6.3. Discussion Of Selectivities Obtained With Various Anions.

In view of the calculations made above it is now possible to make an analysis of the results obtained in these experiments. A factor which must be borne in mind is that ion-pairing in the solution phase takes place between fully solvated ions, and therefore increases as the solvated radius of the ions decrease. The tendency to ion-pairing will

TABLE 33.

THEORETICAL DISTANCES OF CLOSEST APPROACH FOR ALKALINE EARTH PERCHLORATES

Cation	Distance of closest approach
	Å
Mg	7.0
Ca	6.8
Sr	6.8
Ba	6.7

thus lie in the order Ba > Sr $\simeq$ Ca > Mg. Of the two cations employed in these experiments Sr will tend to associate with anions in the solution phase to a greater extent than Mg. It may be assumed that with perchlorate as the anion no ion-pairing occurs with either Mg or Sr in water as solvent, but the effect of substituting an anion such as nitrate, which will associate with the cations, associating with Sr more strongly than with Mg, will be to reduce the tendency for Sr to be forced into the resin phase. Therefore the practical selectivity coefficient k^{Sr}_{Mg} should be reduced. This is in fact observed. The results obtained indicate that in water no ion-pairing takes place between the two cations (Mg and Sr) and the anions perchlorate or chloride, but that a significant degree of ion-pairing does take place between these cations and the anions nitrate and acetate.

With a solvent containing 69% pyridine the assumption that no ion-pairing takes place between the perchlorate anion and the cations is no longer valid. The results indicate, however, that the degree of association of the anions with the cations lies in the order chloride > acetate > nitrate > perchlorate.

The choice of perchlorate as anion is therefore vindicated in both solvents.

5. A POSSIBLE METHOD FOR IMPROVING THE SEPARATION OF THE ALKALINE EARTH METALS BY ION-EXCHANGE CHROMATOGRAPHY

5.1. GENERAL

In the present work the alkaline earth metals were separated by ion-exchange chromatography on Zeo-Karb 225 (chromatographic grade). The method of separation was based on that developed by Honda [75] and has been fully described previously (see page 48). Honda's method was originally used in this work in an attempt to separate a mixture of Mg, Ca, Sr and Ba, but it did not produce a clean separation of Ca from Sr or Sr from Ba. For this reason it was modified and its use in the present work was restricted to the separation of the pairs Mg/Ca, Mg/Sr and Mg/Ba and that of the ions Mg, Ca and Ba from one another.

The results of the selectivity determinations described in chapter 4 reveal that large increases in each of the practical selectivity coefficients k^{Ca}_{Mg}, k^{Sr}_{Mg} and k^{Ba}_{Mg} occur when the pyridine content of the solution phase is increased. This was observed with both Amberlite IRC 50 and Zeo-Karb 225. The increase in the selectivity coefficients suggested that the chromatographic separation of the alkaline earth metals could be improved by introducing pyridine into the eluant used to displace the alkaline earths from the chromatographic column. Some support is lent to this contention by the work of Tsubota [116], who found that the separation factor (practical selectivity coefficient) k^{Sr}_{Ca} on a sulphonic acid resin increased with increasing concentration of organic solvent (methanol or ethanol) in the solution phase. He suggested therefore that, in the presence of these organic solvents, Ca and Sr should be readily separated by a column method.

Therefore, on a basis of both the selectivity results obtained in the present work and the work of Tsubota, it seemed logical that the introduction of pyridine into the eluant solution would lead to an improvement of the method for separating the alkaline earths described by Honda[75].

5.2. SEPARATION OF THE ALKALINE EARTH METALS BY ION - EXCHANGE CHROMATOGRAPHY , USING AQUEOUS PYRIDINE

To provide a standard against which any improvement in the separation of the alkaline earth metals could be measured, a column separation of a solution containing approximately equal quantities of the perchlorates of Mg, Ca, Sr and Ba was performed. The method previously described for the separation of Mg, Ca and Ba (see page 48) was used, with the modification that after the elution of the Ca, the the Sr was eluted with 50 ml of 2.0 M ammonium acetate. Throughout the elution of the column with the various concentrations (1.0 M for Mg, 1.5 M for Ca and 2.0 M for Sr) of ammonium acetate solution, 3 ml fractions of the eluate were collected and later titrated with EDTA, the methods used being those described in 2.3.1. for the titration of the various alkaline earth cations. The volume of EDTA used to titrate each fraction was then plotted against the total volume of eluate in order to determine an elution profile. The results are represented

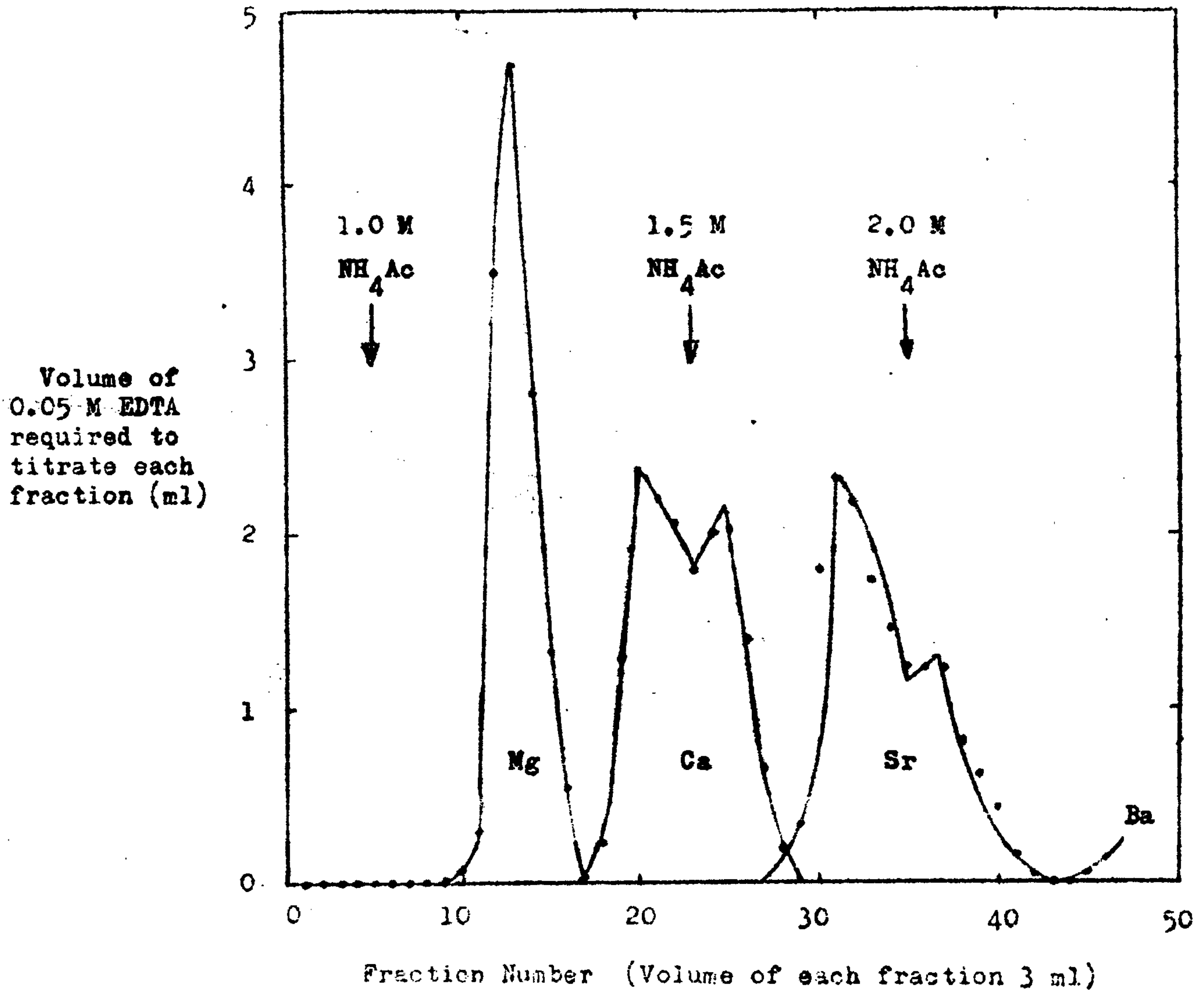

FIG. 10. ELUTION PROFILE FOR THE SEPARATION OF THE ALKALINE EARTH METALS BY ION - EXCHANGE CHROMATOGRAPHY, USING AQUEOUS ELUANTS AND ZEO - KARB 225.

graphically in fig. 10.

The procedure described above was then repeated with eluants consisting of solutions of ammonium acetate in a water/pyridine mixture, which was approximately 75% (by volume) pyridine. The molarity of the eluant solutions with respect to ammonium acetate was in all cases the same as that used previously.

Contrary to expectations the separation of the alkaline earth cations was not improved by eluting with water/pyridine eluants. In fact the separation was far inferior to that obtained previously using aqueous solutions as eluants.

5.3. AN INVESTIGATION OF THE FAILURE TO SEPARATE THE ALKALINE EARTH METALS BY ION - EXCHANGE CHROMATOGRAPHY, USING AQUEOUS PYRIDINE

Three possible explanations for the failure to achieve improved separation of the alkaline earth metals were considered: kinetic effects, elution effects and increased ion-pairing in the solution phase.

Kinetic effects

The rates of ion-exchange in non-aqueous media differ considerably from those in aqueous systems. The rate of ion-exchange in systems with organic solvents is nearly always lower than in comparable aqueous systems [109-113] because particle diffusion is much slower. The rate is particularly slow when swelling is small, and when the solvent has a low dielectric constant and/or a high viscosity. Slow rates of exchange could account for the poor column separations obtained. With pyridine/water solutions, however, it is somewhat doubtful whether this explanation is adequate, since the resins swell significantly in pyridine and it is not a viscous liquid. Furthermore the resin tends to sorb water preferentially, so that the resin phase will contain a significant proportion of water. The pyridine does, however, have a low dielectric constant. In view of these opposing factors it was decided to test this explanation by measuring approximate exchange rates on Zeo-Karb 225 in water and in a water/pyridine mixture.

To each of three identical samples of Mg form Zeo-Karb 225 were added 25 ml aliquots of 0.1 M aqueous ammonium acetate. The mixtures were shaken and, after 1 minute, 10 minutes and 48 hours respectively, the solution phase was separated from the resin phase, by the method described on page 52. The Mg in the solution phase was then determined by EDTA titration (see page 44).

The experiment was repeated with 25 ml aliquots of 0.1 M ammonium acetate solution in which the solution phase composition was 75% pyridine (by vol.) and 25% water.

The rate of desorption of Mg was approximately the same with both solvents, approximately 95% of the final equilibrium value (48 hours) being reached after 1 minute in each case.

From these results it was concluded that rates of ion-exchange in pyridine/water solutions are similar to rates of exchange in aqueous solutions, and that the failure of the proposed method of separation could therefore not be attributed to kinetic effects.

Elution effects

If the eluting power of the ammonium ion increases when the pyridine content of the eluant is increased, the molarity of the ammonium acetate solutions used may have been too great to allow effective separations to be achieved with aqueous pyridine eluants. Also, the presence of pyridine will lead to increased ion-solvent interaction, which will make aqueous pyridine solutions stronger eluting agents than comparable aqueous solutions. Both of these effects will be reflected in the practical selectivity coefficient.

The values of the practical selectivity coefficient of Zeo-Karb 225 for the Mg and ammonium ions in water and in aqueous pyridine were therefore measured in order to determine whether the problem could be ascribed to the increased eluting power of ammonium acetate in aqueous pyridine.

The practical selectivity coefficients were determined by a batch method. Two sets of three 0.7 g samples of air-dry Mg form Zeo-Karb 225 were weighed out. To each of the samples was added 35 ml of ammonium chloride solution. The ammonium chloride solution added to the first set was prepared by diluting 10 ml of 0.1 M ammonium chloride solution with 25 ml of water, while that added to the second set was prepared by diluting 10 ml of 0.1 M ammonium chloride solution with 25 ml of pyridine. The solution phase composition was therefore approximately 70% pyridine (by weight) for the second set. The mixtures were then equilibrated, after which the solution phase was separated from the resin phase and the Mg determined in both solution and resin phases by the methods described previously. Since the original concentration of the ammonium ion in the solution phase was known the practical selectivity coefficients could be calculated. The average values obtained are given below:

Solution phase composition	$k^{Mg}_{NH_4}$
100% Water	7.2
70% Pyridine 30% Water	3.5

It can be seen that a significant change in the practical selectivity coefficient occurs on addition of pyridine to the solvent. The affinity of the resin for the ammonium ion increases relative to that for the magnesium ion, with the consequence that the ammonium ion will in fact be a somewhat stronger eluting agent in aqueous pyridine than in water.

The chromatographic separation of the alkaline earth metals was therefore repeated, using the method described previously, with aqueous pyridine eluant solutions which had the same solvent composition as before but which contained ammonium acetate in one quarter of the concentration previously present. The separation improved somewhat but was still far inferior to that obtained with an aqueous eluant.

Further experiments were performed in which N/4 sodium chloride in an aqueous pyridine solution containing 69% pyridine was used as an eluant. These too failed to achieve any significant improvement in the separation.

It was therefore concluded that while the increased eluting power of the ammonium ion in aqueous pyridine is a contributory factor to the poor separation achieved, it does not play the major role.

Increased ion-pairing in the solution phase

Evidence has been presented in 4.6.3. which supports the contention that a significant degree of ion-pairing takes place between the alkaline earth metals and the acetate anion in aqueous solution. Further, the discussion given in 4.6.2. leads to the conclusion that the degree of ion-pairing increases significantly as the % pyridine in the solution phase increases. Extensive ion-pairing would therefore be expected between the alkaline earth metals and the acetate anion in an aqueous pyridine solution containing approximately 70% pyridine (by weight). The experimental evidence given in 4.6.1. supports this conclusion. Since, as pointed out previously, the degree of ion-pairing increases with decreasing solvated radius of the cation, the tendency to ion-pairing will lie in the order Ba > Sr = Ca > Mg. It would therefore be reasonable to expect that in aqueous pyridine eluants the presence of the acetate anion in the solution phase would tend to increase the affinity of this phase for the ion with the smallest solvated radius. The presence of the acetate anion would therefore reduce the selectivity of the resin in the chromatographic column for the other alkaline earth metals relative to Mg.

5.4. RECOMMENDATION FOR FURTHER WORK

The investigation described in 5.3. has revealed possible reasons for the failure to achieve an improved separation of the alkaline earth cations by adding pyridine to the eluant. A satisfactory solution to the problem would appear to hinge on the development of a suitable eluant for use with aqueous pyridine solutions. This eluant should contain an anion with a low tendency to ion-pairing, such as the perchlorate anion.

6. SUMMARY AND GENERAL DISCUSSION

The main results obtained in the present work will now be summarized and the conclusions drawn will be briefly discussed.

6.1. SWELLING AND SOLVENT SORPTION

The results of the weight swelling and solvent sorption determinations on both Amberlite IRC 50 and Zeo-Karb 225, in various pyridine/water mixtures, which were presented and discussed in chapter3, have led to some interesting conclusions.

Weight swelling is believed to be determined by three factors: the solvation of the fixed groups and counterions, the osmotic pressure difference between the solution phase and resin phase, and the electrostatic repulsion between fixed ionic groups and between charged resin chains. The change in the swelling of the resins as the % pyridine in the resin phase increases may be attributed to the influence of the change in dielectric constant on these three factors. The shape of the curves obtained when weight swelling is plotted against % pyridine in the resin phase, including the maxima through which the swelling of the various salt forms of Zeo-Karb 225 passes when approximately 50% pyridine is present in the resin phase, may also be explained in terms of the effect of the progressive lowering of dielectric constant on the three factors listed above. The weight swelling curves obtained for the two resins were different in shape. This is believed to be attributable to the fact that, in Amberlite IRC 50, ion-pairing between the alkaline earth cations and the carboxylate anion predominates over the other factors affecting swelling for the full range of solvent composition, whereas, in the case of Zeo-Karb 225, ion-pairing between the alkaline earth cation and the sulphonate anion is only predominant when the % pyridine in the resin phase rises above 50%.

The solvent sorption results can not be satisfactorily discussed using only existing theories, which consider only the polarities and the partial molar volumes of the solvents. In order to explain these results adequately it has been found necessary to consider the theoretical consequences of calculations, made in Appendix 1V, which demonstrate that a significant % of the water present in the resin phase is "bound" water, and that this % is lower in Zeo-Karb 225 than in Amberlite IRC 50.

The sorption of solvent by the resin will be governed by the tendency of the system to achieve the greatest overall reduction in free energy. Pyridine, which bonds with water, will therefore move into that phase having the greatest % of "free water" (i.e. the lowest % bound water), namely the solution phase. This tendency has been observed with both resins but, as expected, is particularly marked in the case of Amberlite IRC 50, since this resin has the higher % of "bound" water in the resin phase. The preference of the solution phase for pyridine can therefore be satisfactorily explained in this way.

6.2. SELECTIVITY OF RESINS FOR ALKALINE EARTH CATIONS

The results of the determinations of the practical selectivity coefficients of both Amberlite IRC 50 and Zeo-Karb 225 in equilibria involving the alkaline earth cations were presented and discussed in chapter 4.

The changes in the selectivity coefficient of Amberlite IRC 50 with loading are found to be small. The curves of selectivity coefficient against loading for the Mg/Sr and Mg/Ba systems have slopes opposite in direction to that usually observed in this type of correlation. No explanation for this behaviour can be offered.

The variation with α of the selectivity coefficients of Amberlite IRC 50 for the various pairs of cations is most satisfactorily explained in terms of Reichenberg's model; the effect of increasing is considered to be merely to reduce the average steric separation of the ionized fixed groups. The resultant overlapping of the fields of these groups increases the electrostatic interaction energy while leaving the dehydration energy relatively unaffected.

The investigation of the variation of the selectivity coefficients of both resins with solvent composition has given rise to some interesting conclusions. A feature of the experimental results which was initially found puzzling was that the large selectivity changes observed with both resins as the % pyridine in the solvent was increased were not accompanied by equivalent changes in the relative weight swellings of the various ionic forms of the resins. A correlation between weight swelling and selectivity coefficient usually exists. In view of the absence of this correlation it was deduced that the selectivity changes obtained could only be explained satisfactorily in terms of solution phase effects, particularly ion-solvent interaction, rather than resin phase effects, upon which swelling primarily depends. The Marinsky model can not be applied to this situation, but both Reichenberg's model and the model of Chu, Whitney and Diamond can be used to explain the selectivity changes, on a basis of changes in ion-solvent interaction, in a direct mechanistic manner. The fact that the selectivity coefficients are found to be so dependent on the solvent composition, this dependence stemming directly from ion-solvent interaction, and not indirectly from the influence of the solvent on resin phase ion-pairing, serves to emphasize the importance of the role played by the solvent in the ion-exchange process.

The effect of different anions on the selectivity coefficient k_{Mg}^{Sr} of Zeo-Karb 225 has been found to be significant. The influence of the anion has been attributed to solution phase ion-pairing; it has been demonstrated theoretically that this should occur extensively in pyridine solutions, but only to a small extent in water. The decrease in the selectivity coefficient as the % pyridine is increased may be attributed to the fact that a greater degree of ion-pairing will take place between the solvated strontium ion and a given anion than between the solvated magnesium ion and the same anion. This results from the fact that the strontium ion has a smaller solvated radius than the magnesium ion, so that the probability that a strontium ion will approach within the Bjerrum critical distance of the anion is higher. The results of these measurements vindicate the use of the perchlorate anion in the present work, since this anion shows the smallest tendency to ion-pairing, of those investigated.

6.3. INVESTIGATION OF POSSIBLE IMPROVED METHOD OF SEPARATION OF ALKALINE EARTH CATIONS

The results of the present work indicate the possibility of an improved method for separating the alkaline earth cations by ion exchange chromatography, viz. by using pyridine/water eluant solutions. This possibility has been examined, but the expected improvement has not been observed. An attempt has been made to locate the source of the problem and it has been concluded that the difficulty lies in the increased ion-pairing in the solution phase and greater ion-solvent interaction which result from the addition of pyridine to the eluant. It felt that further investigation could resolve these problems and possibly produce an eluant which will give the desired improvement in the chromatographic separation.

6.4. GENERAL DISCUSSION

The results of the present work serve to emphasize the role of the solvent in the ion-exchange process. It is evident that factors such as ion-solvent interaction and the effect of dielectric constant on ion-pairing have a pronounced effect on ion-exchange behaviour.

The majority of the results obtained can be mechanistically explained in terms of either the Reichenberg model or the model of Chu, Whitney and Diamond. A suggestion for further work in this field is the measurement of the heats of solvation of the various cations in pyridine/water mixtures, which would provide a quantitative test of the Reichenberg model. The results obtained in the present work do not favour either model over the other.

A second line of research suggested by the present work is the development of a suitable pyridine/water eluant for the chromatographic separation of the alkaline earth metals.

APPENDIX 1

CALCULATION OF COMPOSITION OF SOLVENT IN RESIN PHASE FROM DATA OBTAINED IN COMBINED WEIGHT SWELLING AND SORPTION EXPERIMENTS.

P_s - - - g pyridine originally added to solution.

W_s - - - g water originally added to solution.

W_r - - - g water originally on resin.

x - - - g pyridine in solution phase at equilibrium.

y - - - g water in solution phase at equilibrium.

ρ_s - - - mass fraction pyridine in solution phase at equilibrium.

ρ_r - - - mass fraction pyridine in resin phase at equilibrium.

S - - - g solvent (water + pyridine) in resin at equilibrium.

At equilibrium we have:-

$$\rho_s = \frac{x}{x + y}$$

Rearranging we get:-

$$y = x \frac{1 - \rho_s}{\rho_s} \qquad \text{--- (A)}$$

At equilibrium we have:-

$$S = (W_r + W_s - y) + (P_s - x)$$

Substituting in (A) and rearranging we get:-

$$S = W_r + W_s + P_s - \frac{x}{\%_s}$$

$$\therefore \quad x = \%_s (W_r + W_s + P_s - S) \qquad \text{---(B)}$$

At equilibrium we have:-

$$\%_r = \frac{P_s - x}{S}$$

Substituting in (B) we get:-

$$\%_r = \frac{P_s - \%_s (W_r + W_s + P_s - S)}{S}$$

All the quantities on the right hand side of this equation can be obtained directly from experimental measurements, and hence $\%_r$ the percentage by weight of pyridine in the resin phase at equilibrium can be calculated.

APPENDIX 11

DETERMINATION OF MAXIMUM PROBABLE ERROR OF CALCULATED COMPOSITION OF SOLVENT IN RESIN PHASE

The method for determining the maximum probable error is that outlined by Rhodes [114]. He lists the following steps:-

1. Write down the equation correlating the derived result and the observed quantities.
2. Differentiate successively with respect to each of the measured quantities.
3. Divide each partial differential by the original function and multiply each result by the maximum probable error in the measured quantity.
4. Add these results without regard to sign to get the maximum probable error in the derived result.

From Appendix 1 we have:-

$$\%_r = \frac{P_s - \%_s (W_r + W_s + P_s - S)}{S}$$

Rearranging we get:-

$$\%_r = \frac{P_s}{S} + \%_s - \frac{\%_s (W_r + W_s + P_s)}{S}$$

Applying steps 2, 3 and 4 above we get:-

$$\frac{\Delta \%_r}{\%_r} = \frac{\Delta P_s}{P_s} + \frac{4\Delta S}{S} + \frac{\Delta \%_s}{\%_s} + \frac{\Delta W_r + \Delta W_s + \Delta P_s}{W_r + W_s + P_s}$$

To determine the approximate magnitude of the maximum probable this equation was applied to one particular experiment for the determination of the combined swelling and solvent sorption. The experiment selected was that in which to 0.617 g of dry Ca form Amberlite IRC 50 2 ml water and 2 ml pyridine were added.

The results of this experiment are given in Appendix 3, Table 36. Some of the measured quantities are however not given in this Table. For this reason the full list is given below:-

Measured Quantity	Estimated Maximum Error
P_s = 2.00 g	ΔP_s = 0.05 g
S = 0.892 g	ΔS = 0.004 g
$\%_s$ = 0.53	$\Delta \%_s$ = 0.002 g
W_s = 2.00 g	ΔW_s = 0.05 g
W_r = 0.341	ΔW_r = 0.001

Applying the equation given above we get:-

$$\frac{\Delta \%_r}{\%_r} = \frac{0.05}{2.00} + \frac{4 \times 0.004}{0.892} + \frac{0.002}{0.53} + \frac{0.101}{4.34} = 0.070$$

$\therefore$ Maximum probable error in composition of solvent in resin phase is 0.070 x 100 i.e. 7%.

APPENDIX 111

UPTAKE OF SOLVENT BY RESINS (IN SINGLE IONIC FORMS) AT VARIOUS SOLVENT COMPOSITIONS

TABLE 7. H FORM AMBERLITE IRC 50

Equilibrium pyridine content of solution phase		Equilibrium pyridine content of resin phase		log $\frac{\bar{X}\text{ pyridine}}{X\text{ pyridine}}$	Solvent sorbed per m. eq. of dry H form resin			Weight Swelling per g dry H form resin
Wt. %	X pyridine	Wt. %	$\bar{X}$ pyridine		m. moles water	m. moles pyridine	Total m. moles solvent	g solvent
0	0	0	0	-	5.7	0	5.7	1.12
15.0	0.04	58	0.24	0.77	2.8	0.9	3.7	1.31
41.3	0.14	71	0.36	0.41	2.2	1.3	3.5	1.52
70.0	0.35	86	0.58	0.22	1.2	1.6	2.8	1.64
98.8	0.95	100	1.00	0.02	0	1.8	1.8	1.58

TABLE 8. Mg FORM AMBERLITE IRC 50

Equilibrium pyridine content of solution phase		Equilibrium pyridine content of resin phase		$\log \frac{\overline{X}\ \text{pyridine}}{X\ \text{pyridine}}$	Solvent sorbed per m. eq. of dry H form resin			Weight Swelling per g dry H form resin
Wt. %	X pyridine	Wt. %	$\overline{X}$ pyridine		m. moles water	m. moles pyridine	Total m. moles solvent	g solvent
0	0	0	0	-	10.0	0	10.0	1.95
26.4	0.08	10	0.02	-0.60	8.6	0.2	8.8	1.88
52.5	0.20	21	0.06	-0.52	7.3	0.4	7.7	1.81
74.8	0.41	44	0.15	-0.43	5.1	0.9	6.0	1.79
96.4	0.86	64	0.29	-0.45	2.5	1.0	3.5	1.36

TABLE 9. Ca FORM AMBERLITE IRC 50

Equilibrium pyridine content of solution phase		Equilibrium pyridine content of resin phase		$\log \frac{\overline{X}\ \text{pyridine}}{X\ \text{pyridine}}$	Solvent sorbed per m. eq. of dry H form resin			Weight Swelling g per g dry H form resin
Wt. %	X pyridine	Wt. %	$\overline{X}$ pyridine		m. moles water	m. moles pyridine	Total m. moles solvent	g solvent
0	0	0	0	-	8.2	0	8.2	1.60
26.2	0.08	6	0.01	-0.90	7.2	0.1	7.3	1.51
53.5	0.21	15	0.04	-0.72	6.3	0.3	6.6	1.45
75.0	0.41	45	0.16	-0.41	3.9	0.7	4.6	1.38
95.5	0.83	75	0.41	-0.30	1.3	0.8	2.1	0.97

TABLE 10. Sr FORM AMBERLITE IRC 50

Equilibrium pyridine content of solution phase		Equilibrium pyridine content of resin phase		$\log \frac{\overline{X}\ \text{pyridine}}{X\ \text{pyridine}}$	Solvent sorbed per m. eq. of dry H form resin			Weight Swelling per g dry H form resin
Wt. %	X pyridine	Wt. %	$\overline{X}$ pyridine		m. moles water	m. moles pyridine	Total m. moles solvent	g solvent
0	0	0	0	-	7.2	0	7.2	1.41
27.6	0.08	1	0.002	-1.60	6.8	0	6.8	1.35
53.6	0.21	8	0.02	-1.04	5.9	0.1	6.0	1.26
75.8	0.42	30	0.09	-0.67	4.0	0.4	4.4	1.12
96.1	0.85	73	0.38	-0.34	1.0	0.6	1.6	0.70

TABLE 11. Ba FORM AMBERLITE IRC 50

Equilibrium pyridine content of solution phase		Equilibrium pyridine content of resin phase		$\log \frac{\overline{X}\text{ pyridine}}{X\text{ pyridine}}$	Solvent sorbed per m. eq. of dry H form resin			Weight Swelling per g dry H form resin
Wt. %	X pyridine	Wt. %	$\overline{X}$ pyridine		m. moles water	m. moles pyridine	Total m. moles solvent	g solvent
0	0	0	0	-	5.7	0	5.7	1.11
26.4	0.08	4	0.009	-0.95	5.0	0	5.0	1.03
53.0	0.21	9	0.02	-1.04	4.5	0.1	4.6	0.97
75.4	0.42	38	0.12	-0.54	3.0	0.4	3.4	0.94
95.7	0.84	74	0.40	-0.32	0.9	0.6	1.5	0.67

TABLE 12. H FORM ZEO - KARB 225

Equilibrium pyridine content of solution phase		Equilibrium pyridine content of resin phase		log $\frac{\bar{X}\ \text{pyridine}}{X\ \text{pyridine}}$	Solvent sorbed per m. eq. of dry H form resin			Weight Swelling per g dry H form resin
Wt. %	X pyridine	Wt. %	$\bar{X}$ pyridine		m. moles water	m. moles pyridine	Total m. moles solvent	g solvent
0	0	0	0	-	-	-	-	-
19.6	0.05	33	0.10	0.30	23	3	26	2.92
49.1	0.18	48	0.17	-0.04	18	4	22	2.98
74.0	0.40	72	0.37	-0.04	10	6	16	2.98
96.4	0.86	100	0.100	0.05	0	8	8	3.01

TABLE 13. Mg FORM ZEO - KARB 225

Equilibrium pyridine content of solution phase		Equilibrium pyridine content of resin phase		log $\frac{\overline{X}\ \text{pyridine}}{X\ \text{pyridine}}$	Solvent sorbed per m. eq. of dry H form resin			Weight Swelling per g dry H form resin
Wt. %	X pyridine	Wt. %	$\overline{X}$ pyridine		m. moles water	m. moles pyridine	m. moles solvent	g solvent
0	0	0	0	-	31	0	31	2.69
22.9	0.06	25	0.07	0.05	25	2	27	2.84
51.3	0.19	39	0.12	-0.20	20	3	23	2.87
74.4	0.40	65	0.30	-0.11	12	5	17	2.89
98.0	0.95	90	0.69	-0.15	3	7	10	2.80

TABLE 14. Ca FORM ZEO - KARB 225

Equilibrium pyridine content of solution phase		Equilibrium pyridine content of resin phase		$\log \frac{\bar{X}\ \text{pyridine}}{X\ \text{pyridine}}$	Solvent sorbed per m. eq. of dry H form resin			Weight Swelling per g dry H form resin
Wt. %	X pyridine	Wt. %	$\bar{X}$ pyridine		m. moles water	m. moles pyridine	Total m. moles solvent	g solvent
0	0	0	0	-	26	0	26	2.24
23.6	0.06	25	0.07	0.05	21	2	23	2.39
51.9	0.19	36	0.11	-0.23	19	2	21	2.53
75.0	0.41	65	0.30	-0.15	11	5	16	2.65
98.0	0.95	92	0.72	-0.11	2	6	8	2.27

TABLE 15. Sr FORM ZEO - KARB 225

Equilibrium pyridine content of solution phase		Equilibrium pyridine content of resin phase		$\log \frac{\overline{X}\ \text{pyridine}}{X\ \text{pyridine}}$	Solvent sorbed per m. eq. of dry H form resin			Weight Swelling per g dry H form resin
Wt. %	X pyridine	Wt. %	$\overline{X}$ pyridine		m. moles water	m. moles pyridine	Total m. moles solvent	g solvent
0	0	0	0	-	21	0	21	1.82
24.3	0.07	23	0.06	-0.08	19	1	20	2.13
51.5	0.19	37	0.12	-0.20	16	2	18	2.25
75.3	0.41	65	0.30	-0.15	9	4	13	2.30
98.6	0.95	91	0.70	-0.15	2	4	6	1.64

TABLE 16. Ba FORM ZEO - KARB 225

Equilibrium pyridine content of solution phase		Equilibrium pyridine content of resin phase		$\log \frac{\bar{X}\text{ pyridine}}{X\text{ pyridine}}$	Solvent sorbed per m. eq. of dry H form resin			Weight Swelling per g dry H form resin
Wt. %	X pyridine	Wt. %	$\bar{X}$ pyridine		m. moles water	m. moles pyridine	Total m. moles solvent	g solvent
0	0	0	0	-	8	0	8	0.73
24.5	0.07	21	0.06	-0.08	12	1	13	1.27
51.9	0.19	32	0.10	-0.28	11	1	12	1.43
74.4	0.40	65	0.30	-0.11	6	3	9	1.47
98.8	0.95	86	0.58	-0.20	1	1	2	0.79

APPENDIX 1V

CALCULATION OF % BOUND WATER IN ZEO - KARB 225 AND AMBERLITE IRC 50

ZEO - KARB 225 (Mg form)

Exchange capacity of resin = 4.75 m.eq/gm.

Water taken up per g resin = 2.69 gm. (From results obtained with pure water as solvent - see Appendix III)

Number of molecules of water bound to each resin anion[115] ------- 1

Number of molecules of water bound to each Mg ion[115] ------- 7

Since each Mg ion is attached to two resin anions we have:-

1 eq. of resin contains as bound water $= 1 + (\frac{1}{2} \times 7)$ = 4.5 moles water

$\therefore$ 1 g of resin contains as bound water $= \frac{4.5 \times 4.75 \times 18}{1000}$ g water

% bound water $= \frac{4.5 \times 4.75 \times 18}{2.69 \times 1000}$

$= 14\ \%$

A similar calculation can be carried out on the Ca, Sr and Ba forms of the resin using the information tabulated below (weight swellings from Appendix III, hydration numbers from reference [115]). The % bound water obtained from these calculations is also given below:-

Form of Resin	Weight Swelling g/g Resin	Hydration Number	% Bound Water	% Free Water
Mg	2.69	7	14	86
Ca	2.24	5.2	14	86
Sr	1.82	4.7	16	84
Ba	0.73	2.0	23	77

AMBERLITE IRC 50

A similar calculation may be made on Amberlite IRC 50 using a value of 10.9 m.eq/g for the exchange capacity of this resin and making the assumption that the hydration numbers of the ions remain unaltered. The results of this calculation are tabulated below:-

Form of Resin	Weight Swelling g/g Resin	Hydration Number	% Bound Water	% Free Water
Mg	1.95	7	40	60
Ca	1.60	5.2	44	56
Sr	1.41	4.7	47	53
Ba	1.11	2.0	35	65

APPENDIX V

TABLE 17. PRACTICAL SELECTIVITY COEFFICIENT k_{Mg}^{Ca} FOR AMBERLITE IRC 50 IN WATER AT VARIOUS LOADINGS

$\bar{X}_{Mg}$	k_{Mg}^{Ca}
0.80	2.03
0.61	1.96
0.46	1.87
0.30	1.81
0.10	1.77

TABLE 18. PRACTICAL SELECTIVITY COEFFICIENT k_{Mg}^{Sr} FOR AMBERLITE IRC 50 IN WATER AT VARIOUS LOADINGS

$\bar{X}_{Mg}$	k_{Mg}^{Sr}
0.82	0.89
0.69	0.91
0.53	0.91
0.35	0.93
0.21	0.93

TABLE 19. PRACTICAL SELECTIVITY COEFFICIENT k_{Mg}^{Ba} FOR AMBERLITE IRC 50 IN WATER AT VARIOUS LOADINGS

$\bar{X}_{Mg}$	k_{Mg}^{Ba}
0.79	1.12
0.64	1.13
0.46	1.19
0.29	1.23
0.17	1.24

TABLE 20. VARIATION OF PRACTICAL SELECTIVITY COEFFICIENT, WITH α FOR Mg / Ca ON AMBERLITE IRC 50

α	$\bar{X}_{Mg}$	k_{Mg}^{Ca}
1.00	0.36	1.82
0.55	0.33	2.05
0.39	0.32	2.08
0.20	0.32	2.11
0.12	0.32	2.08

TABLE 21. VARIATION OF PRACTICAL SELECTIVITY COEFFICIENT WITH α FOR Mg / Sr ON AMBERLITE IRC 50

α	$\bar{X}_{Mg}$	k_{Mg}^{Sr}
1.00	0.52	0.91
0.48	0.48	1.10
0.40	0.45	1.23
0.20	0.38	1.65
0.12	0.37	1.73

TABLE 22. VARIATION OF PRACTICAL SELECTIVITY COEFFICIENT WITH α FOR Mg / Ba ON AMBERLITE IRC 50

α	$\bar{X}_{Mg}$	k_{Mg}^{Ba}
1.00	0.46	1.19
0.49	0.41	1.46
0.37	0.37	1.67
0.20	0.33	2.02
0.12	0.29	2.41

TABLE 23. PRACTICAL SELECTIVITY COEFFICIENT k_{Mg}^{Ca} FOR AMBERLITE IRC 50 IN PYRIDINE / WATER MIXTURES OF VARIOUS COMPOSITIONS

Equilibrium Pyridine content of external phase		$\bar{X}_{Mg}$	k_{Mg}^{Ca}
Wt. %	$X_{pyridine}$		
0	0	0.42	1.88
31	0.09	0.41	2.84
48	0.17	0.36	3.62
57	0.23	0.38	5.28
69	0.34	0.29	9.3
82	0.51	0.24	15.4

TABLE 24. PRACTICAL SELECTIVITY COEFFICIENT k_{Mg}^{Sr} FOR AMBERLITE IRC 50 IN PYRIDINE / WATER MIXTURES OF VARIOUS COMPOSITIONS

Equilibrium Pyridine content of external phase		$\bar{X}_{Mg}$	k_{Mg}^{Sr}
Wt. %	$X_{pyridine}$		
0	0.00	0.48	0.91
31	0.09	0.46	1.77
48	0.17	0.43	3.05
57	0.23	0.35	5.01
69	0.34	0.33	14.4
82	0.51	0.28	29.6

TABLE 25. PRACTICAL SELECTIVITY COEFFICIENT k_{Mg}^{Ba} FOR AMBERLITE IRC 50 IN PYRIDINE / WATER MIXTURES OF VARIOUS COMPOSITIONS

Equilibrium Pyridine content of external phase		$\bar{X}_{Mg}$	k_{Mg}^{Ba}
Wt. %	$X_{pyridine}$		
0	0.00	0.37	1.20
31	0.09	0.36	3.02
48	0.17	0.30	5.87
57	0.23	0.23	10.3
69	0.34	0.15	31.4

TABLE 26. PRACTICAL SELECTIVITY COEFFICIENT k_{Mg}^{Ca} FOR ZEO - KARB 225 IN PYRIDINE / WATER MIXTURES OF VARIOUS COMPOSITIONS

Equilibrium Pyridine content of external phase		$\bar{X}_{Mg}$	k_{Mg}^{Ca}
Wt. %	$X_{pyridine}$		
0	0.00	0.50	1.46
31	0.09	0.47	1.65
48	0.17	0.43	2.09
57	0.23	0.45	2.32
69	0.34	0.43	2.97
82	0.51	0.40	5.10

TABLE 27. PRACTICAL SELECTIVITY COEFFICIENT k_{Mg}^{Sr} FOR ZEO - KARB 225 IN PYRIDINE / WATER MIXTURES OF VARIOUS COMPOSITIONS

Equilibrium Pyridine content of external phase		$\bar{X}_{Mg}$	k_{Mg}^{Sr}
Wt. %	$X_{pyridine}$		
0	0.00	0.45	1.81
31	0.09	0.40	2.18
48	0.17	0.35	3.25
57	0.23	0.37	4.54
69	0.34	0.33	7.49
82	0.51	0.19	23.7

TABLE 28. PRACTICAL SELECTIVITY COEFFICIENT k_{Mg}^{Ba} FOR ZEO - KARB 225 IN PYRIDINE / WATER MIXTURES OF VARIOUS COMPOSITIONS

Equilibrium Pyridine content of external phase		$\bar{X}_{Mg}$	k_{Mg}^{Ba}
Wt. %	$X_{pyridine}$		
0	0	0.40	3.5
31	0.09	0.39	3.4
48	0.17	0.35	5.8
57	0.23	0.30	8.4
69	0.34	0.31	28

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