THE ION EXCHANGE BEHAVIOUR OF SOME TRIVALENT CATIONS IN AQUEOUS MONOETHANOLAMINE

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BY

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CONTENTS

Page

CHAPTER 1. INTRODUCTION

CHAPTER 2. MATERIALS AND METHODS

CHAPTER 3. CAPACITY DETERMINATIONS

CHAPTER 4. SWELLING DETERMINATIONS

CHAPTER 1

INTRODUCTION

1.1. Objective

Of the numerous investigations of cation exchange resins which have been reported, the majority have been confined to sulphonic acid resins, univalent cations and aqueous solutions. The studies which have been made of ion exchange phenomena in solvents other than water have been concerned mainly with neutral solvents, such as acetone, methanol and ethanol, and mixtures of these solvents with water, although acidic media have been used in some cases[1-7].

The work which is the subject of this thesis formed part of a research programme carried out at the University of Cape Town over the last decade. This research school has investigated various aspects of ion exchange on weak acid ion exchange resins[8], in particular the behaviour of these resins in basic solvents. Since cation exchange resins are acidic, studies of their behaviour in basic media may be expected to yield some interesting results, as the levelling effect of the basic solvents will cause both strong and weak acid resins to be fully ionized.

Macintosh (now Churms) studied ion exchange processes involving the univalent alkali metal ions in the basic solvent monoethanolamine, on the weak acid resin, Amberlite IRC 50, as well as on two **sulphonic** acid resins, Amberlite IR 120 and Zeo-Karb 225 [9,10].

Though the exchange behaviour of divalent ions on sulphonic acid resins has been investigated to some extent [1, 11-13], work on carboxylic acid resins has, with a few exceptions [1, 14-16], been confined to univalent cations. A study of the ion exchange behaviour of the trivalent ions, lanthanum and trisethylenediaminecobalt, in aqueous solutions on the weak acid resin, Amberlite IRC 50, as well as on the sulphonic acid resin, Zeo-Karb 225, was the subject of a thesis submitted to the University of Cape Town in 1965 by Hanley[17]. Recently, Ilsley[18] investigated the ion exchange behaviour of the divalent cations, magnesium, calcium, strontium and barium, on both Amberlite IRC 50 and Zeo-Karb 225 using pyridine/water solvents of varying composition. The ion exchange behaviour of trivalent cations in a non-aqueous solvent, which is the subject of the present thesis, has not been previously investigated.

Monoethanolamine was chosen as the solvent to be used in this investigation because of its basic strength ($K_b = 2.77 \times 10^{-5}$ at 25°C), low dielectric constant (37.72 as compared with 78.3 for water at 25°C) and miscibility with water in all proportions [19,20]. The high viscosity of monoethanolamine was not considered significant in this work, as this property may be expected to affect only rates of exchange, and no kinetic study was included in the work. However, an investigation of ion exchange processes in monoethanolamine/water mixtures of varying composition can be expected to give some indication of the effect of the dielectric constant of the medium on the ion exchange process, since this property will vary considerably as the water content of the solvent changes.

Monoethanolamine is a good solvent for a number of salts of the alkali metals, alkaline earths and lanthanides [21,22], although in this work the solubilities of the trivalent cations were found to be considerably lower than those quoted in the literature (see Section 5.2).

If the monoethanolammonium ion, $CH_2OH.CH_2\overset{+}{N}H_3$, were present in high concentration in monoethanolamine, as a result of the auto-ionization[23]:

$$2CH_2OH.CH_2NH_2 \rightleftharpoons CH_2OH.CH_2\overset{+}{N}H_3 + CH_2\overset{-}{O}.CH_2NH_2$$

then ion exchange processes in the presence of monoethanolamine would be markedly affected by competition for resin sites from the monoethanolammonium ions produced by the solvent, rendering monoethanolamine unsuitable as a solvent in ion exchange studies. However, from the specific conductance of pure monoethanolamine at 25°C (11.0 X 10^{-6} ohm^{-1} cm^{-1}), it has been estimated[23] that the concentration of $CH_2OH.CH_2\overset{+}{N}H_3$ ions is only 1.4 X 10^{-3} mole l^{-1}, and since the concentration of the cations in the ion exchange processes studied in this work was generally about 0.1N, competition for resin sites by $CH_2OH.CH_2\overset{+}{N}H_3$ ions was considered negligible. Further, in the case of ion exchange processes involving resin initially in the hydrogen form, the concentration of monoethanolammonium ions produced by auto-ionization of the solvent will be even lower than 1.4 X 10^{-3} mole l^{-1}, owing to repression of the auto-ionization in the presence of acids[23].

Also, Macintosh[9] has shown that neither the production of monoethanolammonium ions in aqueous monoethanolamine as a result of the reaction :

$$CH_2OH.CH_2NH_2 + H_2O \rightleftharpoons CH_2OH.CH_2\overset{+}{N}H_3 + OH^-$$

nor solvolysis of the cationic forms of a carboxylic acid resin by this solvent occurs to any appreciable extent. Aqueous monoethanolamine is thus a feasible medium for studies of ion exchange processes.

The trivalent cations used in this investigation were yttrium and the lanthanides, lanthanum and neodymium. Lanthanum was chosen since the ion exchange behaviour of this cation in aqueous solutions has been previously studied[14,17] and it was thought that a comparison might prove interesting.

Yttrium and neodymium were selected because of their accessibility and because the ionic radii of these ions and that of lanthanum differ sufficiently to give rise to differences in ion exchange selectivity. Yttrium is not properly a lanthanide, as far as electronic configuration is concerned, nor, strictly, is lanthanum, since it has no 4f electrons, but as regards properties, as Moeller[24] has indicated, yttrium and lanthanum are better discussed with the lanthanides than with any other elements. The magnitude of the lanthanide contraction is such that the ionic radius of the Y^{3+} ion is reached in the holmium-erbium region, and thus by studying the ion exchange behaviour of these three trivalent cations, it was hoped to observe what, if any, effect the lanthanide contraction has upon ion exchange processes.

The nitrate salts of these trivalent cations were used throughout this work, since the solubility of these salts in monoethanolamine is known to be appreciable[22], and because the nitrate ion shows a smaller tendency to form ion-pairs with cations than do most of the common anions.

The univalent cations used in this work were Na^+, H^+ and $CH_2OH.CH_2\overset{+}{N}H_3$, the latter being the "hydrogen ion" in monoethanolamine. In this investigation it has been assumed that any resin initially in the hydrogen form is completely converted to the monoethanolammonium form at equilibrium, in the presence of monoethanolamine. This assumption has been justified by the results of Macintosh[9].

The behaviour of three different cation exchange resins in aqueous monoethanolamine has been discussed in this thesis. The resins studied were the carboxylic acid resin, Amberlite IRC 50, and the two sulphonic acid resins, Zeo-Karb 225 (4-5% D.V.B.) and Amberlite IR 120 (12% D.V.B.). The carboxylic acid resin was of the usual cross-linked polymethacrylic acid type, containing approximately 4-5%

D.V.B., and thus of similar cross-linking to the Zeo-Karb resin. This permitted comparisons to be drawn between the behaviour of a carboxylic acid resin and a sulphonic acid resin of similar porosity. However, the two sulphonic acid resins used in this work differed widely in the degree of cross-linking, allowing the influence of cross-linking on the various processes studied to be ascertained.

1.2. Scope of Investigation

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

1) The weight-swelling of the resins in single ionic forms, in monoethanolamine/water mixtures of varying composition.
2) The affinity sequences shown by the hydrogen and sodium forms of the resins for the trivalent cations in aqueous solution.
3) The affinity sequences shown by the monoethanolammonium and sodium forms of the resins for the trivalent cations in monoethanolamine.

The sorption of solvent by the resins from monoethanolamine/water mixtures of varying composition has not been investigated, as the selective sorption of the more polar solvent by ion exchange resins in mixed solvents has been well established [9,11,25-27].

1.3. Cation exchange resins

A general introduction to the main properties and structural features of cation exchange resins is given below. This is intended to serve as a means of defining some of the more important terms encountered in ion exchange work, which will be used throughout this thesis.

Cation exchange resins are gels consisting of an insoluble macromolecular hydrocarbon framework, or *matrix*, to which are attached **anionic** exchange groups, such as $-SO_3^-$, in the case of the sulphonic acid resins, Amberlite IR 120 and Zeo-Karb 225, and $-COO^-$, in the case of the carboxylic acid resin, Amberlite IRC 50. To maintain electroneutrality an equivalent number of mobile cations, called *counter-ions*, are associated with the negatively charged exchange groups.

Linear hydrocarbon macromolecules containing anionic groups are soluble in water. Ion exchange resins are made insoluble by the introduction of *cross-links*, which interconnect the various hydrocarbon chains, making the resin particle effectively a single giant molecule, too large to dissolve. However, the matrix is elastic and the resin will tend to take up solvent as a consequence of the tendency of the ionic groups to dissolve, the process being known as *swelling*. The lower the degree of cross-linking and the greater the number of fixed ionic groups per unit length of matrix, the greater will be the swelling. Also, association between the counter-ions and the ionic groups, due to either covalent bond formation or ion-pair formation, will reduce the solvation tendency of the exchange sites and hence the swelling. These factors, together with others, will be discussed further in Chapter 4.

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

$$qR_pA^{p+} + pB^{q+} \rightleftharpoons pR_qB^{q+} + qA^{p+}$$

where R represents the resin group. In this case the resin is said to be in the *A-form* initially, and is converted to the B-form. The reaction is thus essentially a metathetical one between an electrolyte in solution, known as the external phase, and an insoluble polyelectrolyte, known as the resin phase. In order to maintain electroneutrality, a counter-ion can leave the resin only when another counter-ion enters 'simultaneously .

The process is, in its true sense, a stoichiometric one and is therefore not a sorption process. The ion exchange process is, however, often accompanied by some sorption. If an electrolyte is sorbed, the ions having a charge of the same sign as the counter-ions on the resin and those having a charge of the same sign as the exchange groups must be sorbed in equivalent amounts, in order that electroneutrality may be preserved; the latter ions are known as co-ions.

The preference of the resin for one cation over another is known as the selectivity or affinity of the resin. The more specific terms used in connection with ion exchange selectivity will be defined and discussed in Chapter 5.

In the case of the three resins studied in this work, the extent of cross-linking, which affects not only the swelling and selectivity but also the mechanical stability of the resins, can be adjusted by varying the amount of the cross-linking agent, divinylbenzene (D.V.B.), added in the polymerisation process. The degree of cross-linking is indicated by the nominal %D.V.B., which refers to the mole percentage of pure D.V.B. in the polymerisation mixture. The components polymerise in a random manner, so that there are broad variations in the degree of cross-linking, and the resins are therefore essentially heterogeneous in nature, as postulated by Attridge [28], Reichenberg and McCauley [29] and Glueckauf et al [30-33]. This means that the charge density and concentration of exchange groups will vary from region to region within the resin, but when averaged over the exchanger as a whole, the effect is not serious.

1.4. Cation exchange in non-aqueous and mixed solvents

Ion exchange can occur in aqueous, non-aqueous or mixed solvents provided that the electrolyte can dissolve and dissociate in the solvent and that no destruction or dissolution of the resin occurs. Water, because of its excellent solvent properties for most inorganic and quite a number of organic acids, bases and salts, has been the solvent employed in most exchange studies. However, solvents such as formamide, methanol, ethanol, isopropyl alcohol, ethylene glycol, anhydrous ammonia, acetone, acetic acid, dioxane, carbon disulphide, benzene, petroleum ether, carbon tetrachloride, monoethanolamine and pyridine have also been used in this field.

An additional factor is introduced in considering ion exchange in mixed solvents, in that the solvent composition of the resin and solution phases may differ if one of the solvent components is selectively sorbed by the resin. This aspect was not studied in the present work because Macintosh [9], working with the same three resins in monoethanolamine/water mixtures, has already shown that :

1) In all cases, the resin shows a preference for water, the preference decreasing as the water content of the external phase increases.

2) The ionic forms of the 12% D.V.B. sulphonic acid resin show a greater preference for water

than the corresponding ionic forms of the 4-5% D.V.B. sulphonic acid resin under the same conditions.

3) The carboxylic acid resin sorbs water selectively to a greater extent than the sulphonic acid resin of similar cross-linking, other factors being equal.

4) For a given resin, the preference for water decreases with increasing ionic radius of the counter-ion.

Both ion exchange and swelling equilibria are strongly affected by the nature of the solvent. The swelling of ion exchange resins in non-aqueous and mixed solvents has been studied by several workers [2,9,25-27,34-38]. Such studies have shown that the swelling of salt forms of ion exchange resins decreases as the dielectric constant of the medium falls; this has been attributed to an increase in ion-pair formation between the resin anions and the counter-ions due to the decrease in the dielectric constant of the medium. However, Phipps and Hume [13] found that the swelling of polystyrene-divinylbenzene Dowex 50 resins in the alkali metal or alkaline earth cationic forms in ammonia was somewhat less than in water, but much greater than in methanol, showing that it is impossible to predict the extent of swelling on the basis of dielectric constant alone.

Ilsley[18] found that the weight-swelling of Zeo-Karb 225 in various single divalent ionic forms in aqueous pyridine solutions increased initially with increasing pyridine content, passed through a maximum when the percentage pyridine was approximately 50% by weight, and then decreased as the pyridine content was increased further. He explained this by proposing that the initial increase in electrostatic repulsion due to the decrease in dielectric constant exceeded the decrease due to reduction of the fixed charges resulting from ion-pair formation; the net increase in electrostatic repulsion caused the initial increase in swelling with decreasing dielectric constant. As the dielectric constant was lowered still further, the ion-pairing became so extensive that it became the dominant factor. A net decrease in electrostatic repulsion resulted, causing the swelling to decrease as the dielectric constant fell, the reverse of the initial trend.

The swelling of ion exchange resins in their H-forms has in many cases been found to increase with increasing concentration of the non-aqueous component of a mixed solvent [1,2,18,34-37,39]. This has been attributed to changes in the nature of the solvated proton as increasing amounts of the organic solvent are added to the medium. Bodamer and Kunin[1], using a variety of organic solvents, found that the swelling of a number of sulphonic Amberlite resins decreased as the proportion of the organic component of the solvent mixture increased, but that the decrease was least in the case of the H-forms of the resins. These workers also noted a decrease in the swelling of Amberlite IRC 50 in the Na-form on increasing the concentration of the organic solvent in the medium, but an increase in the swelling of the H-form of this resin was observed when increasing amounts of ethanol were added to an aqueous ethanol medium.

It has generally been observed that addition of organic solvents to the solution phase enhances ion exchange selectivity [9,25,35,40-43]. A few authors have attempted to explain this in terms of the dielectric constant of the solution phase[42,43], ion association[25-27], solvation of ions[25,35,41], etc.; these theories have been based on limited experimental data. There are, however, some experimental results which are not adequately explained by these theories; for example, reversal of the affinities of lithium and hydrogen[42] and of ammonium and sodium [25,41] with increasing concentration of organic solvent in the solution phase. Athavale et al[44], working with the strong acid exchanger, Amberlite CG-120 Type 1, observed a general increase in selectivity for univalent cations in organic solvents, except for the preference of the resin for lithium relative to that of ammonium, which decreased with increasing concentration of organic solvent in the case of methanol, ethanol and acetone, but increased in the case of 1-propanol and 2-propanol. This shows that the dielectric constant is not the only governing factor, as acetone and 2-propanol have nearly equal dielectric constants and have the same number of carbon atoms.

Ion exchange selectivity depends upon the degree of interaction between the resin anions and the exchanging cations, and also upon the partial molar volumes of the exchanging ions in the resin phase. Both these factors are affected by the nature of the ambient medium. The degree of ionic association depends upon the dielectric constant of the medium, and the partial molar volumes of the ions are determined largely by the degree of ion-solvent interaction. The effect of solvent composition on ion-solvent interaction and on ion-pair formation will be discussed in Section 5.4.1..

CHAPTER 2

MATERIALS AND METHODS

2.1. Resins

Three resins were used in this work: the carboxylic acid resin Amberlite IRC 50, and two sulphonic acid resins, Amberlite IR 120 and Zeo-Karb 225. The Amberlite resins are manufactured by the Rohm and Haas Company, Philadelphia, U.S.A., the Zeo-Karb resin by the Permutit Company Ltd., London.

Amberlite IRC 50 is a polymethacrylic acid resin, cross-linked with 4-5% D.V.B.. Amberlite IR 120 and Zeo-Karb 225 are both sulphonated polystyrene resins, cross-linked with 12% and 4-5% D.V.B. respectively. All three resins are supplied in bead form, the Amberlite resins in the H-forms and the Zeo-Karb resin in the Na-form.

2.1.1. Conditioning

Ion exchange resins, as bottled and dispatched by the manufacturers, often contain soluble monomer and low molecular weight polymer which have not been incorporated into the resin matrix. In order to remove these, a certain amount of pre-treatment of the resins is necessary before they can be used in ion exchange studies.

In the present work this preliminary conditioning was carried out by allowing the resins to stand in 5N NaOH, with occasional stirring, for 24 hours; they were then transferred to columns and washed with distilled water, to remove the NaOH. 2N HCl was then passed through the columns until the resins were completely converted to the H-forms. This was followed by further washing with distilled water and the procedure repeated, the resins being finally washed with distilled water until the effluent gave no precipitate when treated with $AgNO_3$ solution, i.e. until the resins were chloride-free. The resins were all completely in their H-forms at the conclusion of this pre-treatment.

2.1.2. Screening

After conditioning the resins were placed in large evaporating basins, covered with filter paper to prevent the infiltration of dust, and allowed to stand for several days until they were air-dry and free flowing. They were then sieved using a conventional set of standard sieves (B.S.S.); the 44-100 mesh fractions were used in this work.

Hanley [17] used nylon sifting cloths of set porosities, each having a standard number of meshes per inch, to obtain several fractions of resin of different particle size; this ensured that there was no breakdown in particle size during sieving. Particle size plays an important role in the kinetics of ion exchange, but as no kinetic study was undertaken in the present work, screening by means of the conventional set of standard sieves was considered adequate here.

2.1.3. Converting

The Na-form of each resin was prepared by treating the H-form with a solution of NaOH. For this purpose, the resins were shaken with excess 2N NaOH on a mechanical shaker, shaking being continued for at least a week to ensure complete conversion. Due to the very high affinity of Amberlite IRC 50 for the hydrogen ion (see Section 5.4.2.), the lanthanum, neodymium and yttrium forms of this resin were not prepared directly from the H-form, but via the Na-form of the resin, and in order to maintain consistency, the same procedure was applied to the sulphonic acid resins. This was achieved in each case, by first shaking the resin in the H-form with excess 2N NaOH for at least a week, to convert it to the Na-form, and then, after filtering off the resin from the supernatant solution, shaking it for a further week with excess of a 2N solution of the nitrate of the trivalent metal. The resin was then sucked dry on a Buchner funnel and allowed to air-dry for several days.

2.1.4. Drying

In this work it was necessary to use dry resin. There appears to be no standard procedure for drying resins to a constant reproducible state, and various oven temperatures, times and conditions have been stated in the literature [13,25,45-48]. Drying is very important in ion exchange studies, as in order to compare ion exchange resins it is necessary to refer their properties to a standard state, which for cation exchangers is usually chosen as the dry hydrogen form resin.

Helfferich[49] states that the maximum drying temperature for the resins used in the present work is 120°C. Hanley[17] showed that Amberlite IRC 50 may be dried in an oven at 105°C to a constant reproducible state within 24 hours, but that at higher temperatures this resin slowly decomposes. Macintosh[9], working with the same three resins as were used in the present work, dried the H-, Li-, Na-, K- and $CH_2OH.CH_2NH_3$- forms of these resins to constant weight in an oven at 105°C; only the $CH_2OH.CH_2NH_3$-form of the carboxylic acid resin showed signs of decomposition at that temperature, and was therefore dried at 60°C in a vacuum oven.

In the present work, to avoid the possibility of decarboxylation and decomposition of the resins at higher temperatures, all the various ionic forms of the three resins were dried to constant weight in a vacuum oven at 60°C over silica gel for 24 hours, and then stored in vacuum desiccators over phosphorus pentoxide.

2.2. Solvents

In this work two solvents were used, water and monoethanolamine. Distilled water was used in all operations requiring water. The monoethanolamine used, the product of Riedl de Haën of Hanover, Germany, was supplied in a highly purified state, but further purification was considered necessary to minimise the water content. Brewster and his co-workers[23] have shown that distillation of monoethanolamine at atmospheric pressure causes slight decomposition to ammonia and water; the monoethanolamine used in the present work was therefore purified by vacuum distillation at 20 mm Hg and 82°C.

After distillation the monoethanolamine was stored in air-tight containers under dry, CO_2-free nitrogen, since this solvent tends to absorb moisture and CO_2 from the atmosphere. Clarke[50] and Danckwartes et al[51] have shown that the carbonation reaction :

$$\mathrm{CO_2 + 2CH_2OH.CH_2NH_2 \longrightarrow CH_2OH.NHCOO^- + CH_2OH.\overset{+}{N}H_3}$$

takes place even at short contact times, though not to any appreciable extent. Monoethanolamine can thus be regarded as a suitable solvent for ion exchange studies only if exposure to the atmosphere is minimised. Consequently, in the selectivity determinations carried out in this work, where it was necessary to minimise the water content of the solvent (see Section 5.4.1.), the monoethanolamine was exposed only in a dry-box in the presence of magnesium perchlorate and in an atmosphere of dry, CO_2 - free nitrogen.

2.3. Chemicals

All chemicals used in this work were Analytical Reagent (A.R.) grade, and no further purification of these chemicals was attempted. Lanthanum nitrate hexahydrate was obtained from the British Drug Houses Ltd., Poole, England, and the neodymium and yttrium nitrate hexahydrates from Fluka AG, Switzerland. These salts are all deliquescent and were therefore dried under reduced pressure at 60°C over phosphorus pentoxide and stored in a vacuum desiccator over P_2O_5 before use. The NaOH and HCl solutions used in this work were all prepared from fixanols or, in the case of some of the standard HCl solutions, from concentrated A.R. HCl by dilution.

2.4. Analytical methods

2.4.1. Determination of the trivalent cations

The stability constants of the aminepolycarboxylic acid chelates formed by yttrium, neodymium and lanthanum with disodium dihydrogen ethylenediaminetetra-acetate (EDTA) at 20°C are 18.09, 16.61 and 15.50 respectively[52]. This affords a useful method for the determination of these trivalent cations; excess EDTA is added and then back-titrated with standard Zn^{2+} solution. In the present work, only a single trivalent cationic species was present in all cases. The procedure adopted here for the determination of these three trivalent cations was that developed by Hanley[53].

Procedure

25 ml aliquots of a solution in which the trivalent ion concentration was approximately 0.03 M were taken, and each was diluted to 250 ml in a volumetric flask. 25 ml aliquots of the diluted solutions were then taken and

each was diluted to about 100 ml, to reduce the trivalent ion concentration to about 0.00075M. It is essential that the solution be kept acid until excess EDTA is present, since if the pH rises to too high a value, the trivalent metal hydroxides will precipitate. For aqueous solutions, 1 or 2 drops of concentrated A.R.HCl were added to each solution to bring the pH to approximately 1, according to universal indicator paper. In the cases where the trivalent cation concentrations were determined in monoethanolamine, a few ml of concentrated A.R.HCl were required to reduce the pH to 1. About 25 ml of standard 0.01M EDTA was then added to each solution, followed by approximately 50 mg of eriochrome black T indicator. The indicator was not added as a solution, as recommended by Vogel[54], as this procedure was found to give rise to indistinct end-points. An ammonia/ammonium chloride buffer solution [54] of pH 10 was then added dropwise until the solution became blue (pH 8-10). (If the solution does not turn blue when the buffer is added, too little EDTA is probably present. An excess of EDTA must obviously be present before the back-titration can be commenced). The excess EDTA was then back-titrated against a standard 0.01M Zn^{2+} solution. The end-point was indicated by a sharp colour change from blue to pink.

The EDTA was standardised against two primary standards using the solid eriochrome black T indicator as above:

1) Dry calcium carbonate [55].
2) A.R. magnesium sulphate heptahydrate [56].

The Zn^{2+} solution (prepared by dissolving about 0.163 g of A.R. zinc shot in HCl, adding approximately 1M NaOH until the pH was about 6-7 and then diluting to 250 ml) was standardised against the standard EDTA solution.

In the standardisation titrations, the titre values used in the subsequent calculations were the means of 6 separate determinations and were considered accurate to 0.4%.

2.4.2. Determination of monoethanolamine

The composition of monoethanolamine/water mixtures can be found by determination of the monoethanolamine by direct acid-base titration of weighed samples of the solution against standard HCl, or by determination of the water by Karl Fisher titration, or by both methods. In the present work, the monoethanolamine was determined in all cases, and the water concentrations were calculated by difference. The indicator used in the titrations of monoethanolamine against HCl was methyl orange screened with methylene blue.

The HCl was standardised against A.R. anhydrous Na_2CO_3 [57], and NaOH which had been standardised against A.R. sulphamic acid [58]. Here, the titre values, which were the means of 6 separate determinations, were considered accurate to 0.2%.

CHAPTER 3

CAPACITY DETERMINATIONS

3.1. Introduction

The capacity of a resin should be defined in such a way that it is a characteristic constant of the resin and independent of the experimental conditions. One of the most useful ways of expressing capacity is as the scientific weight capacity, which is defined as the number of milliequivalents of counter-ion per gram of resin in a standard state, which for cation exchange resins is the dry hydrogen form. Other definitions of capacity have been given in the literature[59], but will not be discussed here as they have not been used in the present work.

The capacity of an ion exchange resin depends essentially upon the number of ionogenic groups, which contain the exchangeable counter-ions, in a given amount of resin. The capacity of a given resin is therefore constant and independent of the size and shape of the resin particles and the type of counter-ion, except in special cases. Two of these exceptional cases, which give rise to anomalous capacities, will now be discussed, in view of their possible relevance to the present work.

The ionic sieve effect has been observed by several workers[60-64]. This is shown by resins of high or moderate cross-linking towards very large ions, which are believed to be prevented, by virtue of their size, from penetrating to the exchange sites situated in the more tightly cross-linked regions of the resin, so that the capacities of the resins for these larger ions appear to be less than that for smaller ions.

The second effect giving rise to anomalous capacities is that which is sometimes observed with polyvalent ions, when a resin appears to take up the ion in an amount in excess of its scientific weight capacity. Arnold [8] observed that when a lanthanum hydroxide sol was shaken with Amberlite IRC 50 for about 2 months, the uptake of lanthanum by the resin was higher than that corresponding to one-third of a gram atom per exchange group. The effect may be ascribed to the participation of ions such as $La(OH)^{2+}$ in the exchange; in this case a gram atom of lanthanum occupies only two exchange sites instead of the three it would occupy if it behaved as a trivalent ion. Arnold[14] later found that the resin exhibited its normal capacity towards the lanthanides when treated with lanthanide perchlorate solutions, indicating that hydrolysis does not play a major role in these cases.

3.2. Experimental

Sulphonic acid resins react at comparatively fast rates [65] - a contact time of about 20 minutes is usually sufficient to ensure the completion of the reaction. However, rates of exchange on carboxylic acid resins, especially when the resins are initially in their H-forms, are very slow compared with those shown by sulphonic acid resins. This slow rate necessitates contact times of several hours, making capacity determination by a column procedure impractical. Thus in this work, all capacity determinations were carried out by the conventional batch method.

In the case of the weak acid resin, Amberlite IRC 50, with its particularly strong affinity for the hydrogen ion (see Section 5.4.2.), it was necessary to convert the resin into the Na-form before the capacities for the trivalent ions could be determined; for the sake of comparison, the same procedure was adopted for the sulphonic acid resins.

Procedure

The capacities of the resins for sodium were determined as follows: Weighed samples of dry resin in the H-form (about 0.1 g in the case of the carboxylic acid resin and about 0.2 g in the case of the sulphonic acid resins, i.e. approximately 1m. equiv. resin in all cases[49]) were shaken for a week with a mixture of 25 ml of a standard 0.1 N NaOH solution and 25 ml of an approximately 0.1 N NaCl solution (added to reduce any concentration effects). 10 ml aliquots of the supernatant solutions were then removed and titrated against standard 0.1 N HCl, with screened methyl orange as indicator. The back-titration gave the concentration of OH^- ions remaining after neutralisation of some of the OH^- ions by the H^+ ions displaced from the resin by the Na^+ ions. The uptake of sodium by the resins could then be determined and the ion exchange capacities calculated from these figures and the weights of the resin samples.

In order to determine the capacities of these resins for the trivalent cations, the resin samples used in the above determinations were separated from the supernatant solutions by filtration in sintered-glass filter tubes, washed with distilled water to remove any adhering solution, and then washed into clean flasks with distilled water. Each resin was then shaken for a week with 50 ml of a standard 0.1 N solution of the nitrate of the trivalent metal, after which the supernatant solutions were filtered off and the resins washed with 10 ml of distilled water, the washings being added to the filtrates. Each of the solutions so obtained was then diluted to 500 ml in a volumetric flask. This procedure reduces the trivalent ion concentrations to the order of 10^{-3}M. 25 ml aliquots of the diluted solutions were then titrated with EDTA , by the method described in Section 2.4.1., to determine the amounts of the trivalent cations remaining in solution after equilibration, from which the uptake of these ions by the resins and thence the ion exchange capacities of the resins for these ions could be calculated.

Each titration was carried out in triplicate and the determination was repeated with six different samples of each resin for each ion. The quantities used in these determinations were such that any errors resulting from loss of water from the external solutions due to the swelling of the resins were negligible. In the case of the carboxylic acid resin in particular, the times of contact between wash water and resin were reduced as much as possible (definitely less than 10 seconds) to minimise any hydrolysis effects.

3.3. Results

The capacity values for the three resins, which were used in subsequent calculations, are given below in Table 1:

TABLE 1

CATION	CAPACITY (m. equivs. per g of dry resin in H-form)		
	AMBERLITE IRC 50	AMBERLITE IR 120	ZEO-KARB 225
Na	9.87 ± 0.07	4.56 ± 0.06	4.62 ± 0.05
La	9.85 ± 0.07	4.56 ± 0.05	4.63 ± 0.06
Nd	9.70 ± 0.08	4.43 ± 0.06	4.41 ± 0.07
Y	9.43 ± 0.09	4.34 ± 0.07	4.23 ± 0.07

The capacity of each resin for the $CH_2OH.CH_2\overset{+}{N}H_3$ ion was not determined, since Macintosh[9] has stated that, within experimental error, the capacities of these three resins for the $CH_2OH.CH_2\overset{+}{N}H_3$ ion are the same as those for the Na^+ ion.

3.4. Discussion

The values given by the manufacturers for the capacities of Amberlite IRC 50, Amberlite IR 120 and Zeo-Karb 225 are, respectively, 9.95, 4.3 - 5.0 and 4.8 m. equivs. per gram of dry resin in the H-form, but these are not strictly comparable with the present results since testing procedures differed. Capacity is a characteristic of a certain batch of resin under investigation and not of the resin itself in general [48], and it is therefore not surprising to note the variations in the capacity values quoted in the literature for these resins [9,14,16-18,26,29,48,64,66]. However, it is noticeable that the capacity values for the weak acid resin, Amberlite IRC 50, obtained in the present work are approximately 10% lower than the average literature value.

The equivalent weight of styrenesulphonic acid is 184.2, while that of methacrylic acid is only 86.1, and thus the number of functional groups per gram of resin is higher in the case of a polymethacrylic acid resin than it is in that of a polystyrenesulphonic acid resin. Consequently Amberlite IRC 50 has a higher ion exchange capacity per gram of resin than either of the two sulphonic acid resins. No significant decrease in the capacity for a given cation with increasing cross-linking was observed in the case of the two differently cross-linked sulphonic acid resins used in this work, though Hale et al [63] have reported such an effect in the case of the capacities of sulphonated polystyrenes of varying D.V.B. content for various quaternary ammonium ions.

No significant anomalous capacities were observed in this work. The capacities of each resin for the sodium and lanthanum ions were very similar. In each case, the capacities for the trivalent cations were found to decrease slightly with decreasing crystallographic radius of the ion. This may be due to the ionic sieve effect coming into play to some extent, since the order of the hydrated sizes of the trivalent cations will be the reverse of the order of their crystallographic radii (see Section 5.4.1.), and thus the order of decreasing capacity is that of increasing size of the hydrated ions. This is understandable in the case of the sulphonic acid resins where the ions are taken up in their hydrated states (see Section 5.4.2.), but is, perhaps, surprising in the case of the carboxylic acid resin, Amberlite IRC 50, in which ions appear to be present in the unhydrated state in the resin phase (see Section 5.4.2.).

There appears to be no uptake of complexes of the type, $M(OH)^{2+}$, where M= trivalent cation, as reported by Arnold[8] and observed by Hanley[17] in his determinations of the capacity of Zeo-Karb 225 for lanthanum. On the basis of his results, Hanley proposed that approximately two-thirds of the lanthanum on the resin was trivalent, each atom occupying 3 resin sites, and one-third was divalent, with each hydroxo-lanthanum complex occupying 2 resin sites. However, no such effect was observed in the present work with any of the resins and, in agreement with Arnold[14], it may be concluded that hydroxo-complexes of the trivalent cations do not play a part in exchange processes involving the Na-forms of the resins in aqueous solutions of the nitrates of the trivalent metals.

CHAPTER 4

SWELLING DETERMINATIONS

4.1. Introduction

As has been explained in Section 1.3., when an ion exchange resin is placed in a solution it tends to swell until the solvation tendency of the ionogenic groups is balanced by the tension in the resin cross-links. The phenomenon of swelling is a complex one involving a great many factors, the main factors tending to favour an increase in swelling being :

1) Low degree of cross-linking of the resin.
2) High capacity of the resin.
3) Polar solvents.
4) Strong solvation tendency of the fixed ionic groups.
5) Large and strongly solvated counter-ions.
6) Low valence of the counter-ions.
7) Complete dissociation of the ionic groups in the resin.
8) Low concentration of the external solution.

Various theories and models have been developed in an attempt to explain the influence of one or more of the above factors in any particular ion exchange system. Unfortunately, there is no known theory which can take account of all the factors simultaneously, as the importance of the factors in governing swelling varies from case to case. The various theories which have been put forward have been reviewed fairly recently by Helfferich[67] and by Högfeldt[68]. The many widely differing approaches may be broadly divided into two main types : Those based on rigorous abstract thermodynamics, and those based on ion exchange models. The former type are universally applicable to ion exchangers of every conceivable structure, but for practical purposes, their value is limited because, although these treatments give a rigorous description of ion exchange equilibria and require no models with particular assumptions, they provide little insight into the physical causes for the behaviour of the systems. Consequently they will not be discussed in this thesis.

Ion exchange models, with particular properties resembling those of ion exchangers, have been introduced with the object of deriving equations which reflect the action of various physical forces on the ion exchange process. With such models, the effects of particular properties on the behaviour of a system can be analysed. However, the relationships derived from specific models are meaningful only when the pertinent properties of the actual system are adequately represented by the model. Several different ion exchange models will be cited in this thesis.

One of the first ion exchange models to be introduced was that of Gregor[69]. According to this model, the matrix of a resin is considered as a network of elastic springs. Gregor et al[70] later put forward a refined model in which electrostatic interactions were included. This model pictures the ion exchange resin as a series of parallel planar plates carrying a uniform electric charge on their surfaces; the plates are interconnected by elastic springs. Gregor's model is very effective in explaining the trends in swelling observed with the alkali metals on sulphonic acid resins, viz. $Li^+ > H^+ > Na^+ > K^+ > Rb^+ > Cs^+$, where the dominant factor appears to be the size of the solvated alkali metal ion, with the other factors known to affect swelling playing only a minor role.

The elasticity of the springs in Gregor's models is purely mechanical and both models may be called <u>macroscopic</u>, as they do not involve the single ion as a discrete particle. Other models, which may be called <u>molecular</u>, are of a different type, and those of Katchalsky[71,72] and Rice and Harris[73,74] may be cited as typical. In both these models the matrix is represented by cross-linked chains consisting of rigid, rod-shaped segments, each segment carrying one ionogenic group. The elasticity of the matrix is due to the increase in entropy which accompanies coiling of the chains. Both models also include electrostatic forces, in particular the repulsion between neighbouring fixed ionic groups. Rice and Harris consider interactions only between nearest neighbours, without differentiating between groups on the same chain and those on adjacent chains. However in Katchalsky's treatment, which is restricted specifically to weakly cross-linked resins, interactions between all groups on one and the same chain are calculated, whereas interactions between neighbouring chains are disregarded. Another difference between these two approaches is that the Rice and Harris model includes the phenomenon of ion-pair formation, whereas Katchalsky's does not. The model of Rice and Harris explains the swelling sequence observed with the alkali metal ions on a sulphonic acid resin by the fact that those ions having a smaller Debye-Huckel parameter, a^o, can approach the ionogenic groups more closely and therefore form stronger bonds; the resulting high degree of association in the resin leads to a decrease in electrostatic repulsion between the fixed ionic groups, which is accompanied by greater coiling of the chains and hence lower swelling.

These three models are useful in showing how different theories can account in different ways for the observed effects of factors known to affect swelling. Several other models will be mentioned in Sections 4.4. and 5.4. in order to explain the swelling and selectivity results obtained in the present work. The behaviour of ion exchangers in general depends on factors of an almost overwhelming variety, and although different theories when applied to the same phenomenon may well attribute the observed effect to quite different physical forces, they can hardly be classified as 'correct' or 'incorrect', but rather as 'complementary' rather than 'contradictory'.

4.2. Experimental

The weight-swelling of an ion exchange resin in a given solvent is defined as the weight of solvent sorbed by 1 gram of dry resin. Several methods for the determination of this property are described in the literature. These various methods, their precision and limitations have recently been very comprehensively reviewed by Hanley[17], who has classified the various methods into two basic types of approach :

1) Those methods which attempt to obtain a clean separation of the solution from the resin;
2) Those methods which attempt to measure the amount of external solution sorbed by the resin, without separation of the resin phase from the solution phase.

Gregor, Held and Bellin[75] employed suction drying, blotting and centrifugation techniques to achieve clean separation of resin from solution phase. The centrifugation method was later improved by Pepper, Reichenberg and Hale[45] and by Scatchard and Anderson[76]. In this method a known weight of dry resin is equilibrated with the solvent and then centrifuged to constant weight in a sintered-glass filter tube supported in a centrifuge tube, closed with a rubber cap to prevent evaporation of the solvent. From the final weight of the wet resin and and the initial weight of the dry resin, the weight of solvent sorbed by the resin can be found. A control experiment with glass beads of mean size equal to that of the resin particles is usually carried out to correct the final weight of the wet resin for the weight of residual solvent clinging to the surface of the resin particles after centrifugation.

In the second type of approach complete separation is not essential, as the solution phase, and not the resin phase, is analysed after equilibration. One technique of this type is the method of negative absorption, in which the increase in concentration of a reference substance in the external phase, due to loss of solvent from the external phase as a result of sorption by the resin, is determined. Pepper et al[45] measured the uptake of solvent colorimetrically by determining the change in concentration of the acidic dyestuff, Chlorazol Sky Blue FF (Colour Index No. 518), whereas Arnold et al[77] determined weight-swelling polarimetrically by measuring the increase in concentration of an optically active reference solute, methyl α - D - glucopyranoside. The second technique in this group is that of dilution. This technique is basically exactly opposite in principle to the negative absorption method and has three main advantages over this method; namely, that one of the ions already present in the external solution may be used as the reference substance, that the concentration difference can be made very large and that it is not necessary to dry the resin first.

In the present work, where the weight-swellings of the trivalent cationic forms of the three resins in aqueous monoethanolamine of varying composition were determined, the method of centrifugation was unsuitable for two reasons. Firstly, in introducing the resin sample into the filter tube, after equilibration with the solvent, it would be difficult to avoid exposure to the atmosphere, and since monoethanolamine tends to absorb atmospheric moisture, this would lead to high results, particularly where solvents of low water content are concerned. Secondly, the high viscosity of monoethanolamine would necessitate centrifuging the wet resin samples for several hours at 400 g, which would be inconvenient. In view of these difficulties, the centrifugation method was not used in the swelling determinations in the present work. Instead, the negative absorption method used by Arnold et al [77] and Macintosh[9] was employed.

The rotation due to an optically active substance in solution depends upon the length of the polarimeter tube, the wavelength of light used, the concentration of the solution, the nature of the solvent and the temperature of the solution. To take account of all these variables, rotation is usually recorded as the <u>specific rotation</u>, $[\alpha]_D^{25}$, which is defined as the rotation in degrees due to a solution of concentration 1 gram per 100 ml in a 1dm polarimeter tube, the solution being at a temperature of 25°C and monochromatic sodium D light being used, whence

$$[\alpha]_D^{25} = \frac{100 \cdot (\alpha)_D^{25}}{c \cdot l}$$

where, $(\alpha)_D^{25}$ = observed optical rotation at 25°C with sodium D light

c = concentration of optically active solute in g/100 ml

1 = length of polarimeter tube in dm

A Bellingham and Stanley Model A polarimeter and a micropolarimeter tube of length 0.5 dm, with a volume capacity of approximately 2 ml, were used in this investigation. Each polarimeter reading used in the subsequent calculations of weight-swelling was the mean of twenty separate readings and was considered accurate to 0.01°.

Corrections for solvent effect were carried out by determining the polarimetric readings of water, monoethanolamine and various mixtures of these two solvents, in the absence of the glycoside, under the same conditions as were used in the swelling determinations. In this case, the solvent effect was found to be the same over the entire range of solvent composition studied, and the true rotations were obtained by merely subtracting the blank polarimeter values from the observed values.

The methyl α - D - glucopyranoside used in this work was supplied by the British Drug Houses, Ltd., Poole, England. Before use it was dried to constant weight over P_2O_5 at 60°C under reduced pressure and stored in a vacuum desiccator over P_2O_5. The manufacturers claim a specific rotation, $[\alpha]_D^{20}$ of +157° to + 159°. The literature values of the specific rotation of methyl α - D - glucopyranoside vary to a certain extent. Heilbron[78] records $[\alpha]_D^{20}$ = + 158.9°, International Critical Tables give $[\alpha]_D^{16}$ = + 157.9° and Arnold et al[77] found $[\alpha]_D^{25}$ = + 158.7°. In the present work a value of + 158.8° was found for $[\alpha]_D^{25}$ in water, monoethanolamine and in various mixtures of these solvents. This constancy of $[\alpha]_D^{25}$ in solvents of differing composition is somewhat unusual, but in agreement with the findings of Macintosh[9], and was one of the reasons for choosing methyl α -D-glucopyranoside as the reference solute for this work. Other reasons for its choice were that it has a high specific rotation, which facilitates detection of small changes in concentration, and that it does not undergo mutarotation.

Jones et al[79] have reported the absorption of carbohydrates on ion exchange resins, and caution must therefore be exercised in choosing a reference solute for swelling determinations by the polarimetric method, since sorption of the reference solute by the resin to any appreciable extent, will render this method useless. Macintosh[9] has shown conclusively that no appreciable sorption of methyl α -D-glucopyranoside by the resins, Amberlite IRC 50, Amberlite IR 120 and Zeo-Karb 225 takes place under the conditions used in this work. She found that the amount of glycoside taken up by the resin did not exceed 1% of that present in the external solution, so that sorption of this reference solute by the resins will not affect the polarimeter readings to any appreciable extent.

Any hydrolysis of the glycoside to glucose will also markedly affect results obtained by the polarimetric method. As acid conditions favour hydrolysis, this is most likely to occur where strong acid resins are used in solutions of low monoethanolamine content, the tendency being greatest where these resins are used in pure water, under which conditions the acidic strength of the system is at a maximum. This aspect was thoroughly investigated in the present work by means of an iodometric method[80]. The aqueous solutions, which had been equilibrated with ten of the strong acid resin samples used in the swelling determinations, were added to 20 ml aliquots of a standard copper sulphate solution and the concentration of the cupric ion was then determined in each case by the addition of excess KI solution and titration of the liberated iodine against a standard sodium thiosulphate solution, using starch solution, containing potassium thiocyanate to release adsorbed iodine, as indicator. The procedure was then repeated with a further 10 samples of the standard $CuSO_4$ solution, but in this case no filtrates from the resin samples used in the swelling determinations were added. Hydrolysis of the glycoside to glucose will lower the titre values in the first batch of titrations, as the glucose so produced will reduce the copper from the cupric to the cuprous state, and consequently decrease the amount of iodine liberated on addition of excess KI solution. However, no lowering of the titre values was observed, indicating that no appreciable hydrolysis of the glycoside occurred under the conditions used in the swelling determinations in this work.

Macintosh[9] and Pepper et al[45] have found good agreement between swelling results obtained by both the centrifuge and negative absorption methods under exactly the same conditions, which indicates that the accuracy of the negative absorption method is satisfactory. The polarimetric method was thus considered suitable for use in the swelling determinations in the present work.

Procedure

The method requires fairly large quantities of resin and small volumes of solvent, so that the effect of sorption of solvent on the rotation of the solution phase will be sufficiently pronounced to be determined accurately. Consequently, 0.5 gram samples of dry resin were equilibrated with 5 ml portions of a 1% solution of methyl α-D-glucopyranoside in the solvent under consideration. In each case the resin was shaken with the solution in an air-tight flask under dry, CO_2-free nitrogen on a mechanical shaker at 25°C for at least a week. After equilibration the solution phase was transferred to the polarimeter tube and the rotation of the solution measured. The concentration of the glycoside in the external solution at equilibrium was calculated from the value found for the rotation of the solution. From this result, together with the initial concentration of the glycoside in the solution, the loss of solvent from the external phase was calculated, and from the initial weight of dry resin, the weight-swelling of the resin in the particular solvent could be found.

In addition to the solvent uptake, the composition of the external solution was determined in each case. Before the supernatant solution was transferred to the polarimeter tube, three 0.5 ml aliquots were removed, weighed, placed in flasks containing approximately 25 ml of distilled water and kept for solvent analysis by the method described in Section 2.4.2..

The weight-swellings of the lanthanum, neodymium and yttrium forms of the resins, Amberlite IRC 50, Amberlite IR 120 and Zeo-Karb 225, in eight monoethanolamine/water mixtures, ranging from 7% to 100% by weight of water, were determined in this work. The swelling of the resins in solvents of monoethanolamine concentration higher than 93% by weight was not determined because of the extremely slow rates of equilibration at these solvent compositions.

4.3. Results

Tables 2-4 show the values obtained for the weight-swelling of the different cationic forms of the three resins in monoethanolamine/water mixtures of various composition. In all cases the total solvent uptake has been calculated relative to 1 gram of dry resin in the H-form, so that the swellings of the resins in the different ionic forms might be compared. Each weight-swelling result tabulated is the mean value obtained from four separate determinations under the same conditions, and these figures correspond to the points plotted in Figs. 1-3. However, the curves shown in these figures represent those obtained from a computer by applying the method of least squares to all the swelling results obtained in this work, not to the means alone. The results are considered accurate to 8%, which is much higher than the 2% error quoted by Macintosh[9] in using the same method for the alkali metal forms of these resins in the same solvent mixtures. However, this larger percentage error is probably due to the lower degrees of swelling of the resins in the trivalent forms.

TABLE 2A

Uptake of solvent by La-form of Amberlite IRC 50 at various solvent compositions.

EQUILIBRIUM H_2O CONTENT OF EXTERNAL PHASE		TOTAL SOLVENT UPTAKE (g per g dry H-form resin.)
Wt. %	X_{H_2O}	
7.31	0.211	0.41
10.6	0.286	0.46
17.3	0.415	0.54
25.4	0.536	0.65
43.3	0.721	0.81
61.8	0.846	0.90
80.9	0.935	0.96
100	1.000	1.07

TABLE 2B

Uptake of solvent by Nd-form of Amberlite IRC 50 at various solvent compositions.

EQUILIBRIUM H_2O CONTENT OF EXTERNAL PHASE		TOTAL SOLVENT UPTAKE (g per g dry H-form resin.)
Wt. %	X_{H_2O}	
7.43	0.214	0.36
10.8	0.290	0.39
17.8	0.424	0.47
25.7	0.540	0.56
43.6	0.724	0.71
62.2	0.848	0.78
81.2	0.936	0.83
100	1.000	0.95

TABLE 2C

Uptake of solvent by Y-form of Amberlite IRC 50 at various solvent compositions.

EQUILIBRIUM H_2O CONTENT OF EXTERNAL PHASE		TOTAL SOLVENT UPTAKE (g per g dry H-form resin.)
Wt. %	X_{H_2O}	
7.31	0.211	0.32
10.8	0.290	0.35
18.0	0.427	0.42
26.0	0.543	0.53
43.8	0.725	0.63
61.7	0.845	0.74
81.4	0.937	0.79
100	1.000	0.88

TABLE 3A

Uptake of solvent by La-form of Amberlite IR 120 at various solvent compositions.

EQUILIBRIUM H_2O CONTENT OF EXTERNAL PHASE		TOTAL SOLVENT UPTAKE (g per g dry H-form resin.)
Wt. %	X_{H_2O}	
7.48	0.215	0.35
11.0	0.295	0.37
17.0	0.410	0.39
25.9	0.542	0.42
43.3	0.721	0.46
62.4	0.849	0.49
81.2	0.936	0.51
100	1.000	0.52

TABLE 3B

Uptake of solvent by Nd-form of Amberlite IR 120 at various solvent compositions.

EQUILIBRIUM H_2O CONTENT OF EXTERNAL PHASE		TOTAL SOLVENT UPTAKE (g per g dry H-form resin.)
Wt. %	X_{H_2O}	
7.23	0.209	0.33
10.7	0.289	0.35
17.0	0.410	0.37
25.8	0.541	0.40
43.5	0.723	0.46
61.7	0.845	0.49
80.7	0.934	0.51
100	1.000	0.53

TABLE 3C

Uptake of solvent by Y-form of Amberlite IR 120 at various solvent compositions.

EQUILIBRIUM H_2O CONTENT OF EXTERNAL PHASE		TOTAL SOLVENT UPTAKE (g per g dry H-form resin)
Wt. %	X_{H_2O}	
7.35	0.212	0.28
10.7	0.288	0.30
16.8	0.407	0.32
25.7	0.540	0.36
43.5	0.723	0.44
62.2	0.848	0.50
81.7	0.938	0.53
100	1.000	0.56

TABLE 4A

Uptake of solvent by La-form of Zeo-Karb 225 at various solvent compositions.

EQUILIBRIUM H_2O CONTENT OF EXTERNAL PHASE		TOTAL SOLVENT UPTAKE (g per g dry H-form resin.)
Wt. %	X_{H_2O}	
7.39	0.213	0.31
10.8	0.290	0.33
16.6	0.402	0.36
26.4	0.549	0.39
43.4	0.722	0.45
62.4	0.849	0.55
81.4	0.937	0.65
100	1.000	0.69

TABLE 4B

Uptake of solvent by Nd-form of Zeo-Karb 225 at various solvent compositions.

EQUILIBRIUM H_2O CONTENT OF EXTERNAL PHASE		TOTAL SOLVENT UPTAKE (g per g dry H-form resin.)
Wt. %	x_{H_2O}	
7.27	0.210	0.30
10.6	0.287	0.31
16.6	0.403	0.33
25.5	0.537	0.37
44.4	0.730	0.45
62.2	0.848	0.57
81.4	0.937	0.67
100	1.000	0.72

TABLE 4C

Uptake of solvent by Y-form of Zeo-Karb 225 at various solvent compositions.

EQUILIBRIUM H_2O CONTENT OF EXTERNAL PHASE		TOTAL SOLVENT UPTAKE (g per g dry H-form resin.)
Wt. %	x_{H_2O}	
7.48	0.215	0.27
10.8	0.292	0.28
16.7	0.404	0.31
25.6	0.538	0.36
43.8	0.725	0.44
62.6	0.850	0.57
81.4	0.937	0.69
100	1.000	0.79

FIG 1

Variation of weight-swelling with water content of external phase

AMBERLITE IRC 50

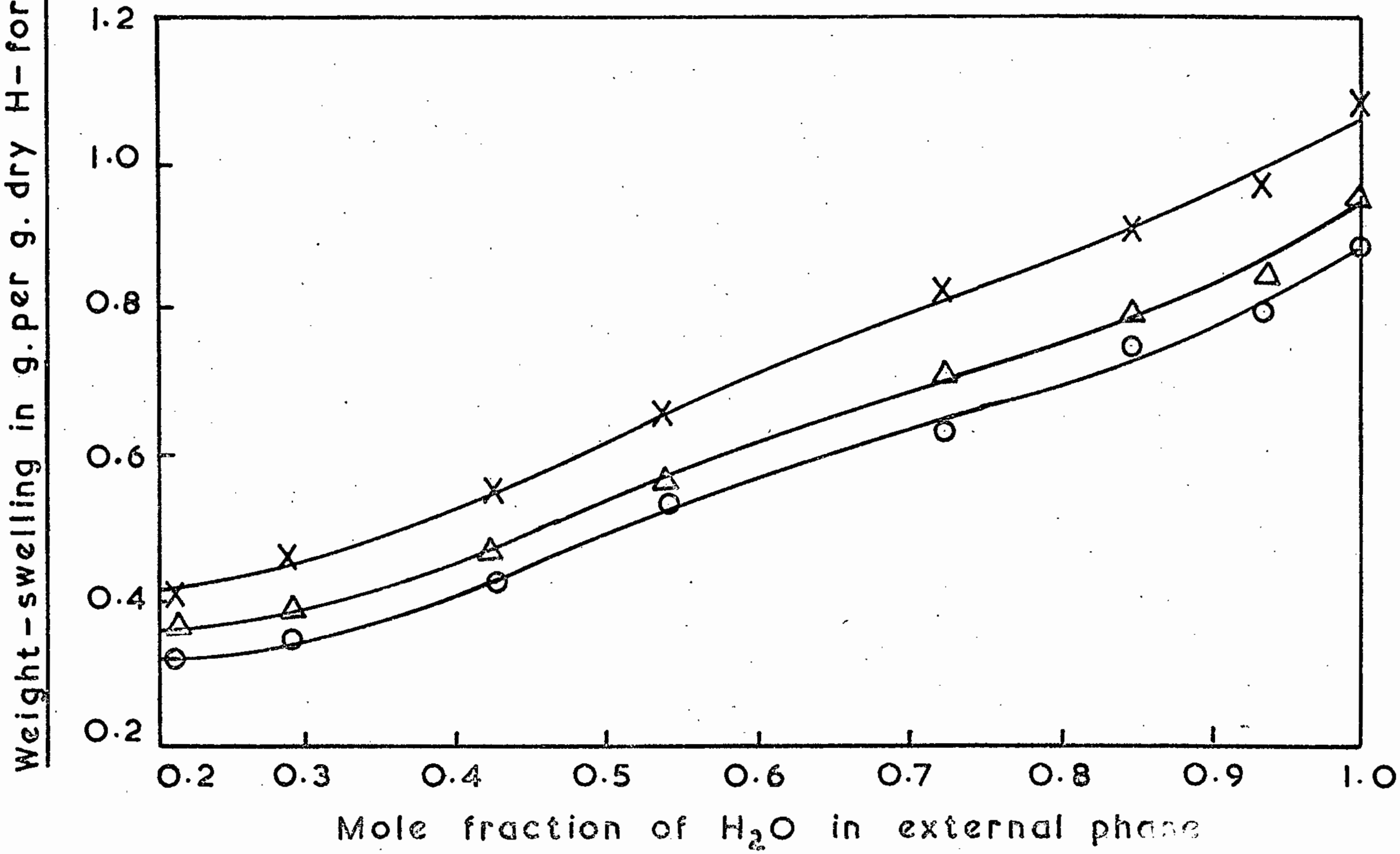


FIG. 2

Variation of weight-swelling with water content of external phase

AMBERLITE IR 120

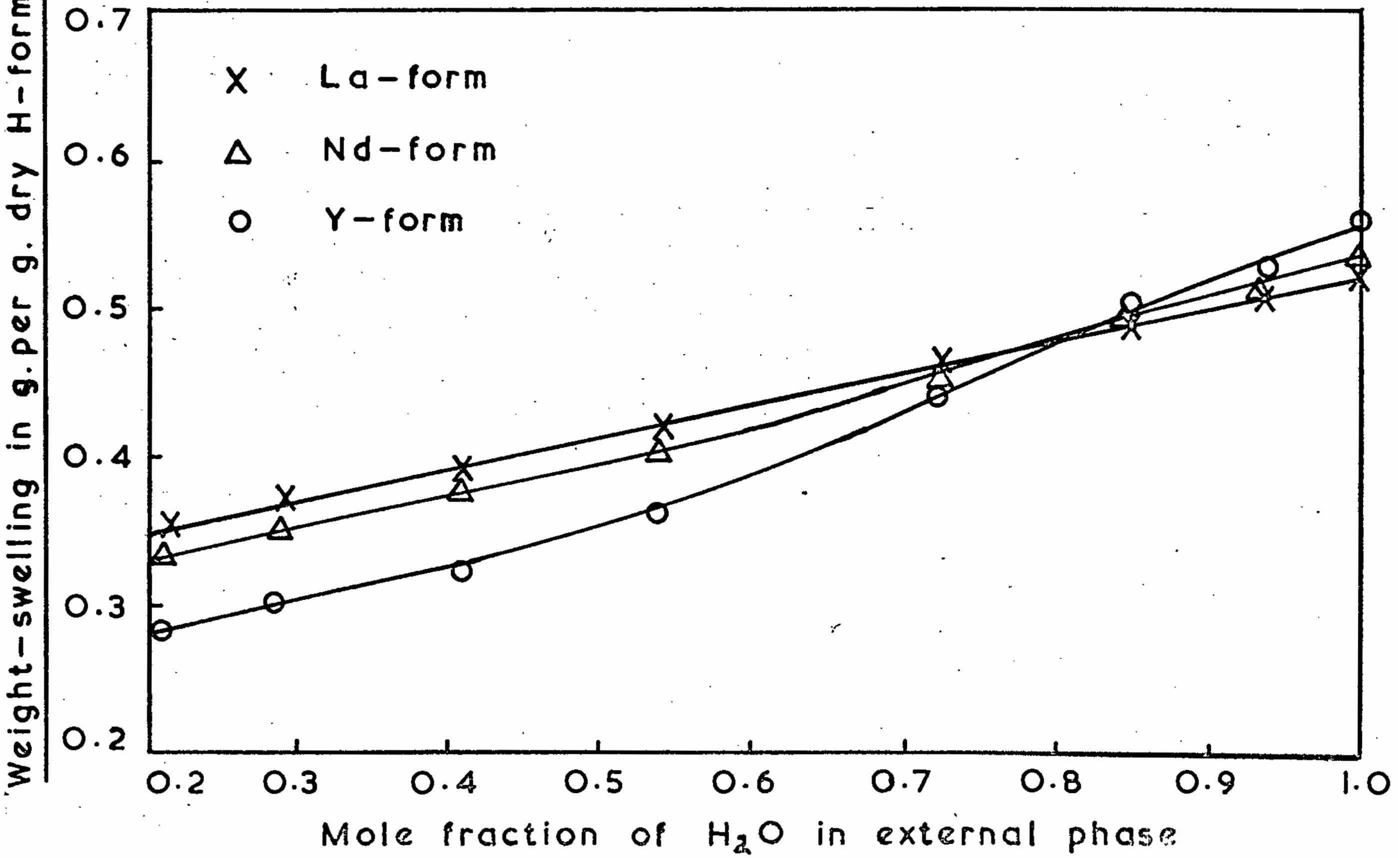
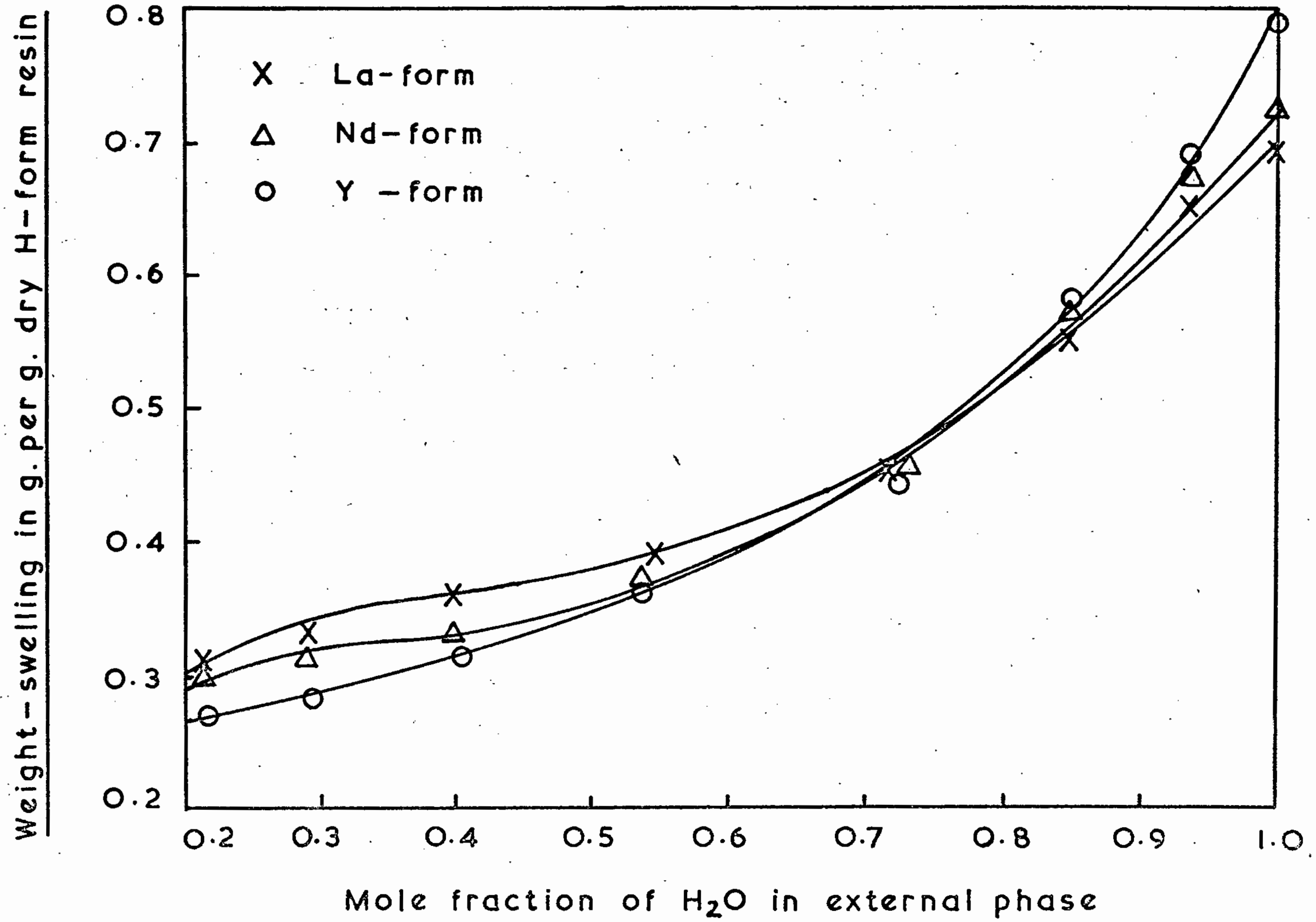


FIG. 3

Variation of weight-swelling with water content of external phase

ZEO-KARB 225 (4-5% D.V.B.)



4.4. Discussion

From the results in Tables 2-4, it can be seen that in all the ionic forms studied, the carboxylic acid resin has a higher weight-swelling at a given solvent composition than either of the sulphonic acid resins; this holds over the entire range of solvent composition investigated. The reason for this is that the carboxylic acid resin, having a higher capacity than the sulphonic acid resins, contains ions in higher concentration in the resin phase, so that the liquid in the resin pores has a greater tendency to dilute itself, and swelling is therefore more pronounced[81].

4.4.1. Effect of composition of external phase on swelling of resins

The effect of the monoethanolamine content of the external phase on the weight-swelling of the three resins in the various trivalent ionic states is shown in Figs. 1-3. In all cases, the swelling of the resins decreases as the monoethanolamine content of the external phase increases. This is in accordance with the results obtained by other workers for the swelling of resins in various salt forms in mixed solvents[1,2,9,25-27,34-39,82,83].

Several effects are believed to be operative in bringing about this deswelling of the resins on addition of increasing amounts of monoethanolamine to the medium. Firstly, a decrease in the solvation tendency of the fixed ionic groups and counter-ions on the resin may be expected to accompany an increase in the monoethanolamine concentration of the solvent. Solvation is governed by the relative strengths of the forces of interaction between the ions and the solvent molecules and those between the solvent molecules themselves. Since strong intermolecular forces are believed to exist in monoethanolamine[23], ion-dipole forces between the ions and the monoethanolamine molecules will tend to be weak. An increase in the concentration of monoethanolamine in the solvent will thus cause a decrease in solvation and consequently in swelling.

Lowering of the dielectric constant of the ambient medium by the addition of monoethanolamine causes an increase in ion-pair formation (see Section 5.4.1.). Gregor[27,47] has attributed the decrease in swelling accompanying an increase in the concentration of the non-aqueous component of a mixed solvent to increased ion-pair formation between resin anions and counter-ions. This ion-pairing gives rise to a decrease in the number of osmotically active ions in the resin, and swelling, which depends on the osmotic pressure difference between the resin and solution phases, will therefore tend to be reduced as the dielectric constant of the ambient medium decreases.

The degree of swelling of a resin also depends on the electrostatic repulsions between neighbouring fixed ionic groups and between charged resin chains, i.e. the electrostatic potential of the polymer chains[74,84]. In media of high dielectric constant, such as water, where there is little association between resin anions and counter-ions, the polymer chain develops a high potential, owing to the large number of ionized resin groups which interact electrostatically with one another. The resin swells in order to decrease the concentration of ionized groups and thus lower the chain potential. If the dielectric constant of the medium is lowered by the addition of monoethanolamine, ionic association between the resin anions and the counter-ions increases, with a resulting decrease in chain potential; the swelling of the resin therefore decreases.

The effect of electrostatic repulsion between fixed charges, which becomes stronger on lowering the dielectric constant[73], provided that the charges are not neutralised by association with counter-ions, causes swelling to increase as the concentration of the non-aqueous component is increased. As mentioned in Section 1.4., Ilsley[18] found that this effect strongly influenced the swelling behaviour of Zeo-Karb 225 in various single divalent ionic forms in pyridine/water mixtures of varying composition. In the present work, however, no increase in swelling with increasing monoethanolamine content of the solvent was observed over any range of solvent composition. It must be concluded, therefore, that the other effects mentioned were predominant at all solvent compositions.

4.4.2. Effect of counter-ion associated with resin on swelling of resins

The counter-ion associated with a resin influences the swelling to a marked extent. In the case of the carboxylic acid resin, the swelling of the different ionic forms studied decreases in the order

$$\text{La-form} > \text{Nd-form} > \text{Y-form}$$

over the entire range of solvent composition investigated. The swelling increases as the crystallographic radius of the counter-ion increases.

In the case of the sulphonic acid resins, however, the swelling behaviour in aqueous monoethanolamine of high monoethanolamine content is completely different from that in water. In water the swelling of the various ionic forms studied decreases in the order

$$\text{Y-form} > \text{Nd-form} > \text{La-form}$$

but in media of high monoethanolamine content the order is reversed. In solvent mixtures of low water content the swelling of the various ionic forms of a sulphonic acid resin follows the sequence of increasing crystallographic radius of the counter-ion, whereas in media of high water content the swelling of the trivalent ionic forms follows the sequence of increasing solvated ionic radius (see Section 5.4.1.), as found by several other workers[11,29,45,47,85].

Thus the critical factors governing the extent of swelling of the various ionic forms of the resins are the ionic size or solvated ionic size of the counter-ion, and variations in these cause differences in swelling by virtue of changes in the effects of the solvation tendencies of the fixed ionic groups and counter-ions, osmotic differences between resin and solution phases, and electrostatic repulsions.

It can be seen from Figs. 3 and 4 that the swelling curves for the different ionic forms of a given sulphonic acid resin cross one another; for both sulphonic acid resins studied this occurs when the mole fraction of water in the external phase lies between 0.80 and 0.84. Macintosh[9], who studied the swelling of the alkali metal forms of the same two sulphonic acid resins in aqueous monoethanolamine, found that these cross-overs of the swelling curves took place at single points, the reversal occurring when the mole fraction of water in the external phase was 0.79 in the case of the 4-5% D.V.B. resin, and at 0.83 for the 12% D.V.B. resin. The similarity between these reversal points and those found in the present work is quite remarkable, especially in view of the much lower degrees of swelling of the trivalent cationic forms studied in the present work.

This low degree of swelling of the trivalent cationic forms of the three resins is probably due to an increase in association between counter-ions and resin groups, giving rise to a low chain potential [74,84], and to a decrease in the amount of 'free' solvent, i.e. solvent not in the form of solvation shells within the resins. The tendency to take up free solvent depends on the number of counter-ions in the resin phase, and this number is divided by 3 when univalent counter-ions are replaced by trivalent ones[87].

Since the swelling of a resin gives an indication of the degree of interaction between the resin anions and the counter-ions, the above results suggest that sulphonic acid resins may show an affinity reversal in aqueous monoethanolamine. However, though this was found to be the case with the univalent cationic forms of these resins[9], it was not observed in the present work (see Chapter 5).

4.4.3. Effect of cross-linking on swelling of sulphonic acid resins

A comparison of Figs. 2 and 3 shows that in media of high water content the 4-5% D.V.B. sulphonic acid resin is much more swollen than the 12% D.V.B. resin under the same conditions. This increase in swelling with decreasing cross-linking, which has been noted in previous work[9,29,45,47], may be attributed to the increase in the flexibility of the resin matrix which must accompany a decrease in cross-linking[45,47,87,88]. A similar trend of decrease in swelling with increase in cross-linking has also been demonstrated for polymethacrylic acid resins of varying D.V.B. content[46,64].

However, in media of high monoethanolamine content, where neither resin swells to a marked extent, the more highly cross-linked resin is the more swollen at a given solvent composition and in a given ionic form. Similar behaviour has previously been observed by Sundheim et al[88] and Macintosh[9]. This unusual swelling behaviour in media rich in monoethanolamine, where the dielectric constant is low, may be attributed to the effect of association between the polymer chains, which is greater in the case of the 4-5% D.V.B. resin than in that of the 12% D.V.B. resin, since the polymer chains are held further apart in the resin of higher cross-linking. Under these conditions, this effect predominates over the restrictive effect of cross-linking on the swelling of the two sulphonic acid resins, so that the resin of higher cross-linking will be more swollen. When the dielectric constant of the medium has risen sufficiently to enable both resins to swell appreciably, so that cohesion between the polymer chains is overcome, the 4-5% D.V.B. resin will swell more than the 12% D.V.B. resin under the same conditions.

Sundheim et al[88] and Macintosh[9] found that the water vapour sorption curves and the swelling curves, respectively, for the univalent cationic forms of the same two differently cross-linked sulphonic acid resins as were used in the present work, crossed when the relative humidity (Sundheim et al) or the mole fraction of water in the external phase (Macintosh) was in the region of 0.35 in all cases, when the resins were in the same ionic forms. The resin of lower cross-linking was less swollen than the more highly cross-linked resin at values below this, while at higher values the reverse was the case. Further, both sets of data indicated that the total number of moles of solvent sorbed per equivalent of resin at the cross-over point was approximately 3 for all ionic forms. It appears, therefore, that the sorption of 3 moles of solvent per equivalent of resin is necessary to overcome the effect of differences in cohesion between these two resins; when this amount of solvent has been taken up, the polymer chains have been forced so far apart that the restrictive effect of cross-linking on swelling just balances the effect of interaction between the polymer chains.

In the present work, however, the swelling curves for the two differently cross-linked sulphonic acid resins in the various trivalent ionic forms were found to cross when the mole fraction of water in the external phase was in the region of 0.7 in all cases. This is probably due to the fact that the number of trivalent cations in the resin phase is only one-third of the number of univalent cations on the resin in a univalent ionic form, giving rise to stronger polymer-polymer interactions and lower degrees of swelling. Consequently, the dielectric constant must rise to a higher value to permit sufficient solvent to be sorbed for the restrictive effect of cross-linking to predominate over the interactions between the polymer chains.

Gregor[69,85] suggested that some of the solvent present in the resin phase is 'bound' solvent, i.e. solvent bound by ion-dipole forces to the various ions present, while the rest is 'free' solvent, taken up as a result of the osmotic activity of the resin and not attached to any of the ions present in the resin phase. When the resin swells, work must be done against the elastic forces of the polymer network, and as a result of this, the increase in volume is not as great as it would otherwise have been, since some of the 'free' solvent is excluded from the resin phase. The elastic forces of the polymer network, and hence the amount of 'free' solvent excluded from the resin phase, increase as the cross-linking of the resin increases. The swelling of resins of high cross-linking should therefore vary less than that of resins of low cross-linking in solutions of varying solvent composition. This has been found to be the case with univalent cationic forms of differently cross-linked sulphonic acid resins[9,45].

It can be seen from Figs. 2 and 3 that the effect of varying the water content of the external phase on the swelling of the various trivalent ionic forms of the 12% D.V.B. sulphonic acid resin is not as pronounced as it is in the case of the 4-5% D.V.B. resin. However, whereas Reichenberg et al[45] and Macintosh[9], working with univalent ionic forms of these resins, found that at any given solvent composition the swelling varied less from one ionic form to another in the case of the more highly cross-linked resin, in the present work, where the trivalent ionic forms were involved, this was found to be so only over a certain range of solvent composition. This difference in behaviour is probably due to variations in the amounts of 'free' solvent within the resins. Glueckauf[89] has shown that the association of almost all water molecules with univalent cations in polystyrene sulphonates is very loose and not related to the co-ordination number of the ions, i.e. most of the sorbed solvent is 'free' solvent. However, in the case of the trivalent cations, the extent of solvation is much greater (see Section 5.4.1.), so that the amount of 'bound' solvent in the resin phase is greater and the amount of 'free' solvent correspondingly less. The effect of exclusion of 'free' solvent from the resin phase will therefore not be as great as in the case of the univalent cationic forms of the resins. The swelling of the trivalent forms of both the differently cross-linked sulphonic acid resins will vary less than that of the univalent ionic forms of the same resins over the range of solvent composition investigated, and in this respect no great difference in the behaviour of the two sulphonic acid resins will be observed.

CHAPTER 5

SELECTIVITY DETERMINATIONS

5.1. Introduction

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

$$qR_p A^{p+} \; + \; pB^{q+} \rightleftharpoons pR_q B^{q+} \; + \; qA^{p+}$$

where R = resin group
A = counter-ion
B = cation originally in the solution phase
p,q = valencies of cations A and B, respectively

As represented in the above equation, ion exchange is a reversible process in most cases, the position of equilibrium depending to a marked extent on the nature of the cations, A and B, on the resin employed and on the nature of the ambient medium. The resin usually exhibits some degree of preference for one ion relative to the other, even when the two ions are present in equivalent proportions – this is the phenomenon of selectivity.

The selectivity of an ion exchange resin in a particular system is usually expressed by means of the so-called selectivity coefficient, which for the above equilibrium is given by :

$$K_A^B = \frac{\left[\overline{B^{q+}}\right]^p \cdot \left[A^{p+}\right]^q}{\left[B^{q+}\right]^p \cdot \left[\overline{A^{p+}}\right]^q}$$

where $[\overline{A^{p+}}]$, $[\overline{B^{q+}}]$ = concentrations of the cations in the resin phase at equilibrium

$[A^{p+}]$, $[B^{q+}]$ = concentrations of the cations in the solution phase at equilibrium

If two counter-ions of different valence are involved, the numerical value of the selectivity coefficient depends upon the concentration scale used.

The preference of the ion exchanger for one of the two counter-ions is often expressed by the practical selectivity coefficient (or separation factor), which for the above equilibrium is defined by :

$$k_A^B = \frac{[\overline{B^{q+}}] \cdot [A^{p+}]}{[B^{q+}] \cdot [\overline{A^{p+}}]}$$

If the cation B is preferred, then the factor k_A^B is greater than unity, if not, the factor is less than unity. The practical selectivity coefficient, like the selectivity coefficient, is usually not constant but depends on the total concentration of the solution, the temperature and the proportion of the two cations on the resin. These two factors, K_A^B and k_A^B , are equal only when the equilibrium is restricted to univalent cations, otherwise, they differ; for example, if the two counter-ions involved are trivalent, then $K_A^B = (k_A^B)^3$. The numerical value of the practical selectivity coefficient is dimensionless and not affected by the choice of concentration units; for this reason, and because more practical results are obtained in this way, all selectivities given in this thesis are reported as practical selectivity coefficients.

The preference of an ion exchanger for one of two counter-ions can also be expressed by two other means; namely, the thermodynamic equilibrium constant, Ka, and the corrected selectivity coefficient, $K'_{B/A}$, which for the above equilibrium are defined by :

$$Ka = K_A^B \times \frac{\bar{\gamma}_B \, . \, \gamma_A}{\gamma_B \, . \, \bar{\gamma}_A}$$

$$\text{and} \quad K'_{B/A} = K_A^B \left(\frac{\bar{\gamma}_A}{\bar{\gamma}_B} \right)$$

for the case of two univalent cations, A and B,

where $\bar{\gamma}_A, \bar{\gamma}_B$ = activity coefficients in the resin phase

γ_A, γ_B = activity coefficients in the solution phase

While activity coefficients of salts in aqueous solution can be determined, the problem of estimating the activity coefficients of the two ions in the resin phase has not yet been overcome. Thus, for practical purposes, K_A^B and k_A^B are used as measures of selectivity rather than Ka and $K'_{B/A}$.

As mentioned in Section 4.1., the phenomena of swelling and selectivity are very complex and to date no really satisfactory theory has been advanced to account for all the factors involved. The complexity of the systems studied in the present work, which involves trivalent cations, 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 in explaining the observed selectivity results. Consequently, in this thesis we shall be concerned mainly with various models which have been put forward to explain particular aspects of ion exchange behaviour. Some of the proposed models have already been mentioned in Chapter 4; several others will be invoked in Section 5.4. in order to explain the selectivity results obtained in the present work.

5.2. Experimental

Since the selectivity of an ion exchange resin varies with the proportion of the two exchanging ions in the resin phase, practical selectivity coefficients for different equilibria are directly comparable only if this proportion is the same in all cases. In this work, it was hoped to determine the practical selectivity coefficients with the two ions present in equivalent proportions in the resin at equilibrium, i.e. $\overline{X}_A = \overline{X}_B = 0.5$, where $\overline{X}$ is the mole fraction of each ion present at equilibrium in the resin phase, and is called the loading of the resin. However, this was not possible in the cases of ion exchange equilibria involving Amberlite IRC 50, initially in the H-form, in water, and of all the equilibria studied in monoethanolamine. The behaviour of the weak acid resin in water was due to its extremely high affinity for the hydrogen ion (see Section 5.4.2.), while that of all the resins in monoethanolamine was due mainly to an ionic sieve effect being brought into play (see Section 5.4.3.), as well as to the limited solubilities of the nitrates of the trivalent metals in monoethanolamine. In the present work, the solubility of these salts was found to be only about one-third of the value of 7.75 g/100g monoethanolamine quoted by Moeller and Zimmerman[22] for the solubility of lanthanum nitrate in monoethanolamine. The solubility of the anhydrous nitrates was closely dependent upon trace quantities of water in the monoethanolamine and therefore, because of the ease with which the latter solvent absorbs water, the results tended to vary, but never approached 7.75g/100g monoethanolamine.

From preliminary experiments, approximate practical selectivity coefficients were estimated, and these values used to calculate the quantities to be used in the final selectivity determinations in order to obtain the required values of the loading, which had to be restricted to $\overline{X}_M = 0.13$ in the case of the weak acid resin in water and $\overline{X}_M = 0.10$ in the case of all three resins in monoethanolamine.

Procedure

A weighed sample of dry resin, approximately 1 m. equiv., was added to 25 ml of a weighed solution containing the calculated weight of the appropriate salt in the required solvent. The resin was then shaken with the solution on a mechanical shaker at 25°C for a week, after which samples of the supernatant liquid were removed and the trivalent metal cation concentrations determined using the method described in Section 2.4.1.. The ionic composition of the resin phase at equilibrium was found by separating the resin from the solution by filtration, centrifuging to remove any adhering solution, eluting the resin with a known volume of 1N HCl and determining the trivalent metal cation concentration in the eluate by the method referred to above. Here, the concentrations of the trivalent cations were determined in both the resin and the solution phases, and the concentrations of the univalent cations calculated by difference.

In the case of the selectivity determinations in monoethanolamine, the monoethanolamine content of weighed samples of the solvents used was determined in each case by the method described in Section 2.4.2..

Owing to precipitation of the hydroxides of the trivalent metals in aqueous monoethanolamine solutions, it was possible to study the ion exchange processes only in distilled water and in monoethanolamine solutions of water content not exceeding 0.2% by weight. The nitrates of the trivalent metals dissolve in anhydrous monoethanolamine to give clear, colourless solutions, but as the water content of the solution is increased, a stage is reached when the hydrous hydroxides, $M(OH)_3 \cdot (H_2O)_n$, where M = trivalent cation, form and precipitate in the basic medium. This effect is generally observed with these ions in basic solvents; for example, Moeller and Cullen[90], in studying the solubility of anhydrous $La(NO_3)_3$ in ethylenediamine solutions, found that at water concentrations above approximately 0.4% precipitation of the hydroxide occurred. However in the present work, by exposing the redistilled monoethanolamine only in a dry-box and by equilibrating the **resins in** the monoethanolamine solutions in air-tight flasks under dry, CO_2-free nitrogen, it was possible to limit the water content of the monoethanolamine to about 0.15% by weight. Under these conditions the monoethanolamine can be regarded as anhydrous, with no appreciable hydroxide formation occurring.

In the analysis of the resin and solution phases for the trivalent metal cations, dilution with distilled water is necessary to achieve the cationic concentration required for the method described in Section 2.4.1.. Although the hydroxides are nearly quantitatively insoluble in water, they are sufficiently basic to dissolve readily in acids. Below pH 6.29 $La(OH)_3(H_2O)_n$ dissolves readily[91], with the neodymium and yttrium hydroxides dissolving at slightly lower pH values [92]. Consequently, sufficient A.R. concentrated HCl was added to the appropriate solutions before dilution was commenced to ensure the complete dissolution of the hydroxides before the EDTA was added.

Though hydroxide formation was observed, hydrolysis of the trivalent metal cations in solution, which decreases in the order $La^{3+} > Nd^{3+} > Y^{3+}$, can not be expected to occur to any appreciable extent in the present work as, unlike the more common tripositive ions, these cations are never extensively hydrolysed[93,94]. Reactions of the type :

$$M^{3+} + H_2O \rightleftharpoons MOH^{2+} + H^+$$
$$2M^{3+} + 2H_2O \rightleftharpoons M_2(OH)_2^{4+} + 2H^+$$
$$3M^{3+} + 5H_2O \rightleftharpoons M_3(OH)_5^{4+} + 5H^+$$

where M = trivalent metal cation, are therefore thought to be of no real significance in explaining the results obtained in the present work.

The ion exchange processes investigated in this work were those involving the resins initially in the H- and Na-forms in water, and the $CH_2OH.CH_2NH_3$- and Na-forms in monoethanolamine, and the trivalent cations in solution. Equilibria involving the resins initially in the trivalent forms with the univalent cations initially in solution were not investigated. The $La^{3+} - H^+$, $Nd^{3+} - H^+$, $Y^{3+} - H^+$, $La^{3+} - CH_2OH.CH_2\overset{+}{N}H_3$, $Nd^{3+} - CH_2OH.CH_2\overset{+}{N}H_3$, $Y^{3+} - CH_2OH.CH_2\overset{+}{N}H_3$, $La^{3+} - Na^+$, $Nd^{3+} - Na^+$ and $Y^{3+} - Na^+$ equilibria were studied in this work. In the case of the $CH_2OH.CH_2NH_3$-forms of the resins, the resins were weighed out in the H-forms, but were converted to the monoethanolammonium forms by the monoethanolamine in the solvent.

When one of the exchanging ions is a coloured species, the selectivity of a resin for two trivalent cations can be determined by a spectrophotometric method, as has been done by Arnold[14]. Thus the $Nd^{3+} - La^{3+}$ and $Nd^{3+} - Y^{3+}$ equilibria can be studied in this manner, since the Nd^{3+} ion is coloured, whereas the other two are colourless. However, investigation of the $La^{3+} - Y^{3+}$ equilibrium is difficult because of the remarkable similarity in chemical and physical properties between these two cations. No chemical method is known for the accurate determination of the concentration of each cation individually in a mixture of both, and separation of one from the other involves many steps and is never complete. Owing to the lack of suitable isotopes with sufficiently long half-lives to enable equilibration to be carried out over a week, the use of a radio-tracer method is not feasible. Of the absorption techniques, neither X-ray fluorescence nor atomic absorption apparatus was available for the present work. An optical spectrograph (Jarrell-Ash Company, Model JA-7101, 3.4 Meter, Plane Grating Spectrograph) was available, however, and an attempt was made to develop a spectrographic method whereby the selectivity of the resin Amberlite IRC 50 for the cations La^{3+} and Y^{3+} could be investigated.

Procedure

For this method a calibration curve is required. Since it was intended to determine the concentration of La^{3+} in the resin phase after equilibrium had been reached, with the concentration of Y^{3+} being calculated by difference, a series of standards, covering the range of La^{3+} ion concentration expected in the resin phase in the equilibrium studies, was prepared. For this purpose, appropriate known weights of A.R. La_2O_3 were added to weighed samples of Amberlite IRC 50 in the H-form. NaF was then added to the mixtures, so that the weight ratio of NaF : (resin + La_2O_3) was 1 : 1, and the mixtures were ground up in an agate mortar, to achieve homogeneity. The mixtures were then placed in silica crucibles which had been dried to constant weight, and the crucibles and contents were weighed and then placed in a furnace at ± 900°C for 12 hours. At this temperature over 99% of the resin is lost through decomposition. The NaF, which is not volatile at this temperature, is added as a fluxing agent and gives some volume to the remnants after ashing, facilitating their subsequent removal from the crucibles. After the crucibles had been removed from the furnace, they were placed in a desiccator over silica gel and allowed to cool to room temperature, after which the ashed remnants were scraped into clean, dry tubes of known weight, reweighed and returned to the desiccator. Known weights of the ashed remnants were then mixed with 5 times their weight of graphite, which is added as a diluent to give the p.p.m. range required for arcing. The mixtures were then arced on graphite electrodes at 10 amps in an inert atmosphere of argon/oxygen, where the ratio of argon : oxygen was maintained at 4 : 1 by means of a Stallwood jet. A 7 step-sector in a 2 : 1 ratio was used, and the spectra were recorded on Ilford N30 ordinary backed photographic plates. From these, the intensities of the lanthanum spectral lines at 4333 and 4328 Å (which were chosen as they are free from interference by other spectral lines) were determined by means of a Hilger microphotometer, each intensity being measured several times. Since there should be no loss of the La^{3+} during any of the steps of the process, the percentage of lanthanum in the arced mixture can be determined in each case. These values were plotted against the intensities of the corresponding spectral lines to yield the working or calibration curve.

This curve was now checked by applying the same procedure to 3 separate samples of weighed resin in the La-form, in which the lanthanum concentration was known. However, differences of up to 50% were observed between these known values and the values of the corresponding lanthanum concentrations read from the calibration curve. For this method to be of any practical use, an accuracy of 5% or better is required, and therefore the method as described above is obviously unsatisfactory.

The investigation of this method was not pursued in the present work, but it is the opinion of the author that refinement of the technique might improve the results obtained by this method; this gives scope for further research. For example, another fluxing agent should be tried, because, although NaF is not supposed to volatise at 900°C (melting point of NaF = 980 - 997°C), a loss in weight of approximately 16% was found when a sample of NaF was heated at 900°C for 12 hours. Calcium fluoride, with a melting point of 1360°C, may be a better fluxing agent. Also the results may be improved by the introduction of an internal standard, such as palladium, into the diluent before arcing.

Since the accuracy of the method as used in the present work was so poor, it was considered futile to study any equilibria by this means. It was eventually decided not to investigate any equilibria involving only the trivalent ions in this work, since the affinity sequences of the resins for the trivalent cations can be demonstrated by reference to the equilibria involving one trivalent and one univalent cation.

5.3. Results

The results of the various equilibrium studies are given in Tables 5 - 8. The practical selectivity coefficients, k_A^M, are defined by :

$$k_A^M = \frac{[\overline{M^{3+}}] \cdot [A^+]}{[M^{3+}] \cdot [\overline{A^+}]}$$

where $[\overline{M^{3+}}]$, $[\overline{A^+}]$ = concentrations of exchanging ions in the resin phase at equilibrium (expressed as mole fractions of total capacity).

$[M^{3+}]$, $[A^{+}]$= concentrations of exchanging ions in the solution phase at equilibrium (expressed in g equivs./litre)

In these tables the symbols M and Et have been used to denote trivalent metal cation and monoethanolammonium ion, respectively, and A-IRC 50, A-IR 120 and Z-K 225 are the abbreviated names of the resins. The ionic composition of the resin at equilibrium is given by the value of $\bar{X}_M$, which denotes the ion fraction of the ion M^{3+}, the displacing ion, in the resin at equilibrium. In the calculation of these practical selectivity coefficients, the capacity value used for each resin was the maximum determined in the present work for that resin, and not necessarily the capacity for the counter-ion initially on the resin.

Each tabulated practical selectivity coefficient is the mean of 4 separate determinations carried out on different samples under the same conditions. The accuracy of the tabulated practical selectivity coefficients is estimated at 7% for those equilibria occurring in water and 10% for those determined in monoethanolamine. The values of the loading, $\bar{X}_M$, for the equilibria in monoethanolamine are all within 5% of 0.100, those quoted for Amberlite IRC 50, initially in the H-form, in water within 5% of 0.136 and the remainder of the equilibria studied in water within 5% of 0.500. Although the practical selectivity coefficients vary slightly with the loading of the resins, the differences in the practical selectivity coefficients are greater than the errors due to this effect and enable the affinity sequences of the three resins for the various ions in water and monoethanolamine to be determined.

TABLE 5

Practical selectivity coefficients, k_H^M, for the resins in pure water.

RESIN	DISPLACING CATION (M^{3+})	$\overline{X}_M$	k_H^M
A-IRC 50	La	0.133	0.0023
A-IRC 50	Nd	0.136	0.0026
A-IRC 50	Y	0.139	0.0030
A-IR 120	La	0.520	14.9
A-IR 120	Nd	0.514	11.5
A-IR 120	Y	0.489	9.2
Z-K 225	La	0.487	12.5
Z-K 225	Nd	0.490	9.6
Z-K 225	Y	0.501	7.0

TABLE 6

Practical selectivity coefficients, k_{Na}^{M}, for the resins in pure water.

RESIN	DISPLACING CATION (M^{3+})	$\overline{X}_M$	k_{Na}^{M}
A-IRC 50	La	0.506	22.1
A-IRC 50	Nd	0.509	25.8
A-IRC 50	Y	0.518	27.0
A-IR 120	La	0.499	19.1
A-IR 120	Nd	0.507	17.3
A-IR 120	Y	0.505	15.6
Z-K 225	La	0.517	15.1
Z-K 225	Nd	0.497	14.4
Z-K 225	Y	0.512	12.9

TABLE 7

Practical selectivity coefficients, k_{Bt}^{M}, for the resins in monoethanolamine.

RESIN	DISPLACING CATION (M^{3+})	EQUILIBRIUM H_2O CONTENT OF EXTERNAL PHASE		$\overline{X}_M$	k_{Bt}^{M}
		Wt. %	X_{H_2O}		
A-IRC 50	La	0.12	0.0041	0.103	0.0148
A-IRC 50	Nd	0.09	0.0030	0.0991	0.0140
A-IRC 50	Y	0.10	0.0034	0.100	0.0123
A-IR 120	La	0.12	0.0041	0.105	0.0132
A-IR 120	Nd	0.07	0.0024	0.101	0.00982
A-IR 120	Y	0.09	0.0030	0.102	0.00881
Z-K 225	La	0.13	0.0044	0.102	0.0336
Z-K 225	Nd	0.09	0.0030	0.105	0.0302
Z-K 225	Y	0.10	0.0034	0.103	0.0275

TABLE 8

Practical selectivity coefficients, k^{M}_{Na}, for the resins in monoethanolamine.

RESIN	DISPLACING CATION (M^{3+})	EQUILIBRIUM H_2O CONTENT OF EXTERNAL PHASE		$\bar{x}_M$	k^{M}_{Na}
		Wt. %	x_{H_2O}		
A-IRC 50	La	0.12	0.0041	0.100	0.0124
A-IRC 50	Nd	0.11	0.0037	0.102	0.0107
A-IRC 50	Y	0.06	0.0020	0.0993	0.00983
A-IR 120	La	0.09	0.0030	0.0991	0.00971
A-IR 120	Nd	0.10	0.0034	0.101	0.00795
A-IR 120	Y	0.13	0.0044	0.0995	0.00691
Z-K 225	La	0.08	0.0027	0.103	0.0139
Z-K 225	Nd	0.13	0.0044	0.105	0.0128
Z-K 225	Y	0.11	0.0037	0.101	0.0114

5.4. Discussion

5.4.1. Solutions of electrolytes in aqueous and non-aqueous media

The affinity sequence shown by a carboxylic acid resin for a series of similar ions is usually determined by the sizes of the unsolvated ions, the order of increasing affinity being that of decreasing size of the unsolvated ions, while in the case of sulphonic acid resins the size of the solvated ion appears to be the important factor, the order of increasing affinity being that of decreasing solvated size; this is discussed further in Section 5.4.2.. In a given series of cations of the same charge, the field strength decreases as the ionic radius increases and thus the ion of smallest crystallographic radius will usually be the largest solvated ion.

The hydrated radii of ions can be calculated from a modification of the Stokes Law equation[95]:

$$r_h = \frac{0.820\,|Z|}{\lambda^o\,\eta^o}\left(\frac{r_h}{r_s}\right)$$

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_h = hydrated radius of ion ($\mathring{A}$)

r_s = Stokes Law radius of ion $= \dfrac{0.820\,|Z|}{\lambda^o\,\eta^o}$ ($\mathring{A}$)

$\left(\dfrac{r_h}{r_s}\right)$ = Stokes Law correction factor.

The 'corrected Stokes Law radius' of the hydrated ion can then be used to estimate its volume. Since the volume of the bare ion itself is negligible compared to the hydrated volume, the average number of water molecules involved in the hydrated entity can be roughly estimated by neglecting the electrostriction of these molecules and ascribing to them the volume of $(30\ \mathring{A})^3$ ordinarily found in liquid water[95].

Values calculated from this equation for the cations studied in the present work are given below in Table 9; these values were calculated by using literature values of the limiting conductances, viscosities, and Stokes Law correction factors[95,96].

TABLE 9

The extent of hydration of the cations.

CATION	CRYSTAL-LOGRAPHIC RADIUS[97]. (Å)	HYDRATED RADIUS (Å)	HYDRATION NUMBER
Na^+	0.95	3.3	5
La^{3+}	1.15	4.5	13-14
Nd^{3+}	1.08	4.6	13-14
Y^{3+}	0.93	4.7	14-15

The values of the hydration numbers reported in the literature vary widely (for example, from 2 tc 70 for Na^+), because some methods of calculation count only the more tightly bound waters, whereas others, such as that of Horne and Birkett[98], who state the hydration number of Na^+ to be 34 at 20°C, include more loosely bound waters also. Padova[99] obtained values of 8.5, 9 and 11 for the solvation numbers of lanthanum, neodymium and yttrium, respectively. In the case of the lanthanides, differences in the values of hydration numbers quoted by different workers may be due to variations in the amount of water actually considered to be bound by hydration and also to the possibility that, as the ions become larger with decreasing atomic number, a second co-ordination number may be introduced, giving rise to changes in the effective radii of the hydrated ions. From their measurements of the conductances of aqueous solutions of lanthanide salts, Spedding et al[100] have suggested the existence of both 9 and 12 co-ordination for the lanthanide ions. Hydration numbers are also affected by the anion present in solution; for example, several workers[101-103] have shown that, in high concentration, the NO_3^- ion interacts with trivalent cations, yielding species with the NO_3^- ion in either the first or the second co-ordination sphere, replacing a part of the water and being partly covalently bound.

The hydration figures given in Table 9 are thus purely qualitative in nature, but serve the purpose of illustrating the tendency to increasing hydration with decreasing ionic size.

The hydrated radius of the NO_3^- ion calculated by the method given above is 2.7 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 nitrate ion and the four cations, calculated from the hydrated radii determined above, are given below in Table 10. The values of the distances obtained are very sensitive to experimental errors, so that it is difficult to determine whether the observed variations are real.

TABLE 10

Theoretical distances of closest approach for cationic nitrates.

CATION	DISTANCE OF CLOSEST APPROACH (Å)
Na^+	6.0
La^{3+}	7.2
Nd^{3+}	7.3
Y^{3+}	7.4

The concept of ion-pair formation must also be considered in any discussion of solutions of electrolytes in aqueous and non-aqueous media. The existence of associated ion-pairs in electrolyte solutions was first postulated by Bjerrum[104] and has been discussed at length by various authors [105-109], and therefore the basic theory will not be reviewed in this thesis. According to Bjerrum[104], the average effects of ion-pair formation in a solution may be calculated on the assumption that all oppositely charged ions within a certain critical distance of each other are associated into ion-pairs, though in reality a fast-moving ion may come within this distance of an oppositely charged ion and pass by without forming an ion-pair. This distance can be calculated from the formula :

$$q = \frac{|Z_1 \quad Z_2| \quad e^2}{2 \varepsilon \; kT}$$

where q = Bjerrum critical distance
Z_1, Z_2 = algebraic values of charges of anion and cation
ε = dielectric constant of medium
k = Boltzmann constant
T = absolute temperature
e = protonic charge

Substituting the appropriate values for a 3 : 1 electrolyte in water into the equation gives :

$$q = \frac{3 \times 1 \times (4.8 \times 10^{-10})^2}{2 \times 78.3 \times 1.38 \times 10^{-16} \times 298 \times 10^{-8}}$$

$$= 10.7 \text{ Å}$$

With monoethanolamine as solvent the value obtained is :

$$q = \frac{3 \times 1 \times (4.8 \times 10^{-10})^2}{2 \times 37.72 \times 1.38 \times 10^{-16} \times 298 \times 10^{-8}}$$

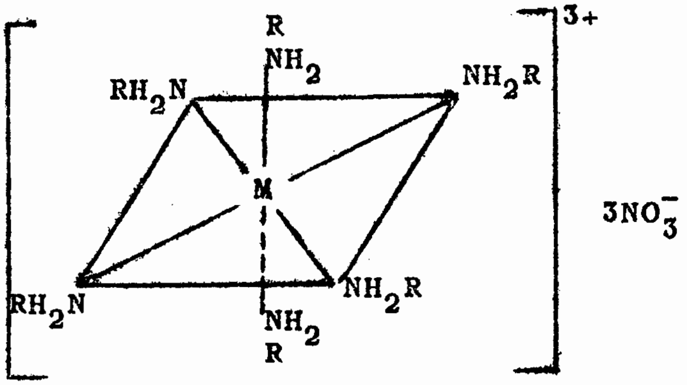
$$= 22.8 \text{ Å}$$

Since the probability of oppositely charged ions approaching within 22.8 Å of each other exceeds that of their approaching within 10.7 Å of each other, many more ion-pairs may be expected to form in monoethanolamine than in water, provided the dilution of the ions is the same in both cases. This leads to the generalisation that lowering the dielectric constant of the medium will increase ion-pairing. Also, from the theoretical distances of closest approach given in Table 10 for the nitrates of the trivalent cations, the tendency for ion-pair formation in both water and monoethanolamine may be expected to be in the order $La^{3+} > Nd^{3+} > Y^{3+}$, provided the concentrations of the ions are the same in all cases. Fuoss[110] has suggested that electrolytes exist almost entirely as ion-pairs in any solvent which has a dielectric constant less than 40. In solvents, such as monoethanolamine, where the dielectric constant is low, there is the possibility of triple ion (+ − +) or (− + −) and even quadrupole (+ − + −) formation occurring, although this is considered unlikely to occur to any appreciable extent at the low concentrations used in the present work.

When discussing solutions of nitrates of trivalent metals in monoethanolamine, apart from the phenomena of ion-pairing and solvation, the precipitation of the hydroxides of the trivalent metals from basic solutions, hydrolysis and the formation of complexes must also be considered. However, as mentioned in Section 5.2., the the conditions employed in the selectivity determinations carried out in this work were such that the monoethanolamine solutions could be considered as anhydrous, with no appreciable precipitation of the hydrous hydroxides or hydrolysis occurring.

The lanthanide ions are known to have a low tendency to complex formation, because, although they carry a high charge, their large size causes them to have a relatively weak field, and their electronic configurations do not provide strongly bonding orbitals. However, in aqueous solutions these ions are readily hydrated, and it is difficult to replace the water molocules by other ligands. It has been observed experimentally that, except for the common aquated ions $[M(H_2O)_n]^{3+}$, lanthanide complexes are limited in number and notably stable only when derived from the strongest chelating agents[111]. Types of complex species formed by ion-pair association exist in solution, where their presence can be inferred from changes in conductance, transference numbers, ion migration or solvent extraction behaviour that follow addition of the complexing group. These species do not, in general, survive through a series of reactions without change, and they are not distinguishable in solid compounds. However, Forsberg and Moeller[112] have recently, by carefully controlling the experimental conditions and maintaining completely anhydrous systems, used the direct reaction of ethylenediamine with a lanthanide (111) salt in acetonitrile to prepare solid compounds of compositions $M(en)_3X_3$ and $M(en)_4X_3$ ($X = NO_3^-$, ClO_4^- , Cl^- , Br^-). Both the ability of ethylenediamine to replace anions in the co-ordination sphere, and the possibility of a co-ordination number of at least 8 for M^{3+} are indicated. Earlier, Moeller[113] stated the existence of isolable non-chelated amine adducts of the type $MX_3.yRNH_2$, but was not specific as to the conditions required or the nature of the species M, X and R in such compounds. However, from this previous work[112,113] and from the results of the present work it seems likely that adducts of the type $M(NO_3)_3.yNH_2CH_2CH_2OH$ where M = La^{3+}, Nd^{3+} or Y^{3+} are formed under the conditions used in the present work, giving rise to complexes such as :

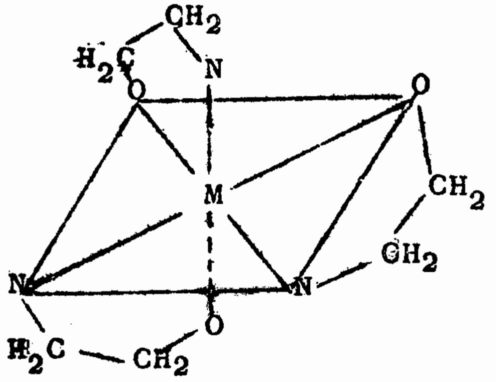
y = 6 →



Type A

where R = $CH_2OH.CH_2-$

or



Type B

The complex of Type A may be expected to be dominant, since Moeller and Zimmerman[114] have shown that, although lanthanide nitrates are not very soluble in anhydrous monoethanolamine, the solutions formed are fairly strongly electrolytic, suggesting the presence of an ionic, rather than a molecular, type of complex. However, conductance data[20,95] indicate that the lanthanide salts are weaker electrolytes in monoethanolamine than in water, probably because of the high viscosity of monoethanolamine and considerable ion-pair formation resulting from the high charge of the cations and the low dielectric constant of the solvent. As water is added, the conductance at a given concentration increases, owing to the formation of the more mobile $M(H_2O)_n^{3+}$ ions.

The fact that these ionic complexes are not stable in contact with water, yielding the hydroxides, indicates that the amines are only weakly held. Moeller[113] states that for a given ligand, a general increase in the stability of the complex with decrease in the crystallographic radius of the cation is observed. The concept of an electrostatic attraction between cation and ligand, which will increase as the crystallographic radius of the cation decreases, thus appears plausible in the case of the lighter lanthanides.

5.4.2. Affinity sequence of resins for cations in water

From the results in Tables 5 and 6, it has been established that for the carboxylic acid resin, Amberlite IRC 50, the affinity sequence for the ions studied is :

$$H^+ > Y^{3+} > Nd^{3+} > La^{3+} > Na^+$$

in both the equilibria, $M^{3+} - H^+$ and $M^{3+} - Na^+$, in water. This is in agreement with the results obtained by other workers[9,14,16,115,116].

The very high affinity of the carboxylic acid resin for the hydrogen ion is due to the weak acidic strength of the resin in water. The affinity of the COO^- groups on the resin for H^+ ions is so great that other cations cannot compete with H^+ ions unless the latter are present at extremely low concentration, and even then replacement of the H^+ ions by other cations is very slow. Because of the high polarisability of the COO^- group, a strong bond, which is thought to be mainly covalent in character, is formed between the hydrogen atom and the oxygen atom available for bonding. This bond is not easily broken, so that replacement of hydrogen by other cations does not take place readily. The polarising power of other cations is not as high as that of hydrogen, owing to their greater size, so that the degree of interaction of the COO^- groups with other cations is not as great, and the bond formed is predominantly ionic in character. In order to obtain loading values of 0.5 in the case of the exchange processes in aqueous solution involving the trivalent cations on Amberlite IRC 50, initially in the H-form, very high concentrations of the trivalent dations would be required. The changes in concentration of the trivalent cations in solution, due to uptake by the resins, would then be so small that they would be extremely difficult to measure. Consequently, the practical selectivity coefficients were determined in these cases at lower values of the loading, as mentioned in Section 5.2..

In the case of the trivalent cations, the order of decreasing affinity is the order of increasing size of the bare, or unsolvated ion. This may be explained in terms of Bregman's "polarisability" theory[117]. Bregman postulates that unsolvated ions take part in exchange on carboxylic acid resins because the COO^- group is more polarisable than the water molecule, so that cation-anion interaction between the cations and the COO^- groups on the resin predominates over ion-solvent interaction, i.e. hydration. Gregor and Frederick[118] have shown by means of potentiometric titrations of polymethacrylic acids with quaternary ammonium bases that the counter-ions are largely held in close proximity to the polyanion chain, with the distances of approach comparable to the sum of the ionic radii. Since the degree of coulombic interaction between the cations and resin groups depends upon the distance of closest approach, the affinity of a carboxylic acid resin for the ions of a given series will increase as the crystallographic radius of the ion decreases.

In the case of the sulphonic acid resins in water, the affinity sequence for the cations studied is :

$$La^{3+} > Nd^{3+} > Y^{3+} > Na^{+} > H^{+}$$

which is in agreement with the results obtained by other workers[9,14,29,119-121].

Here, the resins show no great affinity for the H^+ ion, as the sulphonic acid resins behave as strong acids in water, the resins being readily converted from the H-forms to any other ionic forms. The sulphonate group, SO_3^- , unlike the carboxylate group, COO^-, is less polarisable than water, and thus the H-form of a sulphonic acid resin exists as $RSO_3^-H_3O^+$ in water, where R represents the resin matrix. The H_3O^+ ion is not firmly held by the sulphonate group and is readily replaced by other cations. Thus the difference in behaviour between sulphonic and carboxylic acid resins in water is thought to be due to the difference in polarisability between the SO_3^- group and the COO^- group. In the case of a sulphonic acid resin H^+ ions interact more with the solvent molecules than with the resin groups, while the reverse is the case for a carboxylic acid resin.

Since the sulphonate group is less easily polarised than the water molecule, Bregman[117] considers that hydrated cations take part in exchange on sulphonic acid resins. In the case of the trivalent cations studied, therefore, La^{3+}, which has the smallest hydrated radius will have the highest affinity for a sulphonic acid resin.

The observed affinity sequences for the trivalent cations can also be explained in terms of the model put forward by Chu, Whitney and Diamond[122-125], which considers ion exchange as a competition between the solvent and the resin groups to solvate the cations, the term "solvation" here being extended to include cation-anion interaction as well as ion-solvent interaction. In the case of sulphonic acid resins, the need of the cations for solvation is generally 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 smallest crystallographic radii, i.e. with the strongest solvation tendency, which thus preferentially enter the dilute external phase, forcing the larger ions into the more poorly solvating resin phase. The selectivity order of the sulphonic acid resins will therefore be $La^{3+} > Nd^{3+} > Y^{3+}$, which is confirmed in the present work. In the case of exchange on weak acid resins, this model considers specific cation-resin anion interactions to play an important role in solvating the cations, so that the smallest ions preferentially enter the resin phase, and the affinity sequence observed with sulphonic acid resins is therefore reversed with these resins.

The affinity of both types of resin for the trivalent cations is greater than that for sodium owing to the increased field strength, and hence polarising power, of the trivalent cations by virtue of their higher charge.

The selectivity of the H-form resin for the trivalent cations is much greater in the case of the sulphonic acid resins than with Amberlite IRC 50, owing to the much lower affinity of the SO_3^- group for the H^+ ion, as explained above. On the other hand, when the resins are in the Na-forms, the carboxylic acid resin shows a higher affinity for the trivalent cations than do both sulphonic acid resins. This is because Amberlite IRC 50 has a higher ion exchange capacity than the sulphonic acid resins and therefore, owing to the high concentration of resin groups, the charge density will be higher and ionic interactions between resin groups and counter-ions will be more pronounced in the case of the carboxylic acid resin. The higher field strength of the trivalent ions thus has a more marked effect in this case.

5.4.3. Affinity sequence of resins for cations in monoethanolamine

As mentioned in Section 5.2., under the experimental conditions used it was not possible to study the ion exchange behaviour of the resins in pure anhydrous monoethanolamine, but as the water content was maintained at below 0.15% by weight, so that it caused no appreciable precipitation of the hydroxides of the trivalent metals and did not affect the results to any significant extent, the monoethanolamine used was considered as anhydrous, and not as aqueous monoethanolamine.

In monoethanolamine the affinity sequence of all three resins for the ions studied was found to be

$$CH_2OH.CH_2\overset{+}{N}H_3 > Na^+ > La^{3+} > Nd^{3+} > Y^{3+}$$

where, in the case of the trivalent cations, the decrease in preference follows the decrease in crystallographic radius of the cation. However, Macintosh[9], working with the same three resins, found the affinity sequence for the univalent cations to be :

$$Li^+ > Na^+ > K^+ > CH_2OH.CH_2\overset{+}{N}H_3$$

The variation in the preference trends shown by the resins in these two cases may be explained by the difference in importance of ion-solvent interactions. From conductance measurements, it has been shown that the ion-dipole interaction between alkali metal cations and monoethanolamine molecules is very weak[23]; the ions are not highly solvated and the solvates are not very stable. For this reason the alkali metal ions take part in ion exchange processes in monoethanolamine in the unsolvated state. Thus the smallest bare, or unsolvated cations will be the most preferred in both types of resin. However, as mentioned in Section 5.4.1., the ion-solvent interaction of trivalent cations in monoethanolamine is appreciable, with a certain degree of ion-pair formation, solvation and formation of non-chelated amine adducts of the type $M(NO_3)_3.yNH_2CH_2.CH_2OH$, where M = trivalent metal cation. Ion-solvent interaction may therefore be expected to play a dominant role in determining the affinity sequences of the resins in the present work.

In all cases the trivalent cation with the smallest crystallographic radius is the least preferred in monoethanolamine. The reason for this trend is thought to be the increased stability of the adducts with decrease in crystallographic radius of the cation by virtue of the increased field strength of the cation, rather than to a size effect of the adducts themselves, since the size differences are expected to be negligible when large complexes such as these are considered. This trend may also be explained by means of the model of Chu, Whitney and Diamond[122-125]: the solution phase will be more strongly selective towards those ions with smaller crystallographic radii, which will thus preferentially enter the dilute external phase, with the larger cations being preferentially taken up by the resins. The preference of the trivalent ions for the solution phase will be greater than that of the univalent cations, since the former are more strongly solvated by virtue of their higher charge. Since Na^+ and $CH_2OH.CH_2\overset{+}{N}H_3$ ions are not stably solvated nor complexed by monoethanolamine, they will be preferred by the resins, as was seen in this work. Macintosh[9], and

Davies and Patel[126] have suggested, on the basis of their results, that van der Waals attraction between the resin networks and the organic $CH_2OH.CH_2\overset{+}{N}H_3$ ions favours association between these cations and the resin; this would explain the preference of the resins for the $CH_2OH.CH_2\overset{+}{N}H_3$ ion rather than for the Na^+ ion observed in the present work.

Macintosh[9] found an increase in the selectivity of the resins for the alkali metals with an increase in the monoethanolamine content of the external phase, whereas in the present work, except in the case of Amberlite IRC 50, initially in the H-form, the preferences of the resins for the trivalent cations were found to be lower in monoethanolamine than in water in all cases. The extremely low preference of the H-form of Amberlite IRC 50 for the trivalent cations in water is due to the very high affinity of the resin for H^+ ions (see Section 5.4.2.). However, owing to the 'levelling effect' of a basic solvent, the carboxylic acid resin is fully ionized in monoethanolamine, giving rise to the higher selectivity of the resin in monoethanolamine than in water. Phipps and Hume[13] found that the selectivity coefficients of Dowex 50 for univalent cations were greater in ammonia than in water in all cases, except in the case of the Ag-form of the resin, where the reverse was the case. They suggested that the marked decrease in the selectivity for Ag^+ in liquid ammonia was due to the influence of the strong ammine complex formed by this ion.

In the present work, the much lower selectivities of the resins in monoethanolamine than in water are believed to be due to the introduction of the phenomenon of sieve action. Here, the formation of the non-chelated adducts gives rise to large complexes, which are probably mechanically excluded from the resins by sieve action, i.e. the resin pores are too narrow to accommodate them. Partial, not complete exclusion is observed owing to the heterogeneity of the resin matrix, i.e. some pores are wider than others, and also because of the instability of these adducts, as demonstrated by the formation of the hydroxides of the trivalent metals in the presence of water, which indicates that the amine is only weakly held. As explained in Section 5.4.1., the complexes formed are expected to be ionic in character, and consequently the sieve action is an ionic sieve effect. The phenomenon of counter-ion exclusion by sieve action in ion exchange resins has been demonstrated by several workers[12,60,62,127]. Sieve action is, of course, strongest in highly cross-linked resins, and in the present work, the lowest selectivity for the trivalent cations was shown by Amberlite IR 120, the most highly cross-linked resin.

The preference of the 4-5% D.V.B. sulphonic acid resin for the trivalent cations has been found in the present work to be greater than that of the carboxylic acid resin of similar cross-linking. This may be explained in terms of Gurney's "order-disorder" theory[108], in which all ions with a high charge density are considered as 'order-producing', i.e. they cause the structure of the solvent in their vicinity to be more ordered, while those with a low charge density are 'order-destroying', i.e. the ordered structure of the solvent is destroyed in the vicinity of such ions. According to this theory, the interaction of a cation and an anion of the same ordering character should give rise to a more stable state than the interaction of ions of different ordering character. In the former case, the interaction will be greater and the activity coefficients of the ions will accordingly be lower. According to Gurney, the anion of a strong acid will be order-destroying, while that of a weak acid will be order-producing. Therefore in this work, the SO_3^- group will be order-destroying and the COO^- group, because of its high charge density, i.e. the negative charge being more localised, will be order-producing. The non-chelated amine adducts, formed between the trivalent cations and monoethanolamine, would be considered as order-destroying, in view of their large size and low charge density. Consequently a more stable state is achieved by action of the adducts of the trivalent metals with the SO_3^- groups than with the order-producing COO^- groups, giving rise to a greater preference of the sulphonic acid resin for the trivalent cations than in the case of the comparable carboxylic acid resin.

5.4.4. Effect of cross-linking on selectivity of sulphonic acid resins

In all equilibria studied in water, the 12% D.V.B. sulphonic acid resin has been found to exhibit a higher selectivity for a particular trivalent cation than the 4-5% D.V.B. sulphonic acid resin under the same conditions. When the external solvent is water, the resin of higher cross-linking is less swollen (see Section 4.4.3.), so that the resin phase is more concentrated than in the case of the resin of lower cross-linking. Consequently the activity coefficient ratio of the exchanging ions in the resin phase will be higher, giving rise to higher selectivity. The higher swelling pressure of the 12% D.V.B. resin also contributes to the higher selectivity of this resin.

However in monoethanolamine, the 4-5% D.V.B. sulphonic acid resin is more selective for the trivalent cations than the 12% D.V.B. resin under the same conditions.

As mentioned in the previous Section, formation of the non-chelated amine adducts of the trivalent cations with monoethanolamine causes a sieve action to come into play. The average pore size of the resin matrix will be smaller in the more highly cross-linked resin, so that exclusion of the adducts will be greater and the selectivity for the trivalent cations consequently lower. Macintosh[9] observed an increase in selectivity with cross-linking over the entire range of aqueous monoethanolamine, from 0% to 100% by weight of water, but this is to be expected where ion-solvent interaction is not as dominant a factor as in the present work and where no sieve action was seen to contribute to the exchange processes.

5.4.5. Relationship between selectivity and swelling.

It is difficult to assess any real relationships between the swelling and selectivity results obtained in this work because the practical selectivity coefficients were only determined in water and monoethanolamine, and not, as in the case of the swelling determinations, in aqueous monoethanolamine solutions of varying compositions. A correlation exists between the affinity of an ion exchange resin for a given ion in water and the swelling of that resin in the appropriate ionic state in water. The lower the swelling of a resin in a given ionic state, the greater the affinity of the resin for that cation. This is to be expected from a consideration of the theories of Rice and Harris[74,84] and of Gregor[47,69,85]; a high degree of association between counter-ions and resin anions, giving rise to a low chain potential and a smaller number of osmotically active cations in the resin phase, will result in low swelling.

However, in the case of ion exchange processes in monoethanolamine solutions of high monoethanolamine content, the lower the swelling of a resin in a given ionic state the lower the affinity of the resin for that cation. This difference in correlation from that observed in water is probably due to the dominant role played by ion-solvent interaction in determining selectivity in monoethanolamine; in water this is a contributory factor, but resin anion-counter-ion interaction, which also strongly affects swelling, appears to be the dominant factor. The introduction of an ionic sieve effect in monoethanolamine, which is absent in the case of water, also probably affects the relationship between swelling and selectivity in this solvent.

CHAPTER 6

SUMMARY.

This investigation of the behaviour of cation exchange resins in aqueous monoethanolamine has led to some interesting conclusions regarding the influence of the solvent on ion exchange resins. The main results and conclusions, which have been discussed in detail in the preceding chapters, will now be summarised.

The observed decrease in weight-swelling of the three resins in the various trivalent ionic states with a decrease in the dielectric constant of the ambient medium, by virtue of an increase in the monoethanolamine content of the external phase, may be attributed to :

1) a decrease in the solvation tendency of the fixed ionic groups and counter-ions;

2) an increase in ion-pair formation, resulting in a decrease in the number of osmotically active ions in the resin phase, and an accompanying reduction in the osmotic pressure difference between resin and solution phases;

3) an increase in association between resin anions and counter-ions, giving rise to a lower electrostatic potential of the polymer chains.

The carboxylic acid resin, Amberlite IRC 50, which has a high capacity, contains ions in high concentration in the resin phase, and therefore, the tendency of the pore liquid to dilute itself, and the resulting swelling, are more pronounced than with the low-capacity sulphonic acid resins. In the case of the two sulphonic acid resins, the 4-5% D.V.B. resin is more swollen than the

12% D.V.B. resin in media of high water content, owing to the increase in flexibility of the resin matrix which must accompany a decrease in cross-linking. However, in media of high monoethanolamine content, the reverse is the case, and this may be attributed to the polymer-polymer interaction effect, which is greater in the case of the resin of lower cross-linking, predominating over the matrix flexibility effect in determining the extent of swelling when the degree of swelling is comparatively low[9,88].

The affinity sequence of the carboxylic acid resin, Amberlite IRC 50, for the cations in water is :

$$H^+ > Y^{3+} > Nd^{3+} > La^{3+} > Na^+$$

whereas for the sulphonic acid resins in water, the affinity sequence is :

$$La^{3+} > Nd^{3+} > Y^{3+} > Na^+ > H^+$$

For the carboxylic acid resin the preference for the trivalent cations follows the sequence of decreasing crystallographic radii of the cations, whereas for the sulphonic acid resins the reverse is the case. This is attributed to the polarisability trend :

$$COO^- > H_2O > SO_3^-$$

whereby, in the case of the carboxylic acid resin, the cation with the smallest bare, or unsolvated size is the most preferred, whereas for the sulphonic acid resins, where the need for hydration is greater, it is the hydrated ionic size of the cation which is the critical factor in determining the preference of the resins for the trivalent cations[117]. The trivalent cations are generally preferred to the univalent cations by virtue of their greater field strengths, except in the case of Amberlite IRC 50 in the H-form, where the very high affinity of the resin for the H^+ ion is due to the weak acid behaviour of the resin in water. The sulphonic acid resins in the H-forms, however, behave as strong acids in water, and consequently show a much greater preference for the trivalent cations than does the carboxylic acid resin in the H-form. But when the resins are in the Na-forms, the carboxylic acid resin shows a much higher affinity for the trivalent cations than the sulphonic acid resins. This may be attributed to the high capacity of Amberlite IRC 50, which gives rise to a high charge density as a result of the high concentration of resin groups, so that the ionic interaction between resin groups and cations will be more pronounced in the case of the carboxylic acid resin.

Owing to the 'levelling effect' of a basic solvent, the two types of resin are dissociated to a similar degree in the presence of monoethanolamine. In both cases the H-form of the resin is converted to the monoethanolammonium form in this solvent. In the equilibria studied in monoethanolamine, ion-solvent interaction is seen to play a far more important role than in the same equilibria in water. In monoethanolamine an ionic sieve effect is seen to come into play, whereby the large non-chelated amine adducts of the type $M(NO_3)_3.yNH_2CH_2.CH_2OH$, where M = trivalent cation[113], formed between the trivalent cations and monoethanolamine, are partially excluded from the resins. The instability of these complexes is demonstrated by the formation of hydroxides of the trivalent metals on addition of water to the monoethanolamine solution, showing that the amine molecules are not held very strongly. Due to this fact and also to the heterogeneity of the cross-linking in the resins, partial and not complete exclusion of the trivalent cations is observed. The affinity sequence for the ions shown by all three resins in monoethanolamine is :

$$CH_2OH.CH_2\overset{+}{N}H_3 > Na^+ > La^{3+} > Nd^{3+} > Y^{3+}$$

In the case of the trivalent cations, preference is shown for the cation with the larger crystallographic radius, as the stability of the complexes formed by this cation with monoethanolamine is not so great, owing to the lower field strength of the cation. The univalent cations, which do not interact with monoethanolamine to any great extent, owing to the relatively strong intermolecular forces of attraction between the solvent molecules, are therefore preferred by the resins to the trivalent cations. The greater preference for the monoethanolammonium ion compared with the Na^+ ion is thought to be due to van der Waals forces of attraction between the resin networks and the organic monoethanolammonium ion, which will favour some association between these cations and the resins.

That the preference of the resins for the trivalent cations in monoethanolamine is due to an ionic sieve effect is further indicated by the fact that Amberlite IR 120, the most highly cross-linked resin, shows the lowest preference for these ions. In monoethanolamine the sulphonic acid resin, Zeo-Karb 225, shows a higher affinity for the trivalent cations than does the carboxylic acid resin, Amberlite IRC 50, of similar cross-linking. This is explained by means of Gurney's "order-disorder" theory[108], whereby interaction between the non-chelated amine adducts and the SO_3^- resin groups gives rise to a more stable state than interaction between the adducts and COO^- groups.

In water there exists the relationship that the lower the swelling of a resin in a given ionic state, the greater the affinity of the resin for that cation. This is to be expected from a consideration of the theories of Rice and Harris[74,84] and Gregor[47,69,85], which indicate that a high degree of association between counter-ion and resin anions, giving rise to a low chain potential and a smaller number of osmotically active cations in the resin phase, will result in low swelling. However, in solutions of high monoethanolamine content the reverse relationship is observed, i.e. the lower the swelling of a resin in a given ionic state, the lower the affinity of the resin for that cation. This is thought to be due to the introduction of the ionic sieve effect when the trivalent cations are initially in the solution phase, and to the major role played by ion-solvent interaction, resin anion-counter-ion interaction being only a secondary consideration in ion exchange equilibria involving these trivalent ions in monoethanolamine.

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