48. *Swelling and Exchange Equilibria of Cation-exchange Resins in Aqueous Monoethanolamine.*

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Measurements have been carried out of ion-exchange equilibria and of the amount and composition of solvent sorbed by ion-exchange resins, using mixtures of water and monoethanolamine as solvent media. A carboxylic acid resin and two sulphonic acid resins with different degrees of cross-linking were used. The lithium, sodium, potassium, and monoethanolammonium ions were studied.

With the sulphonic resins the so-called " normal " affinity sequence, $Li^+ > Na^+ > K^+ > HO{\cdot}CH_2{\cdot}CH_2{\cdot}NH_3^+$, is observed in water or solvents of high water content; but when the ethanolamine content is increased this sequence undergoes reversal at a certain solvent composition. The reversed sequence is shown by the carboxylic resin in all solvents. The swelling sequences are in all cases the reverse of the affinity sequences; for the sulphonic resins the swelling sequence undergoes reversal at the same solvent composition as the affinity sequence.

In solvents of low water content the swelling of the sulphonic resins increases with cross-linking. Preferential sorption of water was observed in all cases. The uptake of water increases continuously with increasing water content of the solvent, whereas the uptake of monoethanolamine passes through a maximum.

IN aqueous solution, carboxylic acid cation-exchange resins, owing to their weakly acidic character, differ markedly in many of their properties from sulphonic acid resins. In a solvent more basic than water the levelling effect should eliminate this difference in acid strengths, thereby enabling comparison of other properties of the two types of resin to be made. In the present work, therefore, mixtures of water and monoethanolamine have been used as solvents in the investigation of the behaviour of a carboxylic acid resin and two sulphonic acid resins having different degrees of cross-linking.

Ion-exchange in mixed or non-aqueous solvents has been studied by a number of investigators; some aspects of this work have been reviewed.[1] These studies have been largely confined to neutral solvents, such as methanol and acetone and their mixtures with water. The only acidic solvent which has been used is acetic acid,[2] and the only basic one ammonia. Ion-exchange resins have been used in liquid ammonia to remove unwanted ions in preparative work,[3] and Davies and Patel[4] measured the uptake of ammonia and water from aqueous ammonia by sulphonic acid resins with different degrees of cross-linking and in various cationic forms. Apart from this, no fundamental account of ion-exchange in a basic solvent appears to have been published.

Monoethanolamine was chosen as the basic solvent because it has good solvent properties and is completely miscible with water. In mixtures of this solvent with water, ion-exchange equilibria involving the ions Li^+, Na^+, K^+, and $HO{\cdot}CH_2{\cdot}CH_2{\cdot}NH_3^+$ have been studied, the monoethanolammonium ion being the equivalent of the " hydrogen " ion in the solvents used. Apart from the ion-exchange equilibria, the uptake of solvent by the resins (" swelling ") and the composition of the sorbed solvent have been determined under various conditions.

EXPERIMENTAL

Materials.—The resins used were Amberlite IRC-50, which is cross-linked poly(methacrylic acid), and two polystryenesulphonic acid resins, Amberlite IR-120 and ZeoKarb 225. The latter was known to have a divinylbenzene (DVB) content of 2%; the DVB content of Amberlite IR-120 was estimated as about 12% by comparison of its swelling properties with those of similar resins of known DVB content. The carboxylic resin probably contains 5% DVB[5] but owing to the more open structure of this type of resin it corresponds fairly closely in swelling behaviour to the 2% DVB polystyrene sulphonic acid resin.

The resins were screened while in the H^+-form, the "44—100 mesh" fractions being used in this work. The resins were conditioned by treatment with 5N-sodium hydroxide, water, and 2N-hydrochloric acid, and washed until acid-free. They were in most cases dried to constant weight at 105°. Salt forms of the carboxylic resin were dried at 60° in a vacuum oven as decarboxylation may occur at high temperatures. All samples were stored in a vacuum desiccator over phosphorus pentoxide. The Li^+-, Na^+-, and K^+-forms were prepared by treating the H^+-form with solutions of the alkali-metal hydroxides. The monoethanolammonium form was prepared by treating the H^+-form with a concentrated aqueous solution of monoethanolamine.

Monoethanolamine (C.P. grade) had b. p. 82°/20 mm.; distillation at atmospheric pressure results in slight decomposition to give ammonia and water.[6] The solvent was stored under dry, CO_2-free nitrogen, and was exposed only in a dry-box. In this way the water content could be reduced to 0·05%, but the last trace could not be removed.

AnalaR grades of sodium iodide and potassium iodide, and C.P. grade lithium sulphate were used without further purification. The salts were dried at 58° over phosphorus pentoxide and under reduced pressure. Monoethanolammonium chloride was prepared in solution;[7] dry ammonium chloride is added to monoethanolamine and the liberated ammonia removed under reduced pressure. The reaction is completely stoicheiometric, so that a solution containing any desired concentration of monoethanolammonium ions can be prepared by taking the appropriate weight of ammonium chloride.

Analytical Methods.—Alkali-metal solutions were analysed (estimated accuracy ±2%) by means of a flame photometer (Lange model 6).

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[1] (*a*) Korkisch and Janauer, *Talanta*, 1962, **9**, 957; (*b*) Helfferich, " Ion Exchange," McGraw-Hill, New York, 1962, ch. 10.

[2] (*a*) Bodamer and Kunin, *Ind. Eng. Chem.*, 1953, **45**, 2577; (*b*) Fessler, Ph.D. Thesis, Duke University, Durham, N.C., 1958 (*Diss. Abs.*, 1959, **20**, 520).

[3] Keenan and McDowell, *J. Amer. Chem. Soc.*, 1953, **75**, 6348; Francis, Thornton, Werner, and Hopkins, *ibid.*, 1958, **80**, 6238.

[4] Davies and Patel, *J.*, 1962, 880.

[5] Gustavson, Abstract of papers, Div. of Phys. Chem., 144th Meeting Amer. Chem. Soc., Los Angeles, 1963, p. 48P, Abs. 114.

[6] Brewster, Schmidt, and Schaap, *J. Amer. Chem. Soc.*, 1959, **81**, 5532.

[7] Brewster, Schmidt, and Schaap, *J. Phys. Chem.*, 1961, **65**, 990.

In solvent mixtures of low water content the water was determined by the Karl Fischer method, using a " dead stop " potentiometric titrimeter with a magic-eye indicator.* Titration volumes could be considered accurate to 0·02 ml., corresponding to about 0·005% of water under the conditions used. In mixtures containing more than 40% of water the solvent composition was found by determining the monoethanolamine content by titration (accurate to ±0·2%) of weighed samples with hydrochloric acid.

The capacities of the resins were determined by addition of known amounts of alkali to weighed samples of the H^+-form, the excess being subsequently determined. The quantities and concentrations used were such that the loss of water from the solution due to swelling of the resin caused negligible errors. Determinations were carried out with both sodium hydroxide solutions and monoethanolamine solutions. The capacities obtained with the two bases were in good agreement, indicating that the larger ethanolammonium ions are not excluded from the exchange sites. The capacities were (mg. equiv./g. dry H^+-form): Amberlite IRC-50, 10·70; ZeoKarb 225, 5·07; Amberlite IR-120, 4·84. Each value represents the mean of six determinations, three with each base. The accuracy is estimated at ±0·5%.

Swelling Determinations.—Owing to the high viscosity of monoethanolamine, together with its susceptibility to contamination by atmospheric moisture and carbon dioxide, centrifugation [8] was unsatisfactory for separation of the resin and solvent phase. In order to determine the total solvent uptake, a procedure was developed in which the change of concentration of a reference solute, not absorbed by the resin, was determined. The solute used was methyl α-D-glucopyranoside, and its concentration was determined polarimetrically. This procedure, which is a modification of the " negative absorption " method,[8b] has been fully described.[9] It had the advantage that the transfer of solvent to the polarimetric tube could be carried out in a dry-box. The swelling results found by this method are considered accurate to ±2%.

The composition of the solvent remaining in the external phase after equilibration with the resin was in each case determined. From these results, together with the separate weights of water and ethanolamine initially taken and the results of the swelling determination, the weights of each of the two components of the solvent taken up by the resin phase could be calculated.

Equilibrium Experiments.—In each equilibrium experiment a weighed sample of dry resin, approximately 1 mg. equiv., was added to 25 ml. of a solution containing the calculated weight of the appropriate salt in aqueous monoethanolamine; the system was shaken for 1 week in an air-thermostat at 25°. The supernatant solution was analysed for alkali-metal cations; the ionic composition of the resin was found by elution with 0·1N-hydrochloric acid followed by analysis of the eluate. Only the alkali metals were determined; where the ethanolammonium ion was involved its concentration was found by difference.

From the results of preliminary experiments the quantities could be chosen such that in the final equilibrium the two exchanging ions were present in the resin phase in equivalent amounts; *i.e.*, the ion fraction, X, was always 0·5 (to within 5%). Equilibrium for each pair of ionic species was studied in several different monoethanolamine–water mixtures.

In most cases the determinations were carried out in duplicate, equilibrium being approached from opposite directions in the two determinations; *e.g.*, for the equilibrium $R^-K^+ + Na^+ \rightleftharpoons R^-Na^+ + K^+$, the selectivity coefficient was determined both by adding sodium iodide solution to the potassium form resin and by the converse procedure. Normally the two results were in good agreement and mean values could be taken. In solvents of low water content, however, equilibrium could not be reached at 25° if an alkali-metal ion was initially in the resin phase, since under these conditions exchange proceeds at a negligible rate.[10] Selectivity coefficients for alkali-metal and monoethanolammonium ions could be determined in solvents of low water content only if the resin was initially in the ethanolammonium form, in which case ion-exchange takes place at a finite rate. For equilibria involving only alkali-metal ions, selectivity coefficients could not be determined at 25° when the solvent contained less than 10% of water ($X_{H_2O} = 0·27$). In these cases measurements at 100° together with a comparison of selectivity coefficients between different alkali-metal ions and ethanolammonium

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* The titrimeter used was designed and presented by the Research Department of Messrs. African Explosives and Chemical Industries Ltd., to whom the authors are indebted.

[8] (*a*) Gregor, Held, and Bellin, *Analyt. Chem.*, 1951, **23**, 620; (*b*) Pepper, Reichenberg, and Hale, *J.*, 1952, 3129.

[9] Arnold, Macintosh, and Stephen, *Chem. and Ind.*, 1961, 2051.

[10] Arnold and Churms, unpublished results.

ion gave approximate values so that extrapolation of the selectivity–composition curves (Fig. 3) could be carried out.

RESULTS

The results are shown in Figs. 1—5 and Table 1. In reporting these results the following terms are used. For an ion-exchange equilibrium $R^-B^+ + A^+ \rightleftharpoons R^-A^+ + B^+$, the practical selectivity coefficient $K_B{}^A$ is used, defined as equal to $\overline{[A^+]}[B^+]/\overline{[B^+]}[A^+]$, where the terms in brackets are concentrations, those with superscript bars referring to the resin phase. The abbreviations Ea and Ea$^+$ are used for monoethanolamine and the monoethanolammonium ion, respectively. Solvent compositions are reported as "mole fractions" X_{H_2O} and $\overline{X}_{H_2O}$; these are calculated without considering species other than water and ethanolamine; *i.e.*, $X_{H_2O} = N_{H_2O}/(N_{Ea} + N_{H_2O})$.

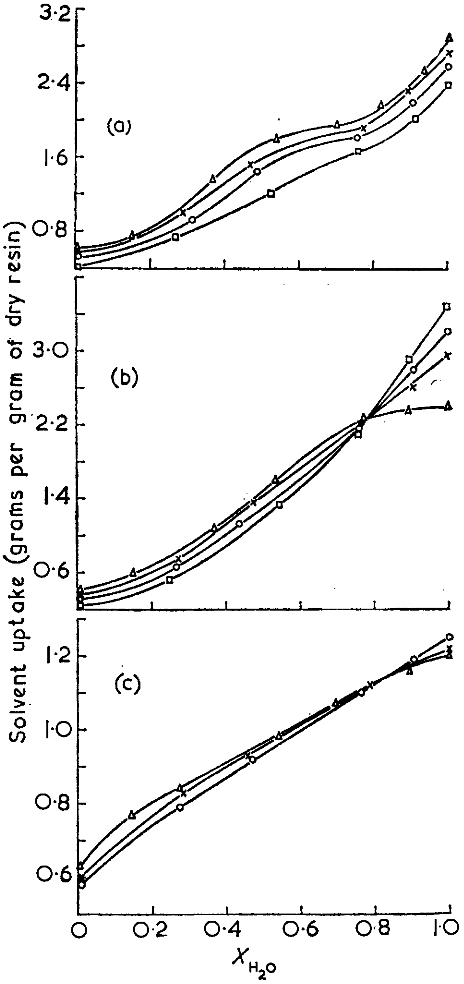

FIG. 1. Variation of weight-swelling with water content of external phase.

△, Ea$^+$; ×, K$^+$; ○, Na$^+$; □, Li$^+$.

(a) Amberlite IRC-50;
(b) ZeoKarb 225 (2% DVB);
(c) Amberlite IR-120.

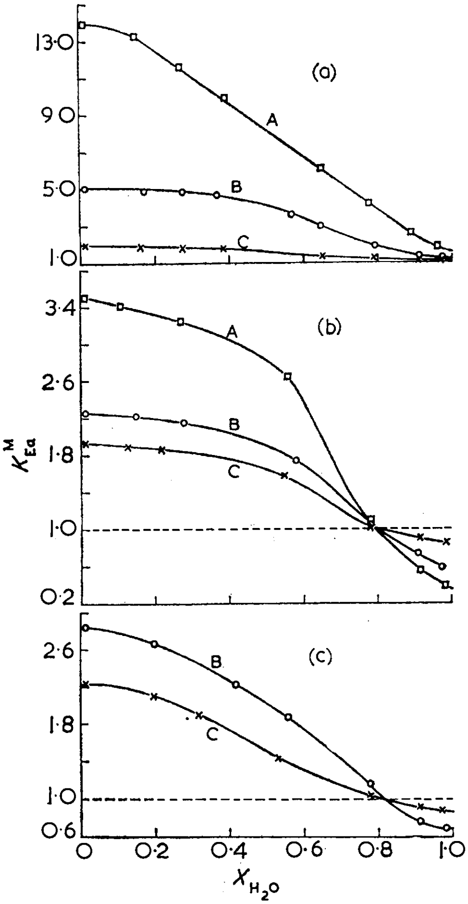

FIG. 2. Variation of selectivity coefficients with water content of external phase.

A, $K_{Ea}{}^{Li}$; B, $K_{Ea}{}^{Na}$; C, $K_{Ea}{}^{K}$.

(a) Amberlite IRC-50;
(b) ZeoKarb 225 (2% DVB);
(c) Amberlite IR-120.

TABLE 1.

Water selectivity of resins.

	$\bar{X}_{H_2O}/X_{H_2O}$										
	Amberlite IRC-50				ZeoKarb 225				Amberlite IR-120		
X_{H_2O}	Ea^+	K^+	Na^+	Li^+	Ea^+	K^+	Na^+	Li^+	Ea^+	K^+	Na^+
0·1	3·20	1·30	1·70	2·30	2·40	1·10	1·20	1·90	2·60	1·20	1·50
0·3	2·02	1·27	1·50	1·67	1·70	1·10	1·13	1·60	1·80	1·17	1·33
0·5	1·49	1·24	1·38	1·44	1·42	1·08	1·10	1·36	1·44	1·14	1·26
0·7	1·30	1·20	1·23	1·26	1·23	1·07	1·09	1·17	1·26	1·12	1·20
0·9	1·11	1·09	1·09	1·10	1·09	1·07	1·08	1·09	1·08	1·08	1·08

The main points emerging from the results are as follows.

(i) In all cases there is a decrease in swelling as the water content of the solvent decreases (Fig. 1); there is also an increase in selectivity (Figs. 2 and 3).

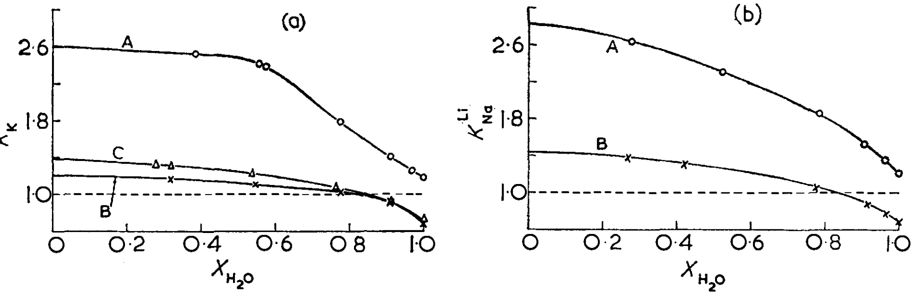

FIG. 3. Variation of selectivity coefficients with water content of external phase.
A, Amberlite IRC-50; B, ZeoKarb 225 (2% DVB); C, Amberlite IR-120.
(a) Sodium–potassium selectivities; (b) Lithium–sodium selectivities.

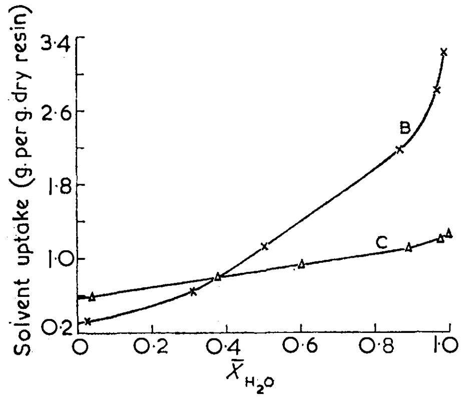

FIG. 4. Weight-swelling of two sulphonic resins at various water contents of the resin phase.

B, ZeoKarb 225 (2% DVB), Na^+-form;
C, Amberlite IR-120, Na^+-form.

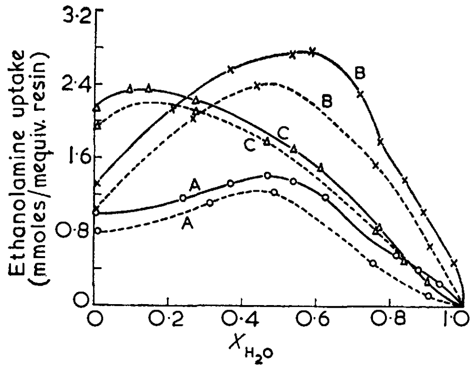

FIG. 5. Variation of ethanolamine with water content of external phase.

A, Amberlite IRC-50;
B, ZeoKarb 225 (2% DVB);
C, Amberlite IR-120.

Full curves, Ea^+-form; broken curves, Na^+-form.

(ii) For different ionic forms of the carboxylic resin the swelling decreases in the order $Ea^+ > K^+ > Na^+ > Li^+$ over the entire range of solvent composition. In the case of the sulphonic resins, however, the order for the different forms depends upon the solvent composition. Over most of the range the order is the same as that for the carboxylic resin, but at high water contents a reversal takes place [Figs. 1(b) and (c)]. For each resin the curves for different ionic forms converge at a single point, this reversal point being at $X_{H_2O} = 0{\cdot}79$ for the 2% DVB resin and at 0·83 for the 12% DVB resin. (When swelling is plotted against the internal water content, $\bar{X}_{H_2O}$, there appears another, higher value of total swelling at which $\bar{X}_{H_2O}$ is the same for the alkali metals, but the curve for the ethanolammonium form is quite different and shows no true cross-over.)

(iii) Over the entire range of solvent composition the carboxylic resin shows the affinity sequence $Li^+ > Na^+ > K^+ > Ea^+$ [Figs. 2(a) and 3]. In the case of the sulphonic resins the sequence undergoes reversal. The curves for the selectivity between the individual alkali-metal ions and the ethanolammonium ion intersect at a single point [Figs. 2(b) and (c)]; since, at this point, $K = 1{\cdot}0$ the position of the ethanolammonium ions is also reversed. The compositions of the external solvent at these reversal points are the same as those found at the corresponding reversal points in the swelling curves. Only below these values of X_{H_2O} is the affinity sequence of the sulphonic resins the same as that of the carboxylic resins. When the selectivity between alkali-metal ions is determined directly (Fig. 3), the reversals appear to occur at slightly higher values of X_{H_2O} (0·82 and 0·84 for the 2 and 12% DVB resins, respectively).

(iv) For a given ionic form the 2% DVB sulphonic resin sorbs more solvent than the 12% DVB resin in most solvent mixtures. In media of high monoethanolamine content, however, the more highly cross-linked resin swells more at a given solvent composition for all ionic forms studied [cf. Figs. 1(b) and (c), and see also Fig. 4].

(v) In all cases the resin sorbs water preferentially, the preference being most marked when the water content of the external phase is low (see Table 1). For the sulphonic resins this preference increases with cross-linking of the resins. For each resin the water selectivity of the different ionic forms decreases in the order $Ea^+ > Li^+ > Na^+ > K^+$.

(vi) The uptake of water by each resin increases continuously with the water content of the external phase, but the amount of monoethanolamine sorbed passes through a maximum. This was found with all the resins and in all ionic forms (typical curves in Fig. 5). The ethanolammonium forms of the three resins take up more ethanolamine than the alkali-metal forms. In almost pure ethanolamine the carboxylic resin takes up less than one mole of solvent per resin site.

(vii) The usual rise in selectivity with increasing cross-linking is observed in the case of the sulphonic resins. This applies even at low water concentrations, where the more highly swollen resin is the one of higher cross-linking.

(viii) At a given solvent composition the carboxylic resin is more selective than the sulphonic resin of comparable swelling (ZeoKarb 225), and is generally more selective than either of the sulphonic resins. Some of the selectivity coefficients for the carboxylic resin reach high values when the water content is low; *e.g.*, K_{Ea}^{Li} is 13·95 and K_{Ea}^{Na} 5·02 in 99·65% monoethanolamine. The carboxylic resin also shows greater selectivity for water than the 2% DVB sulphonic resin.

DISCUSSION

Interaction Sequences of Ions.—The general effects of the organic solvent in decreasing swelling and increasing selectivity have been observed and discussed.[1b, 2b] The most important feature of the present results is that these effects are shown to be more marked with some ionic forms of the sulphonic resins than with others, so that reversals of the swelling and selectivity sequences occur. Thus the so-called " normal " sequence shown by the sulphonic resins in water is reversed not only if the sulphonate group is replaced by a carboxylate group but also if some of the solvent water is replaced by ethanolamine. The basic solvent, which was used in order to increase the effective acid strength of the carboxylic resin and make it comparable with the better-known sulphonic resins, has in fact caused the sulphonic resin to behave like the carboxylic resin in water.

The different swelling and selectivity sequences which occur in ion-exchange and related phenomena have been explained[11] in terms of the energy of interaction of the exchange ions and the fixed sites. In terms of these ideas, the simplest explanation

[11] *E.g.*, (*a*) Eisenman, *Biophys. J.*, 1962, **2**, Suppl. p. 259; (*b*) Report of the National Chemical Laboratory, Teddington, 1961, p. 29.

of the sequences found here is as follows. In pure water, interaction of the carboxylate group and the alkali-metal ions is strong enough to remove, at least partially, the solvation shell around the ions, so that the distance of approach, and hence the interaction energy, is determined by the crystal radii of the ions and is in the order $Li^+ > Na^+ > K^+$. However, the electrostatic force exerted by the sulphonate group, *i.e.*, its " effective field strength," [11a] is less than that of the carboxylate group, and in pure water this group is unable to cause stripping of the hydration shells of the alkali-metal ions. Hence, the order of energy of interaction is the reverse of the above, being now determined by the hydrated radii. On addition of ethanolamine to the solvent the effective field strength of the sulphonate group increases, and at a certain stage solvent-stripping occurs, resulting in a reversal of the interaction order.

The question arises, therefore, as to how the ethanolamine increases the energy of interaction of the ions. Many of the effects of organic solvents on ion-exchange and other electrolytic phenomena have been attributed to a lowering of the dielectric constant. Such an explanation is inadequate to explain how the reversals observed in the present work could be caused by the addition of as little as 15% of monoethanolamine to the solvent. Previous authors studied the effects of ethanol,[12] methanol,[12a] and acetone [12a] on the exchange of alkali-metal ions on sulphonic resins. These solvents have dielectric constants lower than that of monoethanolamine, and, although concentrations of up to 100% of the organic liquid have been used, no reversals in either the swelling or the affinity orders have been observed.

Shabanov, Gorshkov, and Panchenkov [13] reported a reversal in the order of conductances of the Li^+-, Na^+-, and K^+-forms of a sulphonic acid resin when high concentrations (80—100%) of methanol or acetone are added. No reversal in the swelling order was observed, however. The relationship, if any, of conductivity to exchange affinity has not yet been established.[14]

It has been pointed out [15] that the effective field strength in an ion-exchange resin may also be increased if the charged groups are brought closer together so that their electric fields overlap. The shrinking of the resin on addition of the organic solvent would presumably have this effect. However, reversal of the interaction order occurs for Amberlite IR-120 when the swelling has been reduced by only about 10%, whereas on addition of ethanol to the very similar resin Dowex 50 the swelling may be reduced to less than half of its value in water without reversal of the swelling order for alkali-metal forms.[12b]

These comparisons make it seem likely, therefore, that the effect of the ethanolamine is more specific or chemical. Possibly the monoethanolamine molecule, because of its bipolar nature, is able to act as a bridge between the cations and the sulphonate groups; this would, in effect, increase the formation of ion-pairs. (There is evidence [16] that even in water the oppositely charged partners of an ion-pair are separated by a single water molecule.) In this case the distances of separation would be in the same order as the radii of the unhydrated ions. (At the cross-over point for the more highly cross-linked resin there is an average of only 0·5—0·6 mole of ethanolamine per equivalent of resin. This does not, however, necessarily conflict with the above explanation, since it is only necessary for some, not all, of the ions to have reacted with ethanolamine in order to reduce the selectivity coefficient to unity.)

A complete account of the ion-exchange process would have to take into account changes in the free energy of the solution phase as well as of the resin phase.[17] Thus,

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[12] (*a*) Panchenkov and Gorshkov, *Vysokomol. Soedineniya*, 1961, **3**, 177; (*b*) Rückert and Samuelson, *Acta Chem. Scand.*, 1957, **11**, 303; (*c*) Bhatnagar, Arora, and Kurian, *J. Indian Chem. Soc.*, 1963, **40**, 124.

[13] Shabanov, Gorshkov, and Panchenkov, *Russ. J. Phys. Chem.*, 1962, **36**, 1157.

[14] Puri, Duke, and Lomnes, *Iowa State Coll. J. Sci.*, 1956, **31**, 25.

[15] Report of the National Chemical Laboratory, Teddington, 1962, p. 42.

[16] Hamann, Pearce, and Strauss, *J. Phys. Chem.*, 1964, **68**, 375.

[17] Redhina and Kitchener, *Trans. Faraday Soc.*, 1963, **59**, 515.

another group of authors[18] discussed selectivities in terms of the effect of different ions on the structure of water. Effects of this kind could, at least partly, underly the reversals observed here. In a purely aqueous solvent a large ion such as potassium has a disruptive effect on the structure of water and is less favoured in the aqueous phase than the smaller " structure producing " ions such as lithium; hence, potassium is preferred in the less highly structured resin phase. If, however, the structure of the water in the solution phase has already been destroyed by the addition of large molecules such as those of monoethanolamine this effect of the potassium ions would no longer be important. Effects of this type are shown in the different free energies of transfer of alkali-metal ions from water to the more highly structured deuterium oxide.[19]

The fact that the swelling and selectivity cross-over points occur at a single value of the solvent composition in the external phase [*e.g.*, Figs. 1(b) and 2(b)], *i.e.*, at a particular value of the water activity in the two phases, offers more support for an explanation involving the properties of the solvent than for one involving interaction of ethanolamine molecules and ion-pairs. Measurement of heats and entropies of solution of alkali-metal ions in ethanolamine–water mixtures would indicate whether the structure-breaking effects are large enough to account for the observed phenomena.

Quantitative comparison of the selectivity coefficients for lithium with those of the other two alkali metals may be unreliable, since for lithium the sulphate rather than the highly deliquescent iodide was used. It has been shown[20] that different selectivity coefficients in ion exchange result when lithium sulphate rather than a lithium halide is used. It is unlikely, however, that this would affect the above arguments.

The position of the ethanolammonium ion in the affinity sequence demands consideration. On the carboxylic resin or on sulphonic resins in solvents of low water content the sequence is $Li^+ > Na^+ > K^+ > Ea^+$. This is consistent, on most theories, with the fact that the monoethanolammonium ion has the largest ionic radius. On sulphonic resins in solvents of high water content the sequence is completely reversed. This places the alkali metals in order of increasing hydrated radius, but the hydrated ethanolammonium ion is probably larger than the hydrated potassium ion. It cannot, however, be concluded from this that the hydrated radii are not of importance, since it is probable that the binding of the ethanolammonium ion will be enhanced by van der Waals forces of attraction to the hydrocarbon matrix of the resin.

Swelling and Water Sorption.—Another feature of interest is the reversal of the swelling order shown by the two sulphonic resins (Fig. 4); in solvents of low water content swelling increases with degree of cross-linking, which is the reverse of the usual behaviour.[8b,21]

Similar behaviour was observed by Sundheim, Waxman, and Gregor[22] in an investigation of the sorption of water vapour by cross-linked polystyrenesulphonic acid resins. At low relative humidities the amount of water sorbed increased with cross-linking, although at higher relative humidities the expected decrease in sorption with increasing cross-linking was observed. These authors suggested that, at low relative humidities, strong association between the polymer chains occurs, but that the number of close polymer–polymer contacts which may form is reduced if the degree of cross-linking is high; in other words, cross-linking can restrict shrinkage as well as swelling of a resin. For the more highly cross-linked resin, therefore, less work is required to overcome cohesion in the structure when the resin swells. Once sufficient water has been introduced to overcome cohesion between the polymer chains, further amounts of water will be taken up more readily by the resin of low cross-linking.

The results obtained here can be explained in the same way. Neither of the two

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[18] *E.g.*, Holm, *Arkiv Kemi*, 1956, **10**, 461; Chu, Whitney, and Diamond, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1405.

[19] Greyson, *J. Phys. Chem.*, 1962, **66**, 2218.

[20] Panchenkov, Gorshkov, and Kuklanova, *Zhur. fiz. Khim.*, 1958, **32**, 361.

[21] Gregor, Gutoff, and Bregman, *J. Colloid Sci.*, 1951, **6**, 245.

[22] Sundheim, Waxman, and Gregor, *J. Phys. Chem.*, 1953, **57**, 974.

sulphonic resins is swollen to any great extent in solvents of high ethanolamine content, and considerable association between the polymer chains is to be expected, particularly in the case of the 2% DVB resin. Addition of water causes separation of the chains, which is at first more difficult for the 2% DVB resin than for the 12% DVB resin. As the chains separate and the cohesive forces are overcome the swelling becomes equal and eventually higher in the case of the less cross-linked resin. The values of the solvent composition (X_{H_2O}) at the stage where the two sulphonic resins are equally swollen are as follows: Ea^+, 0·26; K^+, 0·31; Na^+, 0·35. Thus, larger counter-ions are more effective in reducing polymer–polymer contacts, so that less water is required to bring about further separation and to reverse the swelling order to its normal sequence.

It is interesting that Sundheim, Waxman, and Gregor[22] found that a 2% DVB sulphonic resin sorbs less water than a 13% DVB resin only when the relative humidity is below about 0·3. For an ideal solution X_{H_2O} is equal to the relative humidity; this accounts for the rough agreement between this relative humidity and the above values of X_{H_2O}. In the present work also the total number of moles of solvent sorbed per equivalent of resin at the swelling cross-over is approximately 3 for all ionic forms, and this again coincides with the observations of the above authors on their 2 and 13% DVB resins. Evidently, the sorption of three moles of solvent per equivalent of resin is necessary to overcome the effect of differences in inter-chain cohesion between a 2% and a 12—13% DVB sulphonic resin.

In these solvents of low water content, the more highly cross-linked resin is not only more swollen but also contains a solvent of higher water content than does the 2% DVB resin. Both of these factors would lead one to expect a lower ion-exchange selectivity for the resin of high cross-linking under these conditions. Nevertheless, the resin of higher cross-linking continues to show the higher selectivity, as in water. This rather surprising fact must be due to the more cross-linked resins having a higher elastic swelling pressure. (Kitchener[23] pointed out that cohesion between polymer chains should not be confused with elastic swelling pressure.) This implies that the pressure–volume term[24] makes an important contribution to the free energy of ion exchange in these solvent mixtures, although its effect is considered negligible in aqueous solutions.[17]

In all cases (Table 1) the resin phase contains a higher proportion of water than the solvent phase; this preference for water increases as the water concentration decreases. Previous investigators[1b] found that the more polar component of the solvent mixture is always sorbed preferentially except in cases where complex-formation is possible between the counter-ions and the less polar solvent.[4] In the present case water may, on account of its small size, be regarded as the more polar constituent of the mixture, even though the dipole moment of monoethanolamine (2·27 D) is somewhat higher than that of water (1·89 D). That the carboxylic resin shows a greater preference for water than the sulphonic resins under the same conditions may be ascribed to the polarisability of the former. In previous work[25] an increase in the preference for water with cross-linking has also been noted.

For the two sulphonic resins an interesting comparison can be made, arising out of the increase of swelling with cross-linking at low water contents. If weight-swelling is plotted against water content of the resin phase there is for each ionic form a " cross-over " point for the two resins; an example is shown in Fig. 4. Since it is the composition of the resin phase which is plotted, at these points both the amounts and the composition of the solvent are identical in two resins of a given ionic form. The conditions at these points are reported in Table 2; it will be seen that in each case the external phase in equilibrium

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[23] Kitchener in " Modern Aspects of Electrochemistry," No. 2, ed. Bockris, Butterworths, London, 1959, p. 98.

[24] Gregor, *J. Amer. Chem. Soc.*, 1948, **70**, 1293; *ibid.*, 1951, **73**, 642; Glueckauf, *Proc. Roy. Soc.* 1952, *A*, **214**, 207.

[25] Davies and Owen, *J.*, 1956, 1676.

with the more highly cross-linked resin is poorer in water. The effect is more marked with ions of lower ionic radius.

TABLE 2.

Conditions for equal swelling in sulphonic resins of different cross-linking.

Ionic form	Ea^+	K^+	Na^+
Weight of solvent sorbed per gram of dry resin (g.)	0·81	0·79	0·79
$\bar{X}_{H_2O}$	0·44	0·31	0·38
Corresponding value of X_{H_2O} for Amberlite IR-120..............	0·23	0·25	0·26
,, ,, ZeoKarb 225	0·25	0·28	0·31

This increased preference for water shown by the more highly cross-linked resin is probably due to its higher swelling pressure, which causes a lowering of free energy when water molecules replace the larger ethanolamine molecules. Since, however, the capacity of the more highly cross-linked resin (4·84 mg. equiv. per g.) is 5% lower than that of the resin of low cross-linking (5·07 mg. equiv. per g.), the results could also be partly due to a salting-in effect.

Sorption of Monoethanolamine.—The total ethanolamine sorbed by each resin passes through a maximum at a certain solvent composition (Fig. 5). Davies and Owen [25] reported a similar variation in the uptake of acetone from mixtures of this solvent with water by sulphonic resins with different degrees of cross-linking. As in the present work, these authors observed a fairly sharp maximum in the uptake of acetone by a resin with low cross-linking (2% DVB), while for a more highly cross-linked resin the maximum was much flatter.

These maxima may be explained as follows. At low water content of the solvent the resins are only slightly swollen and contain little of either of the two solvent constituents. As water is added the swelling increases, making the resin more permeable to the other, larger component. Thus, the amount absorbed increases with the total swelling. On the other hand the tendency of the resin to sorb the non-aqueous component must be expected to decrease as the concentration of the component decreases. The maxima result from the balance between these two opposing tendencies. Since the swelling of more highly cross-linked resins is less affected by the solvent composition, the maximum is reached more readily on addition of water to a resin of higher cross-linking.

The ethanolammonium forms of all three resins sorb more ethanolamine than the alkali-metal resinates in all cases; there is never any reversal of order in this respect. It is probable that this is due to the interaction of ethanolammonium ions with ethanolamine molecules through hydrogen bonding and van der Waals forces in addition to the ion–dipole attraction which is the only type possible in the case of the alkali-metal ions.

From almost pure ethanolamine all ionic forms of the 2% DVB sulphonic resin sorb almost 1 mole of ethanolamine per equivalent of resin, while the sorption by the 12% DVB resin is about 2 moles per equivalent of resin. The higher uptake by the resin with higher cross-linking is due to the greater permeability of this resin in media of low water content, as discussed previously. The uptake of ethanolamine by the ethanolammonium form of the carboxylic resin from almost pure ethanolamine is 1 mole per equivalent of resin, as in the case of the sulphonic resin of similar cross-linking, but that by the alkali-metal resinates is less than this, varying from about 0·6 to about 0·9 moles per equivalent. Howe and Kitchener,[26] in their study of the sorption of water vapour by poly(methacrylic acid) resins, also observed an initial solvent uptake of less than one mole per equivalent of resin, and concluded that in some cases the first molecule was bound to two adjacent carboxylate groups through hydrogen bonds. It appears possible that monoethanolamine can also interact with carboxylate groups in this way. Since the sulphonate group is less polarisable than the carboxyl group, such interaction through hydrogen bonding is unlikely in the case of sulphonic acid resins. For these resins the initial ethanolamine

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[26] Howe and Kitchener, *J.*, 1955, 2143.

uptake is never significantly less than one mole per equivalent of resin. This observation is consistent with the suggestion made earlier that single monoethanolamine molecules may act as bridges between the counter-ions and the sulphonate groups.

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