332. *The Behaviour of Ion-exchange Resins with Mixed Solvents.*

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Data are presented for the swelling of some ion-exchange resins in acetone–water and dioxan–water, and for the distribution of the solvents between the external and resin phases. The use of partition chromatography on ion-exchange columns is illustrated by some experiments with the alkali-metal cations.

In an earlier paper [1] it was reported that when aqueous acetone is in contact with an ion-exchange resin the acetone distributes itself unevenly between the two phases. The present communication describes the experiments from which this result was taken, and discusses some consequences and applications of solvent partition in ion-exchange systems.

Experimental

Materials.—Three sulphonated polystyrene resins, cross-linked with 2·25%, 5·5%, and 10% divinylbenzene, were used. They were of 60—100 mesh and had a capacity of 5·25 equivalents per kg. of dry hydrogen resin. They were cycled three times with 0·5N-sodium hydroxide followed by 0·5N-hydrochloric acid, and after complete conversion into the hydrogen form were washed to constant pH with conductivity water and air-dried. The moisture content was determined by drying over phosphorus pentoxide in vacuum at 80°. Zeo-Karb 225, used in the separation experiments, was treated in the same way. It was a sample in micro-bead form and had a capacity of 5·23 equiv. per kg. of dry hydrogen resin. The Dowex 2 was a commercial sample of 200—250 mesh. It was given a similar pretreatment and was used in the chloride form.

Acetone, of AnalaR quality, was dried over freshly ignited calcium sulphate for 48 hours and was then distilled. The distillate was stored in a dark bottle protected by a calcium chloride tube. AnalaR dioxan was refluxed with sodium and fractionally distilled. The fraction boiling at 101°/760 mm. was stored in the same way. Solutions with water were made up by weight.

Lithium chloride was prepared from lithium carbonate that had been recrystallised four times from conductivity water. The other salts were of AnalaR quality.

Equilibrium Experiments.—Approximately 2 g. of sulphonic acid resin, contained in a sintered-glass crucible, were equilibrated with about 30 ml. of acetone–water for 24 hr. in a closed apparatus. The crucible was then removed, and the resin externally dried by a gentle current of air for a period fixed by preliminary experiments as that after which the rate of loss of weight fell to a small constant value. The composition of the external solution was determined [2] by a density measurement at 25°. The resin was weighed, and then washed free from acetone with water. The acetone in the resulting solution was estimated by Tomada's iodometric method.[3] The whole method of separation and analysis was reproducible to within 0·5% when predominantly aqueous solvents were used; with solvents rich in acetone the error, attributable mainly to the surface drying technique, was ±4%.

Acetone is catalytically decomposed by strong-base resins, so in the experiments with Dowex 2 dioxan–water mixtures were chosen for study. The same equilibrating apparatus was employed, about 5 g. of Dowex 2 in the chloride form being used. The concentration of dioxan in the resulting solution was found by measuring the refractive index of the latter in an Abbé refractometer at 25° with sodium light. The concentration in the resin was obtained by difference, allowance being made for the original moisture content of the resin. Comparison with a previously determined graph enabled the concentration of dioxan to be estimated to within ±0·2%, but the overall error in the equilibrium measurements was as much as ±3% in the solutions rich in dioxan.

Separation Experiments.—20 g. of Zeo-Karb 225 micro-beads in the hydrogen form were introduced as a slurry into a Pyrex-glass tube, 1 cm. in diameter, and formed a column 100 cm. high, resting on a sintered-glass disc. The glass column was closed at the top by a ground-glass stopper through which passed a tube drawn to a fine point. To prevent disturbance of

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[1] Davies and Thomas, *J.*, 1952, 1607.

[2] Int. Crit. Tables, III, 112.

[3] Tomada, *J. Soc. Chem. Ind. Japan*, 1946, **49**, 1.

the resin surface a polythene disc was used to break the fall of drops. The column was conditioned by passing through it 100 ml. of 80% acetone–water at a rate of 20 ml./hr. A solution containing up to 1 milliequiv. each of lithium, sodium, and potassium chloride in the same solvent was slowly added, and formed a pale band at the top of the column. 0·7N-Hydrochloric acid in 80% acetone–water was then run through the column at 20 ml./hr. When alkali-metal cation was detected in the eluate (flame test) 10-ml. fractions were collected and evaporated to dryness on a steam-bath. The residues were heated in an oven at 130° and then dissolved in water. Free acid was determined in this solution by titration with 0·05N-sodium hydroxide and the total chloride by titration with 0·05N-silver nitrate; the difference gave the amount of alkali-metal chloride.

Isotope Fractionation.—10 ml. of 1N-lithium chloride were applied to the top of a column of Zeo-Karb 225, 40 cm. high and 10 cm. in diameter. The lithium was displaced by 0·1N-potassium chloride in 80% acetone–water, which was run on to the column at 5 ml./hr. 10-ml. fractions were collected, and the first and last fractions were examined in a mass spectrometer.

RESULTS AND DISCUSSION

Acetone–Water Equilibria.—In Figs. 1—3 the weights of water and acetone taken up by 1 g. of dry hydrogen resin are plotted against the molar fraction of acetone in the equilibrium solution. For all three resins the water uptake falls continuously. For the 5·5% and 10% cross-linked resins the acetone uptake rises fairly rapidly to a value that thereafter remains virtually constant. In the more lightly cross-linked resin, however, the acetone uptake shows a maximum when the molar fraction of acetone in the equilibrium solution has reached a value of approximately 0·5. Up to this point the total swelling of the resin has not been greatly affected by the presence of acetone but thereafter it falls rapidly and so does the uptake of acetone. An interesting feature of the results is that in each of the three resins the decrease in the amount of water absorbed is proportional, within experimental error, to the molar fraction in the resin phase. This is shown by the points marked by crosses in the diagrams, the same numerical scale of abscissæ now representing the molar fraction of acetone in the resin phase. Since these steep lines must eventually show a very marked change of slope, somewhat as shown by the dotted line in Fig. 1, they seem to imply that not more than about 0·34 g. of water per g. of resin, that is about 4 moles of water per equiv., are firmly held by the resin, the remainder being readily displaced by acetone.

A comparison of the Figures shows, as might be expected, that the more highly cross-linked the resin and the greater its concentration of ionising groups, the more strongly is acetone excluded from the resin phase. This is brought out more clearly in Table 1, which gives for the same experimental points the molar fraction of acetone in the resin phase $\bar{N}$; N, the molar fraction of acetone in the solution in equilibrium with it; and $\bar{f}$, the activity coefficient of the acetone in the resin phase. $\bar{f}$ has been calculated from Morton's vapour-pressure data [4] for acetone–water systems at 20° by means of the equation

TABLE 1.

2·25% D.V.B. resin			5·5% D.V.B. resin			10% D.V.B. resin		
N	$\bar{N}$	$\bar{f}$	N	$\bar{N}$	$\bar{f}$	N	$\bar{N}$	$\bar{f}$
0·043	0·032	8·09	0·053	0·039	7·94	0·050	0·010	29·4
0·083	0·068	6·42	0·103	0·061	8·22	0·103	0·029	17·3
0·118	0·080	6·79	0·135	0·072	8·08	0·218	0·064	10·8
0·143	0·120	5·02	0·212	0·098	7·03	0·310	0·081	9·19
0·240	0·159	4·50	0·310	0·132	5·64	0·400	0·087	8·60
0·358	0·201	3·69	0·433	0·152	5·10	0·503	0·115	6·96
0·512	0·255	3·21	0·610	0·181	4·72	0·585	0·109	7·73
0·525	0·260	3·17	0·750	0·202	4·46	0·605	0·118	7·18
0·715	0·297	3·01	0·775	0·212	4·28	0·725	0·139	6·47
0·883	0·343	2·81	0·900	0·227	4·16	0·750	0·134	6·72
0·945	0·359	2·71				0·790	0·126	7·21
						0·900	0·159	5·94

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[4] Morton, *J. Phys. Chem.*, 1929, **33**, 389.

$fN = p/p_0$, where p is the partial vapour pressure of acetone over a solution of molar fraction N and activity coefficient f, and p_0 is the vapour pressure of pure acetone; the f values were then combined with our results by the equation $\bar{f} = fN/\bar{N}$.

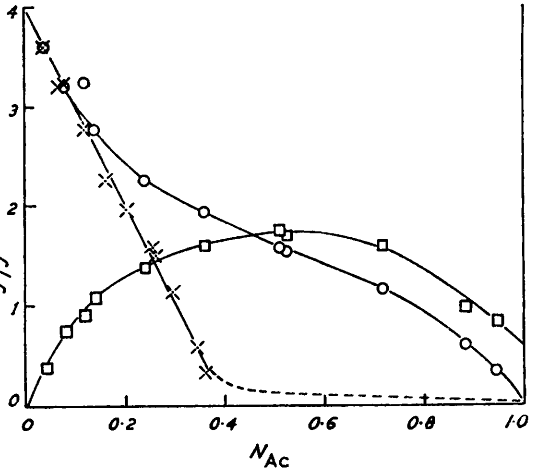

FIG. 1. 2·25% *cross-linked resin* (○ *water*; □ *acetone*).

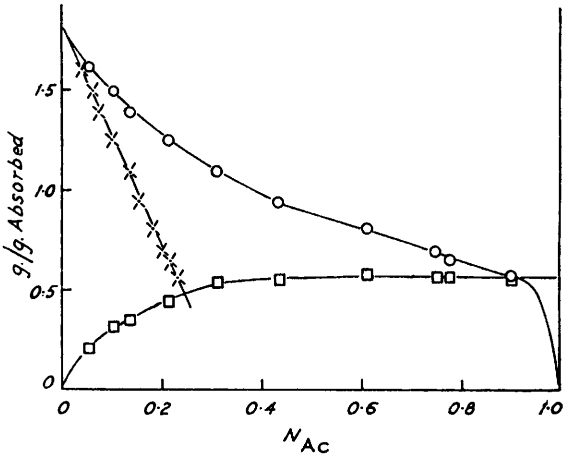

FIG. 2. 5·5% *cross-linked resin* (○ *water*; □ *acetone*).

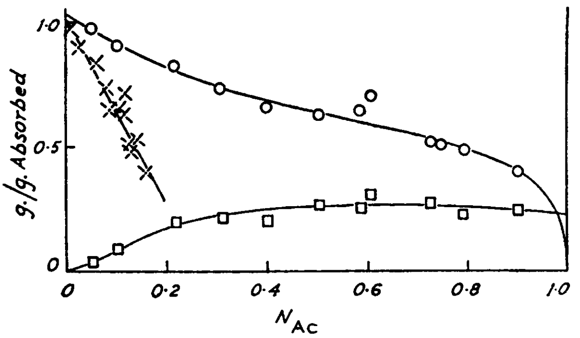

FIG. 3. 10% *cross-linked resin* (○ *water*; □ *acetone*).

Dioxan–Water Equilibria.—The results are in Fig. 4. This shows the same general features as the diagrams for the acetone–water system. The total swelling decreases only gradually until a molar fraction of 0·5 is reached in the equilibrium solution; thereafter decreasing amounts of both solvents are taken up, and the amount of swelling falls off rapidly. The plot of water uptake against the molar fraction in the resin phase is this time perceptibly curved. The rapid change in the slope of this line must occur somewhere below 0·15 g. of water per g. of resin. The capacity of the resin was 3·8 milli-equiv./g., so this result means that not more than 2 moles of water per equiv. are strongly held by the resin in its chloride form.

Partition-Exchange Chromatography.—In ion-exchange chromatography of strong electrolytes the separation of two similar charged solutes in aqueous solution is brought about through: (1) the stronger retention of one of them by the resin, which enables the other to pass through a resin column more rapidly; or (2) the formation of unstable complexes of opposite or zero charge, which are unretarded by the resin and therefore influence, to an extent depending on their stability constants, the net rate of movement of the two solutes down the column. The equilibrium experiments just described show that when a resin has been conditioned with a suitable mixed solvent the resin phase is predominantly aqueous and the ambient solution predominantly organic, so that conditions for partitiom chromatography between two phases of fixed composition are very conveniently set up, and the opportunity arises of using partition effects to enhance the normal separation factors.

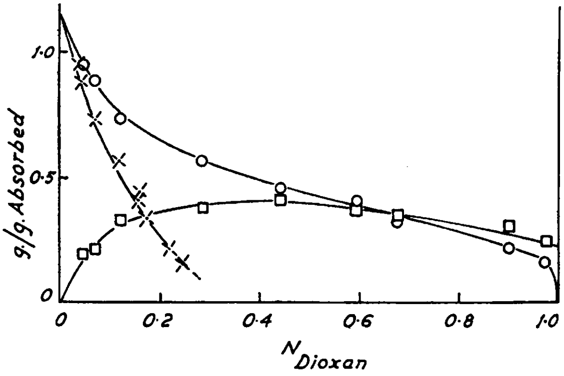

FIG. 4. *Dowex* 2 *resin* (○ *water*; □ *dioxan*).

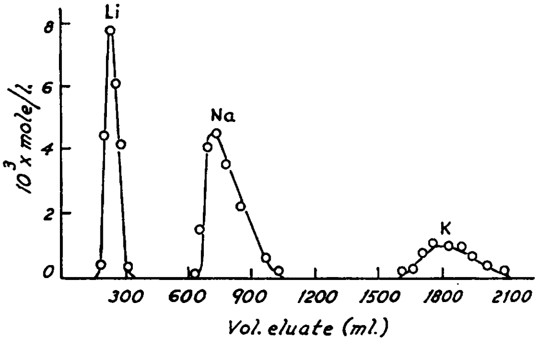

FIG. 5. *Elution curve.*

We have illustrated the possibilities by a separation of lithium, sodium, and potassium chlorides in 80% acetone–water as solvent with 0·7N-hydrochloric acid as eluant. Beukenkamp and Rieman [5] have used aqueous 0·7N-hydrochloric acid in a successful separation of sodium and potassium ions on a column of colloidal Dowex 50, and Kayas [6] has also separated sodium, potassium, and the heavier alkali-metal ions in aqueous solution. Lithium salts are weak electrolytes in acetone, ion-pair formation increasing in the order $K^+ < Na^+ < Li^+$. It was therefore thought probable that the presence of a high concentration of acetone in the ambient solution would increase the rate of flow of lithium salts

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[5] Beukenkamp and Rieman, *Analyt. Chem.*, 1950, **22**, 582.

[6] Kayas, *J. Chim. phys.*, 1950, **47**, 408.

down the column and would facilitate the separation and make the conditions for a successful separation less critical. Our elution curve is given in Fig. 5, and Table 2 shows that the separation procedure is satisfactory.

TABLE 2.

	Lithium	Sodium	Potassium
Milliequiv. introduced	0·365	0·673	0·510
Milliequiv. recovered	0·370	0·680	0·500

The volume of eluate between our sodium and potassium bands is 600 ml., and is much greater than the 140 ml. observed by Beukenkamp and Rieman when using the same concentration of eluting acid. It is likely, therefore, that a complete separation would be obtained over a wider range of conditions when 80% acetone–water is used instead of water as solvent, and that the application of the method to other difficult separations would repay study.

If the dissociation constant of ^{7}LiCl in 80% acetone–water were significantly different from that of ^{6}LiCl the method of partition-exchange would be of great value in the separation of these isotopic species. In the preliminary experiment which we carried out the ^{7}Li/^{6}Li ratios in the first and the final fractions were respectively $11{\cdot}62 \pm 0{\cdot}03$ and $11{\cdot}23 \pm 0{\cdot}03$, which are to be compared with the normal ratio of 11·52. The enrichment is significant, but not very promising. The column was short, and was not used under the conditions of maximum possible efficiency; but the result does not offer hope that the dissociation-constant difference is a very important factor in the solvent we employed.

In the ion-exchange chromatography of weak organic electrolytes in water an additional factor is introduced in the interaction of the organic solute with the resin.[7] The use of mixed solvents to modify the effect of this factor and so improve separations is illustrated in the following paper.

Absorption of Salts from Organic Solvents.—Katzin and Gebert [8] have reported that when air-dried Dowex 1 in chloride form is left in contact with acetone solutions of hydrochloric acid, or of various cobaltous, copper, lithium, or nickel salts, the resin absorbs the electrolyte almost quantitatively. For instance the copper and nickel salts are decolorised, and an originally 0·2M-solution of lithium chloride no longer gives a chloride test with silver nitrate. The authors established that the solute molecule as a whole disappeared from the liquid phase, and that the effect was influenced by the nature of the cations and anions present in the system and also by the water content of the resin. They suggest as possible mechanisms (1) that the acid is adsorbed by free weak base groups (produced by hydrolysis during washing) and (2) that the salts might be adsorbed as negatively charged complex ions. These explanations are rather difficult to accept, as there seems no other evidence for very weak basic groups in Dowex 1 or for the complex anions (especially with lithium) that have to be postulated. On the other hand, effects of the kind observed might be expected as a consequence of the distribution of solvents in the systems studied. Data are lacking for a quantitative test, but it would seem from Fig. 3 that if an air-dried resin of 20% moisture content were immersed in pure acetone, it would absorb acetone to give an inner solution with molar fraction of water of about 0·8, the outer solution remaining virtually pure acetone. Distribution coefficients of the order of 100 in favour of the aqueous phase would then explain the passage of very high percentages of a strong electrolyte from acetone solution into the resins in Katzin and Gebert's experiments.

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[7] Davies, *Biochem. J.*, 1949, **45**, 38.

[8] Katzin and Gebert, *J. Amer. Chem. Soc.*, 1953, **75**, 801.