

262. Cation Exchange with a Synthetic Phenolsulphonate Resin.
Part IV. A Note on Equilibria in Presence of Non-aqueous Solvents.

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Cation exchange occurs readily between a phenol-sulphonate resin and cations in mixtures of water and non-aqueous solvents. The equilibria are found to obey the law of mass action, concentrations being used. More potassium ion passes into the solid phase in the $\text{NH}_4^+ - \text{K}^+$ system in aqueous ethanol and aqueous acetone than in pure water. In aqueous ethanol the logarithm of the equilibrium constant is a linear function of the alcohol concentration; in aqueous acetone the equilibrium constant itself varies linearly with the acetone concentration. This behaviour cannot be explained by differences of hydrated cationic size: however, an explanation may lie in the influence of solvent on the a° values. The effect of incomplete dissociation on the equilibrium constant is very marked with manganous sulphate in aqueous ethanol.

VERY few studies have been made of equilibria between cation exchangers and solutions of salts in the presence of non-aqueous solvents. Only a single set of data appears in the literature (Wiegner and Muller, *Z. Pflanz. Dung.*, 1929, 14, A, 332; Wiegner and Jenny, *Kolloid-Z.*, 1927, 42, 270) in which the solvent was aqueous alcohol and the exchanger a synthetic aluminosilicate. No study has been reported with a resinous exchanger.

The present study has been limited to aqueous ethanol and aqueous acetone as solvents at 25°, but it is clear from the results that the subject is a complex one and considerably more work is necessary before any general rules can be formulated. Certain limitations are set by the extreme scantiness of activity data of salts in the presence of non-aqueous solvents.

In the experiments of Wiegner *et al.* (*loc. cit.*) a calcium zeolite was allowed to come to equilibrium with sodium, potassium, and caesium chlorides dissolved in aqueous ethanol of various concentrations, and the results indicated that more alkali ion passed into the solid phase as the concentration of ethanol was increased, and the exchange became more nearly equal for all the ions. It was shown that the exchange varied linearly with the concentration of ethanol, and this was correlated with the dielectric constant of the mixture, which similarly varies with the concentration of ethanol.

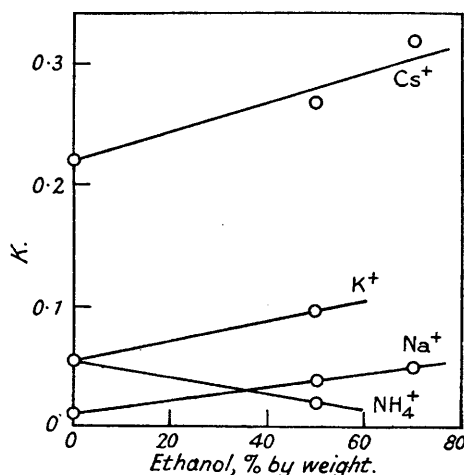
Similar experiments have now been carried out with a calcium resin (prepared from the same resin as that used in Parts I—III) and 0.05N-solutions of sodium, potassium, and caesium chlorides. The results, illustrated in Fig. 1, show that more alkali ion likewise passed into the solid phase with increasing alcohol content of the solvent, in agreement with the findings of Wiegner *et al.* The extent of exchange, however, showed no tendency to become equal for the several ions. The ammonium ion behaved conversely to the alkali ions and showed a reduced affinity as the proportion of ethanol was increased.

This suggests that, in exchanges between ammonium and the alkali-metal ions, the resin would show an increased affinity for the latter by comparison with the former as the ethanol concentration is increased and this, in fact, is found to be the case. Table I shows the values of the stoichiometric equilibrium constants obtained for some alkali-metal ions in 0.1N-chloride solution and the resin initially in the ammonium form. The equilibrium constant is defined by

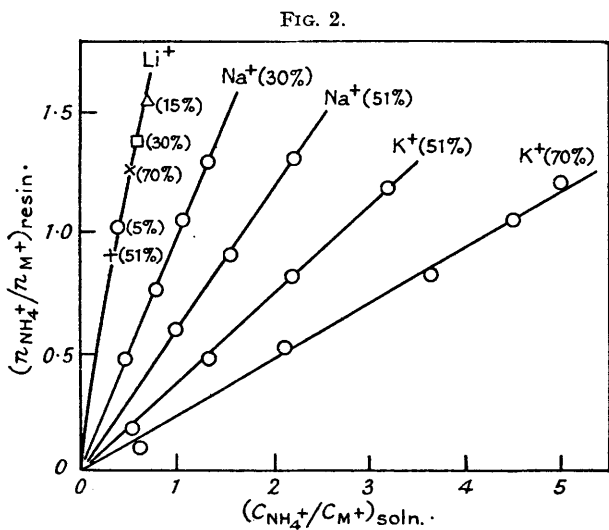
$$K = (n_{\text{M}^+}/n_{\text{NH}_4^+})_{\text{resin}}(C_{\text{NH}_4^+}/C_{\text{M}^+})_{\text{soln.}} \dots \dots \dots (1)$$

and was obtained from the slopes of the straight lines which result on plotting $(n_{\text{NH}_4^+}/n_{\text{M}^+})_{\text{resin}}$ against $(C_{\text{NH}_4^+}/C_{\text{M}^+})_{\text{soln.}}$ (see Fig. 2). (The n terms in these expressions are the number of equivalents of the specified ion in the resin at equilibrium, and the C terms are the corresponding solution concentrations.) A linear relationship exists between the logarithm of the equilibrium constant and the ethanol concentration, although the equilibrium constant of the $\text{Li}^+ - \text{NH}_4^+$ system remains the same as in pure water, even up to 70% alcohol.

FIG. 1.



The $K^+ - NH_4^+$ equilibrium (NH_4 -resin and KCl) has been studied in aqueous acetone solution also. Straight lines were also obtained on plotting the appropriate mass-action functions (equation 1), and the equilibrium constants obtained from these are given in Table II. The change of equilibrium constant with acetone concentration, although in the same direction, is



Figures in parentheses are concentrations of ethanol.

less marked than with ethanol. Further, the equilibrium constant varies linearly with acetone concentration.

TABLE I.

Ethanol concn. (% by wt.).	Equilibrium constant (25°).			Ethanol concn. (% by wt.).	Equilibrium constant (25°).		
	LiCl.	NaCl.	KCl.		LiCl.	NaCl.	KCl.
0	0.40	0.67	1.05	30.5	0.40	1.04	2.04
5.0	0.40	—	—	51.5	0.40	1.67	2.73
15.5	0.40	—	1.47	70.5	0.40	—	4.25

TABLE II.

Acetone concn. (% by wt.)	0	31.0	50.9	71.0
Equilibrium constant (25°)	1.03	1.64	1.97	2.28

TABLE III.

Salt and normality.	Equilm. const. in 51.5% EtOH.	Equilm. const. in H ₂ O.	Salt and normality.	Equilm. const. in 51.5% EtOH.	Equilm. const. in H ₂ O.
BaCl ₂ , 0.1	23.0	5.64	MnSO ₄ , 0.1	0.036	0.82
MnCl ₂ , 0.1	1.14	1.00	„ 0.05	0.44	0.82

Table III shows the equilibrium constants at 25° for an ammonium resin and solutions of barium chloride, manganese chloride, and manganese sulphate in 51.5% (by weight) aqueous ethanol. These are defined by

$$[(C_{NH_4^+})^2/C_{M^{++}}]_{soln.} = K[(N_{NH_4^+})^2/(N_{M^{++}})]_{resin} \dots \dots \dots (2)$$

and are obtained from the slopes of the straight lines which result on plotting the appropriate mass-action functions. (Each N term in this equation is the ratio of the number of equivalents of the cation to the total number of equivalents of the two cations in the resin phase; the C terms are the concentrations of the ions in the solution phase, in eqivs per l.) A comparison of the figures with those obtained in pure water shows that barium ion in 0.1N-chloride solution has a higher affinity for the resin in 51.5% aqueous ethanol than in pure water, while manganese ion in 0.1N-chloride shows almost the same affinity as in water. On the other hand, the latter ion in 0.1N-sulphate solution shows a very much lower affinity in the aqueous-alcoholic solution than it does in water—comparable, in fact, with that of lithium. In 0.05N-solution the affinity

is greater, by comparison with that in 0.1N-solution, than is predicted by the mass-action equation (2), as indicated by the different K .

Discussion.—The results expressed in Table I could perhaps be explained on an assumption, similar to that of Wiegner *et al.* (*loc. cit.*), that the alkali-metal ions are dehydrated by the alcohol to a greater extent than is the ammonium ion. This theory seems to be untenable, however, as measurements of the mobilities of the potassium and the ammonium ions, carried out in aqueous-ethanolic solution containing 51.5% by weight of alcohol, showed these to be very nearly equal, *viz.*, 50.1 and 51.5, respectively, just as they are in pure water. Consequently, the hydrated radii must be practically equal. It is possible, however, that the a° values of the two ions have changed to different extents in the alcoholic solution, and since the equilibria are determined by these values rather than by hydrated radii, this would account for the observed effect. Unfortunately, no data exist from which these values can be calculated and it is, accordingly, impossible to test this theory.

Certainly the different behaviour of the lithium ion precludes any correlation with dielectric constant as attempted by Wiegner (*loc. cit.*), since this would presuppose a similar variation with alcohol concentration in each case.

Similar considerations evidently apply to the $\text{NH}_4^+\text{-Ba}^{++}$ equilibrium. The behaviour of the manganous ion in sulphate solution, however, indicates that here the "affinity" is largely determined by the degree of dissociation of the manganous sulphate. The low value of the equilibrium constant in 0.1N-alcoholic solution is evidently the result of the very slight ionisation of the manganous sulphate, few manganese ions being available to pass into the resin phase. Dilution increases the ionisation and more of these ions therefore pass into the solid phase than is predicted by equation (2), and a different equilibrium "constant" is obtained in 0.05N-solution. An indication of the very small dissociation of manganous sulphate is the difficulty with which it dissolves in the aqueous alcohol solution. Manganous chloride, and especially barium chloride, on the other hand, dissolve readily.

It is interesting to speculate upon the state of ionisation of the metal salts of the resin. Whereas the degree of dissociation of an aqueous electrolyte changes with the addition of a non-aqueous solvent, that of the resin salt must apparently be supposed the same in the presence of all solvents. According to present theory, incomplete dissociation of a salt in solution is not generally due to the existence of covalent linkages, but to the presence of ion pairs, triple ions, etc. (see, *e.g.*, Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," 1943, pp. 183 *et seq.*). Presumably a similar situation exists in the resin salts, which may, therefore, be regarded as completely ionised but almost entirely undissociated.

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