Solvent Effects on Ion Exchange Equilibria. Part I.

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Introduction

It has been found that the addition of non-electrolytes to the ion exchange system generally causes shifts in equilibrium, which depend on the composition of the solvent system, the ionic species, etc. These effects have been studied in detail from the physico-chemical point of view, and some noticeable regularities have been found, thus suggesting that simple and well-defined procedures may be added to the list of ion exchange techniques.

The fact that only a few papers on this subject have as yet been published indicates that this aspect has been somewhat overlooked in the past. Some decades ago Wiegner et al[1] studied the ion exchanges between a calcium zeolite and various alkali chlorides dissolved in aqueous ethanol, and observed that more alkali ions passed into the exchanger as the concentration of ethanol was increased and that the exchange became nearly equal for all ions at higher concentrations of alcohol. The problem remained untouched until a recent investigation by Kressman and Kitchener[2]; they studied the effect of the addition of an organic solvent on the exchange of alkali ion, using a phenolsulfonate resin. It was found that with the calcium resin-alkali salt system in aqueous ethanol the logarithm of the equilibrium constant increased linearly with the ethanol percentage, whereas with the $NH_4^+-K^+$ system in aqueous acetone the equilibrium constant itself changed linearly with the acetone concentration. More recently Okuno, Honda and Ishimori[3] investigated the exchange of alkali ions by sulfonated styrene type resins (H-form) in aqueous solutions containing various quantities of methanol or ethanol. They observed that the difference in the equilibrium constants of various alkali ions became greater as the alcohol concentration was increased. Their results have been reconfirmed by the more detailed study of the same system carried out in our laboratory under the collaboration of Kakihana and his co-workers.

A short note on our results has already been published[4] and the application of these to analytical and preparative chemistry has been discussed elsewhere.[5] Therefore the present paper will be limited to the physico-chemical treatment of the problem.

Experimentals and Results

(i) **Properties of the Resin Used.**—Amberlite IR-120 was used. Conventional techniques were employed for the conversion of the resin to the H-form, regeneration, determination of the exchange capacity per gram of dry resin, etc.

When the H-resin granules, which had been dried at 100°C under 15 mm Hg to constant weight, were allowed to absorb water vapor at 100 per cent relative humidity at room-temperature during ten days, it uptook 0.9 gram of water per gram of dry resin. To determine the exchange capacity of the resin, 0.1N solutions of potassium chloride in water, and 20, 40, 60, 80 and 100 per cent methanol or ethanol were used. This was found to be 5.10 ± 0.02 meq. per gram of dry resin, independent of the alcohol concentration of the solution used, that is, the total capacity was uninfluenced by the addition of alcohol.

(ii) **Experimental Procedures.**—The measurements were carried out under the following conditions. The alkali chloride was dissolved in the aqueous solution containing a known amount of alcohol, to yield 0.05, 0.1, or 0.2N salt/l. solutions. An adequate amount of the H-resin was added to 50 ml. of the salt solution, and subsequently the vessel containing the exchange system was kept shaken at 25 ± 0.05°C until the equilibrium had been attained. An aliquot portion of the solution was then analyzed for the hydrogen ion. The mole ratio of an alkali ion to hydrogen ion in the resinous phase at equilibrium was kept around unity by varying the quantity of the resin added. To avoid error due to the instability of the H-resin, the exchange capacity of the resin sample was simultaneously determined with each measurement of the exchange equilibrium.

(iii) **Apparent Equilibrium Constant.**—The exchange reaction involving metal ion M^+ and hydrogen ion H^+ is written as,

$$M^+ + HR = H^+ + MR.$$

The apparent exchange equilibrium constant, K_H^M, is given by

$$K_H^M = \frac{[H^+][MR]}{[M^+][HR]} \tag{1.1}$$

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[1] G. Wiegner and H. Jenny, *Kolloid-Z.*, **42**, 268 (1927).

[2] T. R. E. Kressman and J. A. Kitchener, *J. Chem. Soc.*, **1949**, 1211.

[3] H. Okuno, M. Honda and K. Ishimori, *Bunseki-Kagaku* (*Japan Analyst*), **2**, 430.

[4] T. Sakaki and H. Kakihana, *Kagaku* (*Science*), **23**, 471 (1953).

[5] H. Kakihana, Chemical Industry (Kagaku Kogyo), Symposium Kogyo-Keisoku.

TABLE I

EFFECT OF ALCOHOL (25°C)

Salt	Conc. (N)	Alkali chloride—H-resin (Amb. IR-120)				
LiCl	0.2	Wt. % of methanol	0	30.0	50.0	
		K_H^{Li}	0.84_4	1.45	2.15	
	0.1	Wt. % of ethanol	0	21.8	36.7	40.5
		K_H^{Li}	0.80_3	1.32	2.18	2.37
NaCl	0.05	Wt. % of methanol	0	13.5	29.5	47.0
		K_H^{Na}	1.70	2.86	5.07	10.7
	0.2	Wt. % of ethanol	0	14.0	32.0	
		K_H^{Na}	1.84	3.33	8.15	
KCl	0.1	Wt. % of methanol	0	13.5	21.5	
		K_H^K	3.61	4.74	6.65	
	0.2	Wt. % of ethanol	0	14.0	34.0	
		K_H^K	3.74	5.25	17.8	

The mole ratio, $[MR]/[HR]$, was kept at 0.85–1.10 for Li^+ and Na^+, and at 1.86–2.30 for K^+.

where the bracket [ ] represents the analytical concentration of each species in eq./l.

The equilibrium measurements were carried out with 0.2N, 0.1N and 0.05N alkali chloride solutions containing various amounts of alcohol. A part of the results is given in Table I as typical data illustrating the solvent effects. It is to be noted that the following features may be deduced from these results.* First, for the same metal ion and for the equal content of alcohol, K_H^M is always greater in aqueous ethanol than in aqueous methanol; secondly, the value of K_H^M becomes higher as the alcohol concentration is increased, and finally, the sequence of the magnitude of K_H^M is $K^+ > Na^+ > Li^+$, provided that the alcoholic solutions are of identical concentration.

Discussion

(i) The Free Energy Change of Ion Exchange and the Dielectric Constant of Solution.

—In the system of aqueous alkali chloride solution and the sulfonic acid exchanger, it has been found by Boyd, Schubert and Adamson,[6] and ascertained by Kressman and Kitchener[7] that the apparent free energy change** accompanied by ion exchange is inversely proportional to the hydrated radius of the exchangeable ion. This regularity is conveniently represented by the following equation;

$$-\Delta F'_{MR} = RT \ln K_H^M, \qquad (1.2)$$

$$= B + \frac{C_m}{D_s \cdot a_M} \qquad (1.3)$$

where $-\Delta F'_{MR}$ represents the apparent free energy change, B and C_m are constants, and D_s and a_M are the dielectric constant of solution and the hydrated radius of M^+ ion, respectively.

Fig. 1–1. shows the graph of $-\Delta F'_{MR}$ against $1/D_s$ for each ion. The values of $-\Delta F'_{MR}$ have been calculated from the data according to Eq. (1.2). Since the salt concentration is too low to give a notable influence on the values of D_s, they have been estimated from the alcohol concentrations of solutions, using results from macroscopic measurements.[8]

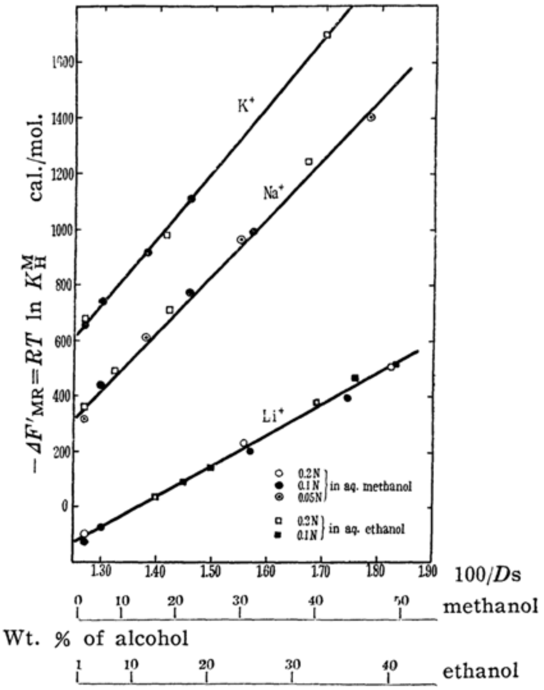

Fig. 1–1

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* See also the data given in reference 3).

6) G. E. Boyd, J. Schubert and A. W. Adamson, *J. Am. Chem. Soc.*, **69**, 2818 (1947).

7) T. R. E. Kressman and J. A. Kitchener, *J. Chem. Soc.*, **1949**, 1190.

** The free energy which these authors have used is nearly equal to the apparent free energy.

8) G. Åkerlöf, *J. Am. Chem. Soc.*, **54**, 4125 (1932).

This manner of plotting apparently gives a straight line for each ion in the range of $D_s>55$. In order to let Eq. (1.3) represent the linear relationship between $-\Delta F'_{MR}$ and $1/D_s$, a_M must be kept invariable through the region of D_s in Fig. 1-1. It might be possible that owing to the preferential hydration of the ion the value of a_M is essentially uninfluenced by the addition of alcohol up to a concentration of 40 or 50 per cent in weight. When the alcohol content is increased and consequently the reciprocal of D_s exceeds the region shown in Fig. 1-1 the free energy vs. $-1/D_s$ curve, losing the linearity, reaches a maximum and falls sharply as $1/D_s$ approaches the value of absolute alcohol, as illustrated in Fig. 1-2.

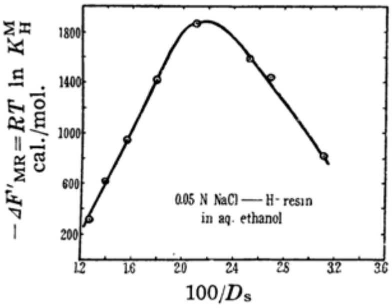

Fig. 1-2

This fact leads us, as the natural consequence, to the viewpoint that the ion may gradually lose its apparent affinity for water molecules in higher alcohol concentrations.

Furthermore it is to be noted that the slope of the line shown in Fig. 1-1 is characteristic to each ion and indifferent to the kind of coexisting alcohol, and that, as is expected from Eq. (1.3), the order of its magnitude is $K^+>Na^+>Li^+$, which is equal to the sequence of the value of K^M_H or $-\Delta F'_{MR}$ in aqueous solution. It goes without saying that these results are consistent with the observations stated in section II (iii).

(ii) **The Effect of Urea.**—It is interesting to examine the effect caused by the addition of non-electrolytes, such as urea, which contrary to the case of alcohol, increase the dielectric constant of solution.

According to Eq. (1.3) the value of K^M_H is expected to decrease with the addition of urea. This is supported by the results listed in Table II, which illustrates the data on the system of Amberlite IR-120 and urea in 0.1N sodium chloride at 25°C. Though Eq. (1.3) seem to coincide with the facts in this case as well, close examination reveals that the agreement of the equation with experiments is only qualitative. If the data on D_s of aqueous urea solutions[9] are inserted into Eq. (1.3), the constants of which have beeen determined from Fig. 1-1, then, the value of K^M_H is found to be by far greater than that observed, that is, K^M_H appears to be more sensitive to the presence of urea than to that of alcohol. This discrepancy may be formally eliminated by admitting that the gradient C_m in Eq. (1.3) is generally dependent on the species of the non-electrolyte added, so far as a_M can not be assumed to decrease rapidly with the concentration of urea. But it must be taken into consideration that this simple empirical equation is inadequate for quantitative usage, since it lacks sufficient theoretical basis.

TABLE II
EFFECT OF UREA (25°C)
0.1N NaCl—H-resin
(Amberlite IR-120)

Conc. of urea (Wt. %)	K^{Na}_H
0	1.68
0.8	1.31
1.6	0.93
2.4	0.77
3.2	0.70
4.0	0.44
6.0	0.37

In conclusion, Eq. (1.3) represents semi-quantitatively the effect of the addition of non-electrolytes on ion exchange equilibria. However, this cannot correlate successfully the free energy change with the valency of the exchangeable ion. Hence, further work is necessary to establish a relationship, which is not only consistent with the mentioned facts but also more generally applicable; this will be attempted in the ensuing paper.

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[9] J. Wyman Jr., *J. Am. Chem. Soc.*, 55, 4116 (1933).