# *Solvent Effects on Ion Exchange Equilibria. Part II.*

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In the preceding paper⁽¹⁾ it was pointed out that a semi-quantitative relationship exists between the free energy change of univalent ion exchange and the dielectric constant of the solution. The present paper is concerned with a more general regularity which governs the solvent effects on the exchange of polyvalent ion.

## The Free Energy Change of Univalent Ion Exchange

The present discussions are limited, for simplicity, to the case in which the exchange groups of resin have the same ionization constant. Then, the free energy change, $\Delta F^\circ$, for the reaction of the type

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

is written

$$RT \ln K_a = -\Delta F^\circ, \qquad (2.\ 1)$$

where $K_a$ is the thermodynamic equilibrium constant and is expressed as

$$K_a = K_H^M \cdot \frac{f_H \cdot f_{MR}}{f_M \cdot f_{HR}} \qquad (2.\ 2)$$

where $f_i$ shows the activity coefficient of i species. Now let us specify by the symbol $(X)_o$ the value of the quantity $X$ to be measured in aqueous solution—resin system, and by $(X)_m$ that in the system of aqueous alcohol—resin; then, from Eqs. (2. 1) and (2. 2), we get

$$(\Delta F'_{MR})_o - (\Delta F'_{MR})_m = (\Delta F^\circ)_o - (F^\circ)_m - RT\left\{\ln\frac{(f_H)_m}{(f_H)_o} - \ln\frac{(f_M)_m}{(f_M)_o}\right\} - RT\left\{\ln\frac{(f_{MR})_m}{(f_{MR})_o} - \ln\frac{(f_{HR})_m}{(f_{HR})_o}\right\} \qquad (2.\ 3)$$

The second term on the right-hand side of the above equation is readily evaluated by the Debye-Hückel theory, assuming that the solvated radii are kept constant indifferently of the addition of alcohol. The result of the calculation shows that this term contributes only a little to the total value of the difference in $-\Delta F'_{MR}$ shown in Fig 1–1 of the preceding paper.

It is difficult to estimate, without any assumption, the value of the third term, but it does not seem to be so unreasonable to assume that under the present experimental conditions this term is not so great when compared with the preceding term.

Thus,

$$(\Delta F'_{MR})_o - (\Delta F'_{MR})_m \approx (\Delta F^\circ)_o - (\Delta F^\circ)_m, \qquad (2.\ 4)$$

or

$$RT \ln \frac{(K_H^M)_m}{(K_H^M)_o} \approx RT \ln \frac{(K_a)_m}{(K_a)_o} \qquad (2.\ 5)$$

## A Simple Model of Ion Exchange

Let us consider the free energy change of ion exchange, based upon a simple model. When an ion is brought into the resin phase and is fixed, either loosely or tightly, by one of the ionic groups, the solvent molecules attached to the ion may be more or less detached from it; the ion fixation may be accompanied by the desolvation process to a certain extent. This process can be analyzed into the three steps shown in Fig. 2–1. Step 1 represents the partial desolvation of ion in the solution having Ds; the ion enters the resin phase through step 2; and in step 3 the charge of the ion is neutralized by an ionic group of the opposite sign. Each step is accompanied by the free energy change $\Delta F_1$, $\Delta F_2$ and $\Delta F_3$, respectively. It seems that among these free energy changes the second and the third do not vary with the species of exchangeable ion, that is, it is likely that the difference in the resultant free energy change between a pair of exchangeable ions is predominantly determined by that in the magnitude of $\Delta F_1$.

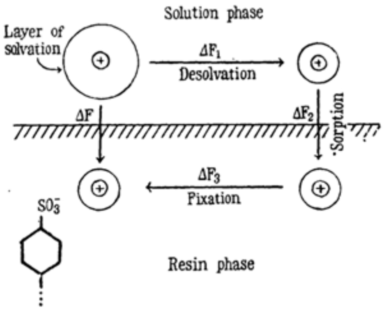

Fig. 2–1

The work of step 1 may be essentially of an electrical nature, so that, as a rough ap-

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1) This Bulletin, **28** 217 (1955).

proximation, it can be regarded as being proportional to the solvation number of the ion and inversely proportional to the dielectric constant of the medium.

If the solvation number is tentatively replaced by the hydration number in the case of the solution of the lower alcohol concentration, we obtain the following equation as the final result of the above considerations;

$$(\Delta F^\circ)_o-(\Delta F^\circ)_m=C_n\cdot(n_H-n_M)\cdot\left\{\frac{1}{(D_s)_m}-\frac{1}{(D_s)_o}\right\}, \tag{2.6}$$

where $n_H$ and $n_M$ are the hydration numbers of hydrogen ion and metal ion, and $C_n$ is a constant which depends upon the species of the solvent added and that of the resin used.

Combining Eqs. (1. 2), (2. 4) and (2. 6),

$$RT\ln\frac{(K_H^M)_m}{(K_H^M)_o}\approx C_n(n_H-n_M)\cdot\left\{\frac{1}{(D_s)_m}-\frac{1}{(D_s)_o}\right\}. \qquad (2.\ 6)$$

or, in general

$$RT\ln K_H^M\approx B+(n_H-n_M)\cdot\frac{C_n}{D_s}, \qquad (2.\ 8)$$

where $B=C_n(n_H-n_M)/(D_s)_o$.

Here the hydration numbers of exchangeable ions are adopted as parameters in place of their hydrated radii in Eq. (1. 3). When the values proposed by Stokes and Robinson[2] are introduced for $n_H$ and $n_M$, it is readily found that Eq. (2. 8) agrees with the experimental results, obtained in the case of univalent ion exchange.

### Polyvalent Ion Exchange

The apparent equilibrium constant $K_H^M$ for the exchange reaction of the type

$$M^{Z+}+zHR^+=zH^++MR_Z$$

is written as

$$K_H^M=\frac{(H^+)(MR_Z)^{1/2}}{(M^{Z+})^{1/Z}(HR)}\cdot\left\{\frac{v}{V}\right\}^{\frac{Z-1}{Z}} \qquad (2.\ 9)$$

where $z$ is the valency of metal ion, $V$ and $v$ are the volume of the solution and that of the solvent in the resin phase accessible to the ion in it, respectively, and ( ) represents the absolute quantity (equivalent) of each species found in each phase.

From Eq. (2. 9)

$$RT\ln K_H^M=RT\ln\frac{(H^+)\cdot(R_ZM)^{1/Z}}{(M^{Z+})^{1/Z}(RH)}+\left\{\frac{z-1}{z}\right\}RT\ln\left\{\frac{\mathrm{v}}{\mathrm{V}}\right\}. \qquad (2.\ 10)$$

If the same consideration as in the case of univalent ion exchange is applied to this case, it leads us to

$$RT\ln K_H^M\approx B+(n_H-n_{M/Z})\frac{C_n}{D_s}. \qquad (2.\ 11)$$

The volume of free solvent in the resin phase, $v$, is a rather indefinite quantity, though $RT\ln K_H^M$ cannot be evaluated unless the value of $v$ is determined. But, fortunately, when $RT\ln K_H^M$ is plotted against $1/D_s$ with constant $v$, the slope of the curve is unaffected by the value of v. Thus, it is possible to check the validity of Eq (2. 11). The measurements were carried out on the resin-alkali earth chloride systems in aqueous ethanol under the same conditions as stated in the preceding paper, except that one gram of the resin (dry weight) was added to the solution in each measurement. This procedure may assure us of the constancy of $v$, since the value of $v$ is likely to be insensitive to the variation of alcohol concentration. But at the same time it follows that the mole ratio of the two species in the resin phase is no longer maintained at a constant value.

The plot of the data suggests in this case, too, the existence of the linear relationship between $RT\ln K_H^M$ and $1/D_s$ in the range of $D_s>55$. Moreover it is found that the relative value of $RT\ln K_H^M$ increases more rapidly for the heavier ion. By comparing the linear parts of the curves obtained for alkali and alkali earth ions, it is found that the order in the magnitude of the slope is

$K^+>Na^+>\frac{1}{2}Ba^{++}>\frac{1}{2}Sr^+>\frac{1}{2}Ca^+Li^+>\frac{1}{2}Mg^{++}$,

which comes into line with the sequence expected from Eq. (2. 11) and the values of $n_H$ and $n_M$ given by Stokes and Robinson.[2] These facts do not directly lead to the conclusion that the treatment given Section II is entirely adequate. Because of the complexities of the probem it is impossible at present to provide an exact quantitative expression of the phenomena associated with the solvent effects. The probem has been treated rather in a qualitative manner in Section II; a series of assumptions has been introduced either explicitly or implicitly, and several factors have been neglected for the sake of simplicity in the course of the computations. Therefore, Eq. (2. 8) or (2. 11) is to be regarded not as a theoretical formula but as a semi-empirical one. But it may be admitted that Eq. (2. 11) is a useful representation reflecting the general tendency of the solvent effects.

### The Value of "$v$"

It was pointed out in the preceding report that the metal ion having the greater value

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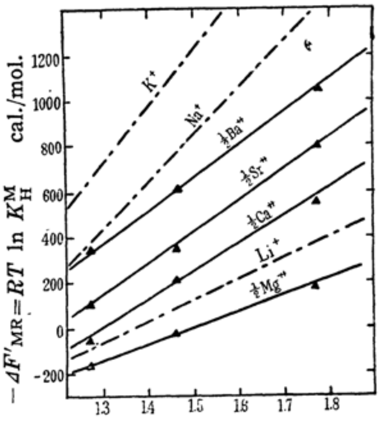
[2] R. H. Stokes and R. A. Robinson, *J. Am. Chem. Soc.*, 70, 1870 (1948).



100/$D$s

Fig. 2–2

of $RT\ln K_H^M$ in aqueous solution exhibits the more rapid increase of $RT\ln K_H^M$ with $1/D_s$. Consequently, in the graph of $RT\ln K_H^M$ plotted against $1/D_s$, the lines of barium, strontium and calcium ions should lie between those of sodium and lithium ions, and the line of magnesium ion should be found below that of lithium ion.

Since the first term of the right hand side of Eq. (2. 10) has been known from the experiment, the value of the second term must be determined so that the above requirements may be satisfied. By this procedure 0.20—0.25 ml. is found for the value of $v$ per one gram of dry resin.

This result shows nothing but the fact that the ion behaves as if it were surrounded by this volume of free water in the resin phase. Besides, the value of $v$ presumably depends upon the species of the ions in the resin and their quantities. But the found value seems to be not far from the real value of the free water in the resin.

Fig. 2–2 shows the results obtained by using this value for $v$.

## Summary

The effect of the addition of non-electrolytes to the ion exchange system has been studied. It has been found that the dielectric constant of the solution gives a profound effect on the ion exchange equilibrium and that in the case of lower concentrations of alcohol a linear relationship exists between the apparent free energy change and the reciprocal of the dielectric constant. A working equation has been proposed to account for the relationships between the free energy change, dielectric constant, ionic species and valency of exchangeable ion.

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