Activities of the Components in Ion Exchangers

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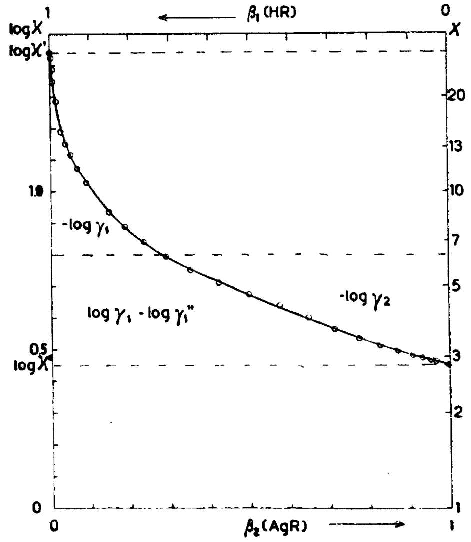
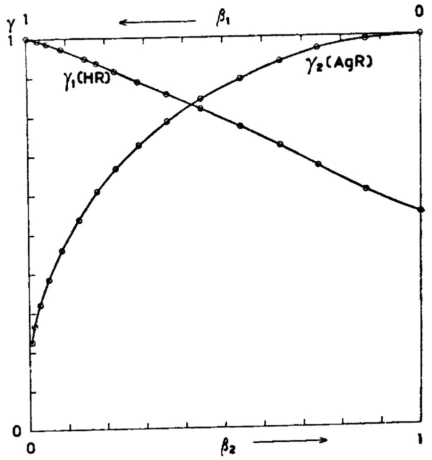
An ion exchanger (R^-) containing two different ions A_1^+ and A_2^+ certainly cannot be considered as an ideal solid solution of the components A_1R and A_2R. If it were, the law of mass action could be applied to the exchange reaction with an aqueous solution:

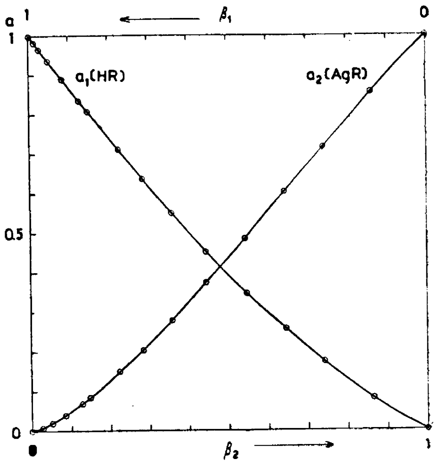
$$A_2^+ + A_1R \rightleftharpoons A_1^+ + A_2R \qquad (1)$$

inserting the molar fractions β_1 and β_2 of A_1R and A_2R for their activities. The quotient $\varkappa$ in equation (7) below is, however, found to vary considerably with β_1 and β_2.

In describing the deviations from ideality, it seems desirable to eliminate the aqueous solution and use quantities that refer to the ion exchanger only. This can be done if the ion exchanger is formally regarded as a solid solution of A_1R and A_2R, and the activities a_1 and a_2, and activity factors γ_1 and γ_2 of the components are given for varying composition. This way of representation will be analogous to that used for the components of liquid mixtures.

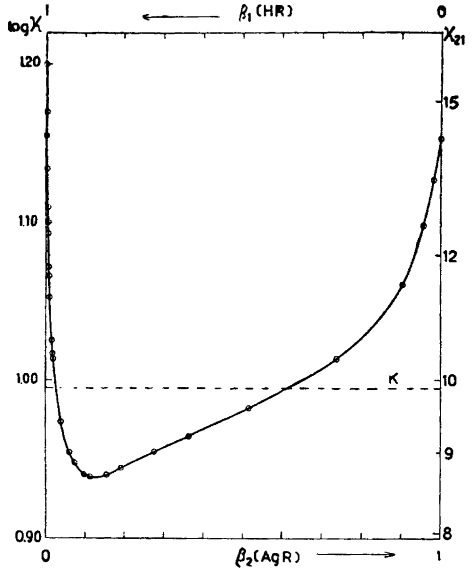


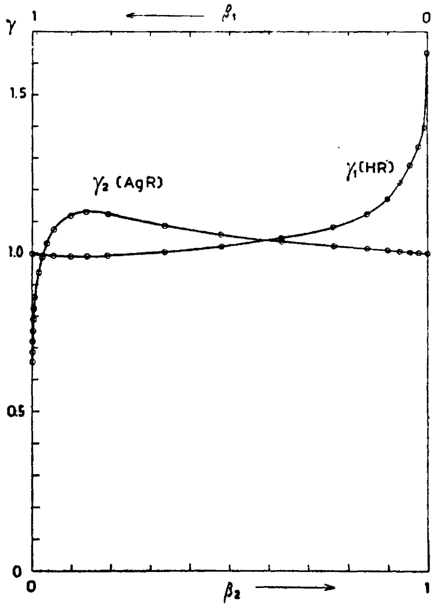




Figs. 1—3. Equilibria of H+ (1) and Ag+ (2) on Wofatit KS.

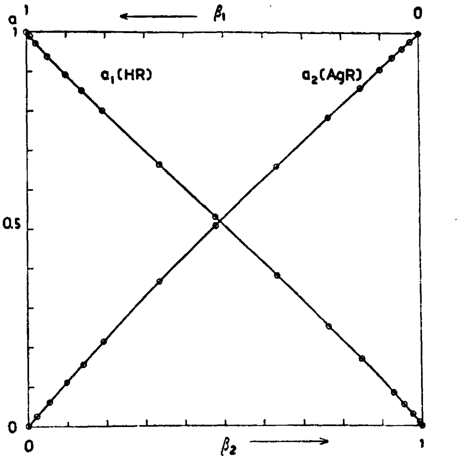
Fig. 1: Log $\varkappa$ as a function of β. For $\beta < 0.04$ the points were calculated from elution curves, for the smaller β from static measurements. Fig. 2: Activity factors γ_1 and γ_2. Fig. 3: Activities a_1 and a_2 of the components HR and AgR of the solid.





Figs. 4–6. Equilibria of H+ (1) and Ag+ (2) on Dowex 50.

Fig. 4: Log $\varkappa$ as a function of β. Fig. 5: Activity factors γ_1 and γ_2. Fig. 6: Activities a_1 and a_2 of the components HR and AgR of the solid. — Observe that log K is the average value of log $\varkappa$. (Fig. 4).



Let us assume that the two ions are univalent, that the total concentration is a_0 in the aqueous solution and s_0 in the sorbent, and that their molar fractions are α_1, α_2 in the solution and β_1, β_2 in the sorbent. Then in the aqueous solution the concentrations are:

$$[A_1^+] = \alpha_1 a_0;\ [A_2^+] = \alpha_2 a_0;\ \alpha_1 + \alpha_2 = 1 \quad (2)$$

and the activities, introducing the activity factors f_1 and f_2

$$\{A_1^+\} = f_1\alpha_1 a_0;\quad \{A_2^+\} = f_2\alpha_2 a_0 \quad (3)$$

In the sorbent, using pure A_1R and A_2R as standard states

$$[A_1R] = \beta_1 s_0;\ [A_2R] = \beta_2 s_0;\ \beta_1 + \beta_2 = 1 \quad (4)$$
$$\{A_1R\} = a_1 = \gamma_1\beta_1;\ \{A_2R\} = a_2 = \gamma_2\beta_2 \quad (5)$$

We define the thermodynamic equilibrium constant K_{21} of (1) and its inverse value K_{12} by

$$K_{21} = K_{12}^{-1} = \frac{\{A_1^+\}}{\{A_2^+\}} \cdot \frac{\{A_2R\}}{\{A_1R\}} = \frac{f_1\alpha_1 \cdot \gamma_2\beta_2}{f_2\alpha_2 \cdot \gamma_1\beta_1} \quad (6)$$

Equilibrium measurements will not give K_{21} directly but the equilibrium quotient $\varkappa_{21}$

$$\varkappa_{21} = \varkappa_{12}^{-1} = \frac{\{A_1{}^+\}}{\{A_2{}^+\}} \cdot \frac{[A_2R]}{[A_1R]} = \frac{f_1 a_1 \beta_2}{f_2 a_2 \beta_1} = $$
$$= K_{21} \cdot \frac{\gamma_1}{\gamma_2} \qquad (7)$$

Gibbs-Duhem's equation gives

$$\beta_1 \text{ dln } (\gamma_1 \beta_1) + \beta_2 \text{ dln } (\gamma_2 \beta_2) = 0 \qquad (8)$$

From (4), (7), and (8) we find

$$\text{dln}\,\gamma_1 = \beta_2 \text{ dln}\,\varkappa_{21};\ \text{dln}\,\gamma_2 = -\beta_1 \text{ dln}\,\varkappa_{21} \quad (9ab)$$

For brevity we set $\varkappa_{21} = \varkappa$; $\beta_2 = \beta$, $\beta = 1-\beta$ and denote by $\varkappa'$, γ_1' ($= 1$) and γ_2' the values at $\beta = 0$ (pure A_1R), by $\varkappa''$ γ_2'' and γ_2'' ($= 1$) those at $\beta = 1$ (pure A_2R). Moreover we transfer (9a, b) to decadic logarithms and get:

$$\log \gamma_1 = \int_{\varkappa'}^{\varkappa} \beta \text{ dlog}\,\varkappa \qquad (10\text{ a})$$

$$\log \gamma_2 = -\int_{\varkappa''}^{\varkappa} (1-\beta) \text{ dlog}\,\varkappa \qquad (10\text{ b})$$

We have measured the equilibria of H^+ ($= 1$) and Ag^+ ($= 2$) on two ion exchangers, Wofatit KS and Dowex 50, for a wide range of β values. The curves $\varkappa(\beta)$ are given in Figs. 1 and 4. For Wofatit KS the calculations were made in the following way. First, log $\varkappa$ was calculated for round β values by means of (10 a). The corresponding area is marked out in Fig. 1. Then the thermodynamic constant K was obtained from (7) which gives:

$$\log K = \log \varkappa'' - \log \gamma_1'' \qquad (11)$$

Now for each β, log γ_2 was obtained from (7)

$$\log \gamma_2 = \log K + \log \gamma_1 - \log \varkappa \qquad (12)$$

For Dowex 50 the calculations of γ_1 and γ_2 were analogous though complicated by the minimum in $\varkappa$. (Fig. 4.)

The results are given in Figs. 2, 3, 5 and 6. When a number of curves a_i (β) are known, it will be tempting to try to explain them in analogy with liquid mixtures, by association, dissociation, compound formation (and perhaps by inhomogeneity of one of the components).

The generalization to multivalent ions is easily made.

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