

## Activities of the Components in Ion Exchangers

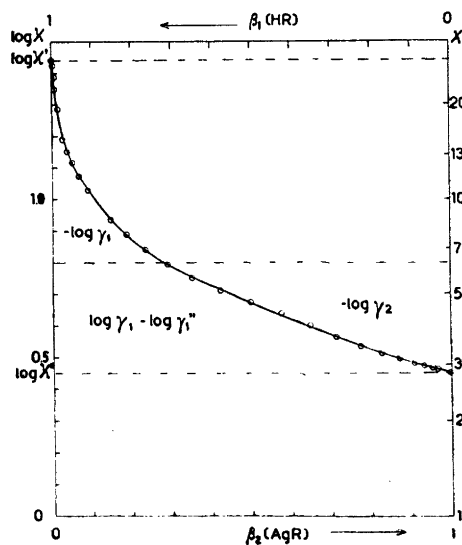
ERIK EKEDAHL, ERIK HÖGFELDT,  
and LARS GUNNAR SILLÉN

FOA, 1, Ulriksdal; Inst. of Inorg. Chem.,  
Univ. of Stockholm; CTH, Gothenburg,  
Sweden

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:

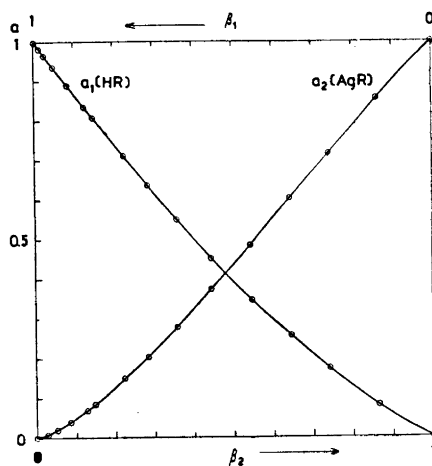
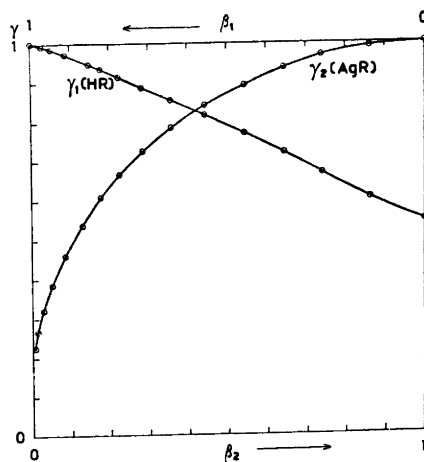


inserting the molar fractions  $\beta_1$  and  $\beta_2$  of  $A_1R$  and  $A_2R$  for their activities. The



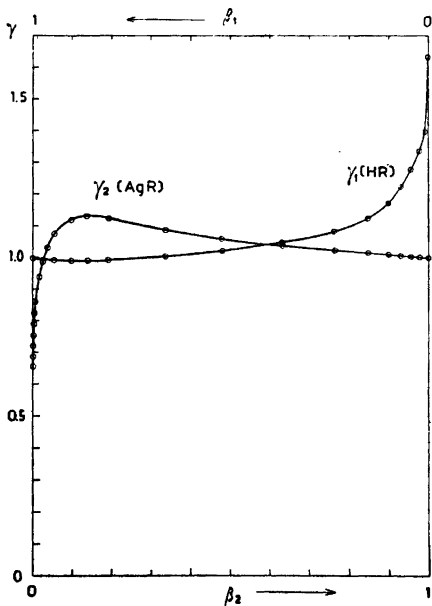
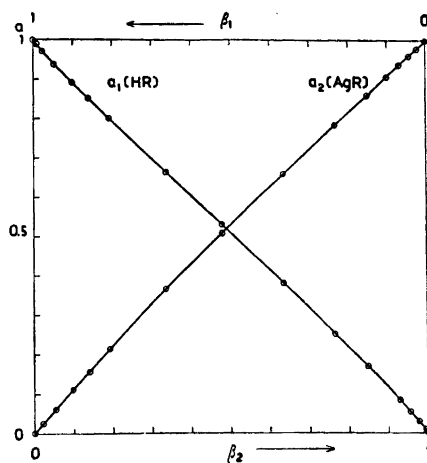
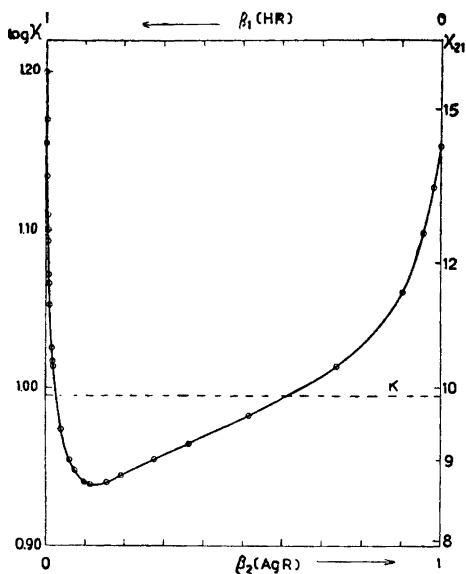
quotient  $\kappa$  in equation (7) below is, however, found to vary considerably with  $\beta_1$  and  $\beta_2$ .

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  $\gamma_1$  and  $\gamma_2$  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:  $\log \kappa$  as a function of  $\beta$ . For  $\beta < 0.04$  the points were calculated from elution curves, for the smaller  $\beta$  from static measurements. Fig. 2: Activity factors  $\gamma_1$  and  $\gamma_2$ . Fig. 3: Activities  $a_1$  and  $a_2$  of the components HR and AgR of the solid.



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  $a_1, a_2$  in the solution and  $\beta_1, \beta_2$  in the sorbent. Then in the aqueous solution the concentrations are:

$$[A_1^+] = a_1 a_0; [A_2^+] = a_2 a_0; a_1 + a_2 = 1 \quad (2)$$

and the activities, introducing the activity factors  $f_1$  and  $f_2$

$$\{A_1^+\} = f_1 a_1 a_0; \{A_2^+\} = f_2 a_2 a_0 \quad (3)$$

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

$$K_{21} = K_{12}^{-1} = \frac{\{A_1^+\}}{\{A_2^+\}} \cdot \frac{\{A_2R\}}{\{A_1R\}} = \frac{f_1 a_1 \cdot \gamma_2 \beta_2}{f_2 a_2 \cdot \gamma_1 \beta_1} \quad (6)$$

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

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

Fig. 4:  $\log \kappa$  as a function of  $\beta$ . Fig. 5: Activity factors  $\gamma_1$  and  $\gamma_2$ . 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  $\log \kappa$ . (Fig. 4).

$$\begin{aligned} \kappa_{21} &= \kappa_{12}^{-1} = \frac{\{A_1^+\}}{\{A_2^+\}} \cdot \frac{[A_2R]}{[A_1R]} = \frac{f_1 a_1 \beta_2}{f_2 a_2 \beta_1} = \\ &= K_{21} \cdot \frac{\gamma_1}{\gamma_2} \end{aligned} \quad (7)$$

Gibbs-Duhem's equation gives

$$\beta_1 \, d \ln (\gamma_1 \beta_1) + \beta_2 \, d \ln (\gamma_2 \beta_2) = 0 \quad (8)$$

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

$$d \ln \gamma_1 = \beta_2 \, d \ln \kappa_{21}; \quad d \ln \gamma_2 = -\beta_1 \, d \ln \kappa_{21} \quad (9ab)$$

For brevity we set  $\kappa_{21} = \kappa$ ;  $\beta_2 = \beta$ ,  $\beta = 1 - \beta$  and denote by  $\kappa'$ ,  $\gamma_1'$  ( $= 1$ ) and  $\gamma_2'$  the values at  $\beta = 0$  (pure  $A_1R$ ), by  $\kappa''$ ,  $\gamma_2''$  ( $= 1$ ) those at  $\beta = 1$  (pure  $A_2R$ ). Moreover we transfer (9a, b) to decadic logarithms and get:

$$\log \gamma_1 = \int_{\kappa'}^{\kappa} \beta \, d \log \kappa \quad (10 \, a)$$

$$\log \gamma_2 = - \int_{\kappa''}^{\kappa} (1 - \beta) \, d \log \kappa \quad (10 \, b)$$

We have measured the equilibria of  $H^+$  ( $= 1$ ) and  $Ag^+$  ( $= 2$ ) on two ion ex-

changers, Wofatit KS and Dowex 50, for a wide range of  $\beta$  values. The curves  $\kappa(\beta)$  are given in Figs. 1 and 4. For Wofatit KS the calculations were made in the following way. First,  $\log \kappa$  was calculated for round  $\beta$  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:

$$\log K = \log \kappa'' - \log \gamma_1'' \quad (11)$$

Now for each  $\beta$ ,  $\log \gamma_2$  was obtained from (7)

$$\log \gamma_2 = \log K + \log \gamma_1 - \log \kappa \quad (12)$$

For Dowex 50 the calculations of  $\gamma_1$  and  $\gamma_2$  were analogous though complicated by the minimum in  $\kappa$ . (Fig. 4.)

The results are given in Figs. 2, 3, 5 and 6. When a number of curves  $a_i(\beta)$  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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