May, 1987] Bull. Chem. Soc. Jpn., 60, 1613—1615 (1987)

Additivity Law for the Activity of a Counter Ion in Ion-Exchange Resin

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(Received November 8, 1986)

The ion-exchange resin–electrolyte solution equilibria were studied on the basis of thermodynamics. The experimental results showed that the external salt activity divided by the co-ion concentration in the ion-exchange resins was linear against the co-ion concentration in the resin. The equilibria were consistently explained by a partition coefficient of salt distribution with the additivity law for the counter ions in the ion-exchange resin. A thermodynamic expression for the ion-exchange reaction was also discussed.

It is of importance to elucidate the behavior of ions in the ion-exchange resin in order to understand the ion transport through the charged membrane and the ion-exchange reaction.

Teorell[1] and Meyer and Sievers[2] explained the membrane potential across a charged membrane by applying the Donnan relation[3] to the membrane surface-electrolyte solution equilibria. Later, the ion concentration in the Donnan relation was replaced by the ionic activity.[4] However, the problem of the change in the activity coefficients of the ions in the ion-exchange resin with the external electrolyte solution has remained unsolved.[5]

On the other hand, it is well-known that the counter-ion activity in a polyelectrolyte solution with an added electrolyte obeys the additivity law;[6] that is, the total activity of counter ions is best expressed as a sum of the independent contributions of counter-ion activities from the polyelectrolyte and the added salt.

Toyoshima et al.[7] treated the membrane properties on the assumption of the additivity law for counter ions in the membrane, disregarding the partition factor. Unfortunately, however, they did not verify the additivity law experimentally.

Since the ion-exchange resin may be regarded as a polyelectrolyte, it is possible to elucidate the salt partition between an ion-exchange resin and an external electrolyte solution on the basis of thermodynamics by taking the additivity law into account.

This paper will describe the theory and the experimental evidence.

Theory

The thermodynamic treatment of the ion-exchange resin-single electrolyte solution equilibria leads to:

$$\bar{a}_{\pm}/a_{\pm} = K \tag{1}$$

and:

$$-\boldsymbol{R}T \ln K = \bar{\mu}^{\circ}_{\pm} - \mu^{\circ}_{\pm} + \pi\bar{V}_{\pm} \tag{2}$$

where the overbars refer to the membrane phase; $a_{\pm}$ denotes the mean electrolyte activity; K, the partition coefficient; $\boldsymbol{R}$, the gas constant; T, the absolute temperature; $\mu^{\circ}_{\pm}$, the standard chemical potential; π, the swelling pressure, and $\bar{V}_{\pm}$, the mean partial molar volumes of electrolytes, which are assumed identical in both the resin and external-solution phases.

By applying the additivity law[6] to the counter ion α in the membrane with a fixed charge concentration of $\bar{X}$, the activity of the counter ion, $\bar{a}_{\alpha}$, is expressed by;

$$\bar{a}_{\alpha} = (\bar{\gamma}_{f}|Z_{f}|\bar{X} + \bar{\gamma}_{\alpha}|Z_{\beta}|\bar{C}_{\beta})/|Z_{\alpha}| \tag{3}$$

where $\bar{\gamma}_{f}$ denotes the activity coefficirent of ion α referred to the fixed charge; Z_{f}, the valency of the fixed site; $\bar{\gamma}_{\alpha}$, the activity coefficient of the ion α referred to the Donnan salt present in the interstitial space; Z_{β}, the valency of the co-ion; $\bar{C}_{\beta}$, the co-ion concentration, and Z_{α}, the valency of the ion α. The activity of the co-ion β, $\bar{a}_{\beta}$, is given by a usual expression;

$$\bar{a}_{\beta} = \bar{\gamma}_{\beta}\bar{C}_{\beta} \tag{4}$$

where $\bar{\gamma}_{\beta}$ denotes the activity coefficient of the co-ion. By combining Eq. 1 with Eqs. 3 and 4, we obtain;

$$\begin{aligned}(a_{\pm})^{(\nu_{\alpha}+\nu_{\beta})}/(\bar{C}_{\beta})^{\nu_{\beta}} \\ = (\bar{\gamma}_{\pm}/K)^{(\nu_{\alpha}+\nu_{\beta})}[(\bar{\gamma}_{f}|Z_{f}|\bar{X}/\bar{\gamma}_{\alpha} + |Z_{\beta}|\bar{C}_{\beta})/|Z_{\alpha}|]^{\nu_{\alpha}}\end{aligned} \tag{5}$$

where ν_{α} and ν_{β} are the stoichiometric coefficints of the counter ion and the co-ion respectively and $\bar{\gamma}_{\pm}$, the mean activity coefficient of the Donnan salt.

For the system composed of a symmetric electrolyte and a resin having ion-exchange sites with $|Z_{f}|=1$, Eq. 5 is reduced to:

$$(a_{\pm})^{2}/\bar{C}_{\beta} = (\bar{\gamma}_{\pm}/K)^{2}(\bar{\gamma}_{f}\bar{X}/|Z_{\alpha}|\bar{\gamma}_{\alpha} + \bar{C}_{\beta}) \tag{6}$$

Thus, for a symmetric electrolyte, $(a_{\pm})^{2}/\bar{C}_{\beta}$ is linear against $\bar{C}_{\beta}$, providing that $\bar{\gamma}_{\pm}/K$ and $\bar{\gamma}_{f}/\bar{\gamma}_{\alpha}$ are constant.

Experimental

Materials. The anion-exchange membrane used in the present study was a styrene–divinylbenzene copolymer with a quarternary ammonio group developed by the Asahi Chemical Co., Ltd., and coded as CA-1, 0.2 t. The ion-exchange capacity was 1.70 meq. (g dry membrane)$^{-1}$; the water content, 0.37 g H_2O (g dry membrane)$^{-1}$, and the thickness, 0.225 mm. This membrane was prepared without any other supporting polymer and was of a homogeneous distribution of functional groups within the membrane. The cation-exchange resins were commercial ones, coded as Dowex 50W−X2, −X8, and −X12, whose water contents were 0.75, 0.59, and 0.53 g H_2O (g dry resin)$^{-1}$ respectively and whose ion-exchange capacities were 1.8, 3.2, and 3.8 meq. (g dry resin)$^{-1}$ respectively. The degrees of cross linkage and the water contents of these cation-exchange resins are also different from each other. Pure inorganic salts and twice-distilled water were used for preparing the salt solutions. The concentrations of the electrolyte solutions varied from 0.5 to 3 mol dm^{-3}.

Procedure of Experiments. A membrane of 2×2 cm^2 preconditioned with a test solution was dipped into a 100-ml test solution for 5 days. After equilibration, the solution which had adhered to the membrane was removed by the filter paper; then the Donnan salt was extracted 5 times with 10 ml of distilled water, each extraction being carried out for 1 day. All the extracts were then gathered, and the concentration was determined by measuring the electric conductance of the solution. The Donnan-salt concentration was calculated from the concentration of the extract and the geometry of the membrane determined after equilibration with the test solution. The procedure for determining the ion concentrations in the cation-exchange resin has been described elsewhere.[8] The experiments were carried out at 25±1 °C.

Results and Discussion

The experimental results are shown in Figs. 1 and 2 where the activity data of the external electrolyte solutions were taken from the text book.[9] It is shown in these figures that $(a_\pm)^2/\bar{C}_\beta$ is linear against $\bar{C}_\beta$. This indicates that $\bar{\gamma}_\pm/K$ and $\bar{\gamma}_f/\bar{\gamma}_\alpha$ may be regarded as constants. These values, as estimated from Figs. 1 and 2, are cited in Table 1, together with the ratio of $\bar{\gamma}_f/\bar{\gamma}_\alpha$ to $K/\bar{\gamma}_\pm$, $(\bar{\gamma}_f/K)(\bar{\gamma}_\beta/\bar{\gamma}_\alpha)^{1/2}$.

Table 1 shows that the values of $K/\bar{\gamma}_\pm$ and $\bar{\gamma}_f/\bar{\gamma}_\alpha$ are smaller than unity except for those of $MgSO_4$, while their ratios are of the same order of magnitude. This table also indicates that co-ions in the anion-exchange membrane, Na^+ and K^+, exert different effects on the thermodynamic parameters and that the variation in the cation-exchange resin gives rise to a change in the thermodynamic parameters.

Since $\bar{\gamma}_\pm$ and $\bar{\gamma}_\alpha$ may be regarded as less than unity, both K and $\bar{\gamma}_f$ values for all electrolytes may be deduced to be less than unity. The small values of $\bar{\gamma}_f$ for the uni-univalent electrolyte, a measure of the counter-ion condensation caused by an array of charged sites as a polyelectrolyte, may also be considered to indicate a strong trapping of counter ions by charged sites. The low K values may be ascribed to the co-ion repulsion by charged sites in addition to the exclusion effect due to the resin matrix with a hydrophobic nature. The anomalous values of $K/\bar{\gamma}_\pm$ and $\bar{\gamma}_f/\bar{\gamma}_\alpha$ for $MgSO_4$ may be due to a stronger interaction of magnesium ions with sulfate ions than with charged sites as deduced from the extremely low activity coefficient of $MgSO_4$ in an aqueous solution, an order of 10^{-2}. In fact, the ratio of $\bar{\gamma}_f/\bar{\gamma}_\alpha$ to $K/\bar{\gamma}_\pm$ for $MgSO_4$ was comparable to those for the other

Table 1. Thermodynamic Parameters in the Ion-Exchange Resin-Electrolyte Solution Equilibria

Ion-exchange resin	Electrolyte	$K/\bar{\gamma}_\pm$	$\bar{\gamma}_f/\bar{\gamma}_\alpha$	$(\bar{\gamma}_f/K)(\bar{\gamma}_\beta/\bar{\gamma}_\alpha)^{1/2}$
CA-1 0.2 t	NaCl	0.316	0.015	0.047
	KCl	0.895	0.056	0.063
	$MgSO_4$	6.76	2.15	0.318
Dowex 50W-X12	NaCl	0.121	0.038	0.314
50W-X8	NaCl	0.250	0.074	0.296
50W-X2	NaCl	0.543	0.230	0.424

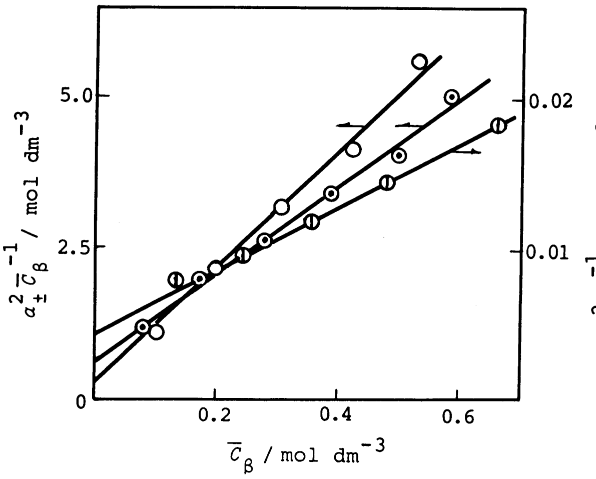

Fig. 1. $a_\pm^2\bar{C}_\beta^{-1}$ vs. $\bar{C}_\beta$ plot for the anion-exchange membrane-electrolyte solution equilibria.
Membrane CA-1 0.2 t; Electrolyte, O:NaCl, ◉:KCl. ⦶:$MgSO_4$

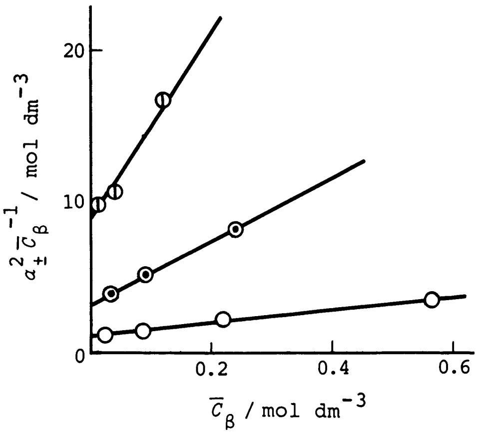

Fig. 2. $a_\pm^2\bar{C}_\beta^{-1}$ vs. $\bar{C}_\beta$ plot for the cation-exchange resin-sodium chloride solution equilibria.
Cation-exchange resin, O: Dowex 50 W-X2, ◉: Dowex 50 W-X8, ⦶: Dowex 50 W-X12.

electrolytes as is shown in Table 1. This may indicate that the interactions of Mg^{2+} and $MgSO_4$ with the ion-exchange resin are not anomalous. Assuming $\bar{\gamma}_\alpha=\bar{\gamma}_\beta=\bar{\gamma}_\pm$, the ratio is reduced to $\bar{\gamma}_f/K$, which expresses the ratio of the counter ion-charged site interaction to the electrolyte-resin interaction.

So far, the difference in the standard chemical potential of an ion between the resin and the external solution has been ignored in thermodynamic treatments of the equilibria.[5] This may, in general, not be valid, since the resin-electrolyte solution equilibria are heterogeneous.

It is likely that $\bar{\gamma}_\pm$ as well as $\bar{\gamma}_\alpha$ varies with the concentration of Donnan salt. Thus, the constant values of $K/\bar{\gamma}_\pm$ and $\bar{\gamma}_f/\bar{\gamma}_\alpha$ observed in the present study may be regarded as apparent ones. A constant value of $K/\bar{\gamma}_\pm$ will be realized if the swelling pressure term is cancelled by $\bar{\gamma}_\pm$. On the other hand, a constant value of $\bar{\gamma}_f/\bar{\gamma}_\alpha$ can not thus be explained, since $\bar{\gamma}_f$ is regarded constant in terms of the additivity law.[6] The apparent constancy of $\bar{\gamma}_f/\bar{\gamma}_\alpha$ is probably related to the fact that the total counter ion concentration did not change so remarkably as the concentration of Donnan salt.

For the ion-exchange reaction:

$$M^+ + NR \rightleftharpoons N^+ + MR$$

where R is the ion-exchange site, we obtain, from Eqs. 1 and 2:

$$\bar{a}_M a_N/\bar{a}_N a_M = K_N^M \tag{7}$$

The equilibrium constant, K_M^N, is given by:

$$-\boldsymbol{R}T\ln K_N^M = (\bar{\mu}_M^0-\mu_M^0) - (\bar{\mu}_N^0-\mu_N^0) + \pi(\overline{V}_M-\overline{V}_N) \tag{8}$$

where the subscripts M and N refer to the M and N ions respectively. Since the difference in the ionic molar volume is small, the contribution of the swelling pressure term may be ignored unless the swelling pressure is extremely high.

It is well-known that the selectivity coefficinet for an ion-exchange reaction varies with the composition of the ions involved in the reaction.[5] This indicates the changes in the activity coefficients of ions with the composition. Even in this case, the additivity law may also provide a way of elucidating the behavior of counter ions in the ion-exchange reaction. A more detailed study will be required to establish thermodynamic treatments concerning the ion-exchange resin-electrolyte solution equilibria.

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