Univalent-Bivalent Ion-exchange Equilibria on Some Permselective Membranes

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(Received June 3, 1963)

This study was undertaken in connection with preferential ion transport in electrodialytic ion transfer through permselective membranes and therefore the ion pairs studied were selected from those encountered in natural waters: Cl/SO$_4$ in the case of anion exchange resins and Na/Ca in the case of cation exchange resins.

In the equilibrium state the electrochemical potential of each mobile particle is equal inside and outside the resin. If a constant partial molar volume is assumed for each particle it may be shown$^{1)}$ that for the ion i:

$$E_i=\overline{\varphi}_i-\varphi_i=\frac{1}{z_i\boldsymbol{F}}\left[\boldsymbol{R}T\ln\frac{a_i}{\overline{a}_i}-\pi V_i\right] \tag{1}$$

in which E is the Donnan potential, φ the electrical potential, z the electrovalency of the ion, $\boldsymbol{F}$ Faraday's constant, $\boldsymbol{R}$ the gas constant, T the absolute temperature, a the single ion activity, π the swelling pressure and V the partial molar volume; barred symbols refer to the resin phase. Helfferich$^{1)}$ applies Eq. 1 to both the competing counterion species i and j, assuming $\overline{\varphi}_i=\overline{\varphi}_j$ and therefore $E_i=E_j$, and assuming a constant π. Tye$^{2)}$ has pointed out that counterions and co-ions are on different electrical potentials and the same, although possibly less so, should hold for two different counterions i and j. Therefore we will equate φ_i and φ_j rather than E_i and E_j:

$$\varphi_i=\varphi_j \tag{2}$$

Combining Eqs. 1 and 2:

$$\ln\left[\frac{a_j}{\overline{a}_j}\right]^{z_i}\left[\frac{\overline{a}_i}{a_i}\right]^{z_j} =-\frac{\pi}{\boldsymbol{R}T}[z_jV_i-z_iV_j]-\frac{z_iz_j\boldsymbol{F}}{\boldsymbol{R}T}[\overline{\varphi}_i-\overline{\varphi}_j] \tag{3}$$

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1) F. Helfferich, *Ionenaustauscher*, Vol. 1, *Verlag Chemie*, Weinheim/B (1959), pp. 133, 154.

2) F. L. Tye, *J. Chem. Soc.*, **1961**, 4784.

In the exchange of i and j not only the two counterions are involved but also a certain amount of water and therefore we replace in Eq. 3 the difference in partial molar volumes by the total volume change (in the resin) involved in the exchange of i and j, $(z_j\overline{V}_i - z_i\overline{V}_j)$. Furthermore, it will be assumed that π is proportional to the equivalent fraction $\overline{X}_j$ of j in the resin:

$$\pi = \pi_i + \overline{X}_j(\pi_j - \pi_i) \tag{4}$$

in which π_i and π_j denote the swelling pressures in the single ionic forms of the resin. When the single ion activities in Eq. 3 are replaced by molalities according to

$$a_i = f_i m_i, \text{ etc.} \tag{5}$$

and the molalities are in turn replaced according to

$$X_i = \frac{z_i m_i}{z_i m_i + z_j m_j}, \text{ etc.} \tag{6}$$

and defining the relative affinity coefficient $K_j{}^i$ by:

$$K_j{}^i \equiv \left[\frac{X_j}{\overline{X}_j}\right]^{z_i} \left[\frac{\overline{X}_i}{X_i}\right]^{z_j} \tag{7}$$

then, combination of 3−7 and conversion to logarithms gives:

$$\begin{aligned} \ln\, k_j{}^i = {} & (z_j - z_i) \ln \frac{z_i m_i + z_j m_j}{z_i \overline{m}_i + z_j \overline{m}_j} \\ & + \ln \frac{f_i{}^{z_j}}{f_j{}^{z_i}} + \ln \frac{\overline{f}_j{}^{z_i}}{\overline{f}_i{}^{z_i}} - [z_j\overline{V}_i - z_i\overline{V}_j] \\ & \times \frac{\pi_i + \overline{X}_j[\pi_j - \pi_i]}{\boldsymbol{RT}} - \frac{z_i z_j \boldsymbol{F}}{\boldsymbol{RT}}(\overline{\varphi}_i - \overline{\varphi}_j) \end{aligned} \tag{8}$$

The first term on the right hand side is the external/internal concentration ratio term which disappears when $z_i = z_j$. This term is mainly responsible for the increase in affinity for multivalent ions (compared with univalent ions) when the external total electrolyte concentration is decreased. The term varies slightly with $\overline{X}_j$ because of the amount of water involved in the exchange, which causes m_i and m_j to change with $\overline{X}_j$.

The second term is the external activity coefficient ratio term which is somewhat dependent on X_j and therefore also on $\overline{X}_j$ and, depending on the ionic species involved, the term can change considerably with external concentration.

The thired term is the internal activity coefficient ratio term which is difficult to estimate; one should be very cautious when considering an analogy with concentrated electrolyte solutions.

The fourth term is the pressure-volume term which is dependent on $\overline{V}$ and therefore on total external concentration (increased swelling of the resin at lower external concentration) and, as shown, it is also dependent on $\overline{X}_j$.

The last term is the electrical term which can be expected to be quite independent of external concentration and $\overline{X}_j$.

Experimental

Ion exchange resin membranes used were:

	Cation exchanger	Anion exchanger
Permaplex[3]	C-20	A-20
T. N. O.[4]	C-60	A-60
A. M. F.[5]	3129 B-56	3129 B-96
A. C. I.[6]	Yes	Yes
C. S. I. R.[7]	—	TA

From each membrane four circular pieces with a diameter of 1.5 in. were cut and brought to the sodium or chloride form with several amounts of 2 N sodium chloride after which the samples were rinsed with distilled water. The pieces were then equilibrated for two days with renewed amounts of mixed solutions of sodium chloride and calcium chloride (0.15N) or sodium chloride and sodium sulfate (0.5N, 0.15N or 0.01N). In a number of cases ohmic resistance measurements were carried out on the membranes in the equilibrating solution. On each piece of membrane measurements were made on two different small areas (2.3 cm²) and for each material the reported values are the average of eight measurements.

Equilibration and Resistance Measurements at 25°C. —The four pieces of each material were weighed together after thorough blotting with filter paper. Calcium was then displaced from the cation exchange resins by leaching with 25 ml. amounts of 1N sodium chloride and calcium was determined by complexometric titration with EDTA. Chloride and SO_4 were displaced from the anion exchange resins by leaching with 25 ml. amounts of 2 N sodium nitrate. Chloride in the leach was determined by Mohr titration and SO_4 by complexometric titration using photometric endpoint detection. The NO_3 form of the membranes was weighed. The membranes were in the complete sodium or chloride form before each new equilibration with a mixed solution. All equilibrations were carried out with the same four pieces of material. Finally, the membranes were rinsed free of absorbed electrolyte and dried to constant weight sodium or chloride form in a vacuum desiccator over phosphorus(V) oxide.

Results and Discussion

Change in Water Content.—The weight of the samples varied linearly with internal

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3) The Permutit Co., Ltd., England.

4) Central Technical Institute T. N. O., Netherlands.

5) American Machine & Foundry Comp., U. S. A.

6) Asahi Chemical Industry, Japan.

7) J. R. Parrish and R. Stevenson, S. A. Council for Scientific and Industrial Research, S. A. Pat. 2793/60; Brit. Pat. 907079.

TABLE I. CHANGE IN WATER CONTENT IN ION EXCHANGE

Increase in water content in the replacement of:	Total external electrolyte concn., N	Permaplex	T. N. O.	A. M. F.	A. C. I.	C. S. I. R.
Ca by Na, g. mol./g. eq.	0.15	0.4	4.7	1.1	1.1	—
Internal molality of Na-form, g.-eq./1000 g. H_2O	0.15	3.4	2.0	9.3	7.5	—
Cl by SO_4, g. mol./g. eq.	0.01	2.4	1.3	2.7	2.0	1.8
	0.15	2.5	1.3	2.7	1.9	—
	0.50	2.2	1.5	2.6	3.4 ?	1.1
NO_3 by SO_4, g. mol./g. eq.	0.01	5.7	4.3	4.9	4.0	3.9
	0.15	5.4	3.9	4.9	3.6	—
	0.50	4.9	3.5	4.3	3.9	2.9
Internal molality of Cl-form, g.-eq./1000 g. H_2O	0.01	5.5	7.0	6.2	4.3	5.3

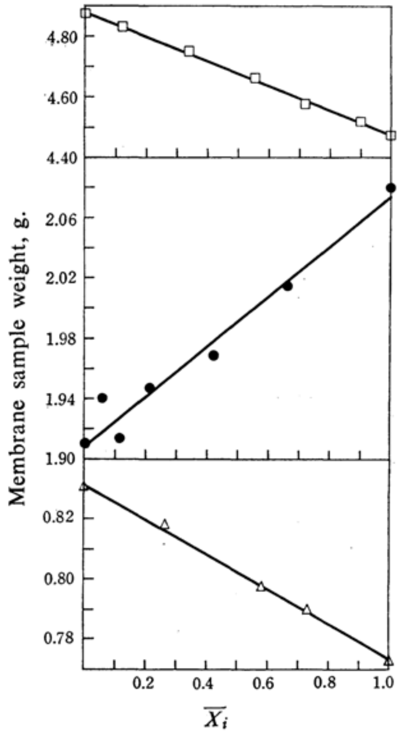

Fig. 1. Weight change of membrane samples.
i=Monovalent ion
△ A. M. F. 3129 B-96, Cl/SO_4,
● T. N. O. C-60, Na/Ca,
□ Permaplex A-20, Cl/SO_4

counterion composition, examples being shown in Fig. 1. After correcting for the change due to the counterions themselves it was possible to arrive at the constant amount of water involved in the exchange of i and j. The constancy is the basis for Eq. 4. As indicated by Boyd et al.[8] the amount of water involved is not necessarily constant in resins with low degrees of crosslinking; the resin membranes are usually highly crosslinked.

The observed water content changes have been summarized in Table I. In the cation exchange resins the amount of water involved in the Ca/Na exchange tends to be low in the resins of high internal molality. The hydration of the ions in the resin decreases with increasing internal molality (degree of crosslinking).[9]

The result for Permaplex C-20 seems to deviate, but it should be remembered that these heterogeneous membranes contain liquid interstices between the ion exchange resin grains embedded in the inert matrix. This leads to a higher water content for the membrane than for the resin itself[10] and consequently to a low calculated internal molality. It may also lead to low values for the change in water content, if the volume changes of the resin particles are partly compensated by changes in the size of the interstices.

In the anion exchange resins the amount of water involved in the Cl/SO_4 or NO_3/SO_4 exchange decreases, in general, with increasing external electrolyte concentration, i. e., with decreasing swelling of the resin and consequently an increasing internal molality. The correlation of water content change with the internal molalities of the different membranes is less clear and it should be remembered that, although in general the high concentration of fixed ions is due to crosslinking, the degree of crosslinking itself should still be taken into account. The C. S. I. R.-T. A. resin, for instance, is very highly crosslinked but does not have the highest concentration of fixed ions.

In general, we may conclude that the amount of water involved in ion exchange is dependent

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[8] G. E. Boyd, S. Lindenbaum and G. E. Myers, *J. Phys. Chem.*, **65**, 577 (1961).

[9] H. Ohtaki, K. Gonda and H. Kakihana, This Bulletin, **33**, 293 (1961); *Z. Electrochem*, **67**, 87 (1963).

[10] D. K. Hale and D. J. McCauley, *Trans. Faraday Soc.*, **57**, 135 (1961).

on the amount of water present in the resin and on the rigidity (crosslinking) of the polymer network.

Conductivity.—Conductances were measured only in 0.15 N solutions. The results are given in Figs. 2 and 3. In the cation exchange resins interaction is noticeable only at high calcium loading. The calcium form of the resin is less swollen and the observed effect could be explained by an uneven distribution of counterions through the resin, caused by heterogeneity in the crosslinking of the resin.

The form of the curve obtained for the heterogeneous Permaplex C-20 membranes can be explained as follows. At low $\overline{X}_{\mathrm{Ca}}$ the calcium ions in the membrane will be located mainly inside the resin particles and then they cannot hinder the movement of Na^+ on the particle surface. If surface transport makes up a large portion of total transport, the conductivity of the membrane decreases little when only a small amount of calcium is present. Evidence that surface transport is indeed important in heterogeneous membranes comes from selective ion transport in a d. c. field, in which the transport ratios are more in favor of the common monovalent ions than would be expected from the ratios of internal concentrations and mobilities. At high $\overline{X}_{\mathrm{Ca}}$ the calcium ions are present on the particle surface as well (area of little crosslinking) and the interaction is then similar to, though possibly less than, that in homogeneous membranes.

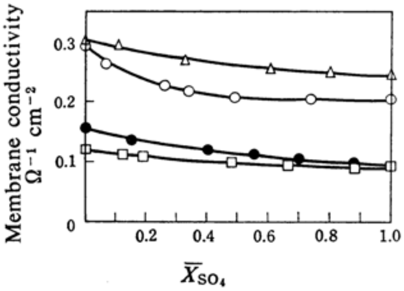

Fig. 2. Membrane conductivity at 25°C in 0.15 N NaCl/$\mathrm{Na_2SO_4}$ solution.

△ A. M. F. 3129 B-96
○ A. C. I.
● T. N. O. A-60
□ Permaplex A-20

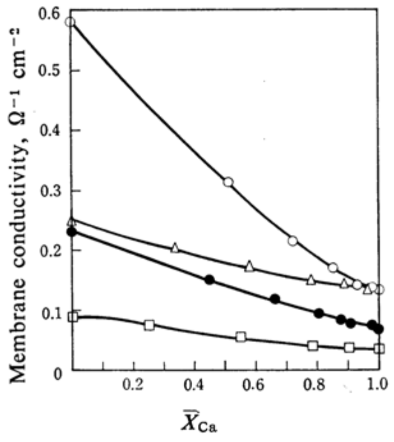

Fig. 3. Membrane conductivity at 25°C in 0.15 N NaCl/$\mathrm{CaCl_2}$ solution.

△ A. M. F. 3129 B-56
○ A. C. I.
● T. N. O. C-60
□ Permaplex C-20

In the anion exchange resins the interaction is strong at any $\overline{X}_{\mathrm{SO_4}}$, particularly in the A. C. I. membrane. The chloride form of the resin is less swollen and the observed effect could again be explained by an uneven distribution of counterions through the resin. In this case the ions causing the highest swelling of the resin are the less mobile (bivalent) ions, and the differences in the conductivities of the two single ionic forms of the resin are considerably smaller than in the case of Ca/Na in the cation exchange resins in which the less mobile (bivalent) ions cause the lowest swelling. Conductivities appear to give some indication of the electrostatic forces between fixed ions and counterions.

Ion Exchange Equilibrium. — The relative affinity coefficient $K_{\mathrm{Ca}}^{\mathrm{Na}}$ is given in Fig. 4 and $K_{\mathrm{SO_4}}^{\mathrm{Cl}}$ is given in Fig. 5. In both types of resin K varies with $\overline{X}$ and in the discussion of Eq. 8 several reasons have already been indicated. This equation does not incorporate the influence of heterogeneity in the resin. This heterogeneity can have several causes. If the fixed ions are of a different chemical nature (e. g., $-\mathrm{COO}^-$ and $-\mathrm{SO_3}^-$), then the resin is bifunctional[11] and $K_j{}^i$ changes sharply at $\overline{X}$ corresponding to the fraction of fixed ions of one kind; or, fixed ions of identical chemical nature are attached to the polymer network in different positions.[12-14] Reichenberg and McCauley[15] attributed the strong dependence of K on $\overline{X}$ in highly crosslinked resins to heterogeneity in the degree of crosslinking through the resin (sometimes interpreted as a range of pore sizes[16,17]); the result

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[11] J. P. Cornaz and H. Deuel, *Helv. Chim. Acta*, **39**, 1227 (1956).

[12] I. H. Spinner, J. Ciric and W. F. Graydon, *Can. J. Chem.*, **32**, 143 (1954).

[13] G. E. Myers and G. E. Boyd, *J. Phys. Chem.*, **60**, 521 (1956).

[14] O. D. Bonner, V. F. Holland and L. L. Smith, ibid., **60**, 1102 (1956).

[15] D. Reichenberg and D. J. McCauley, *J. Chem. Soc.*, **1955**, 2741.

[16] K. Uberreiter and G. Kanig, *J. Chem. Phys.*, **18**, 399 (1950).

[17] Ref. 1, p. 13.

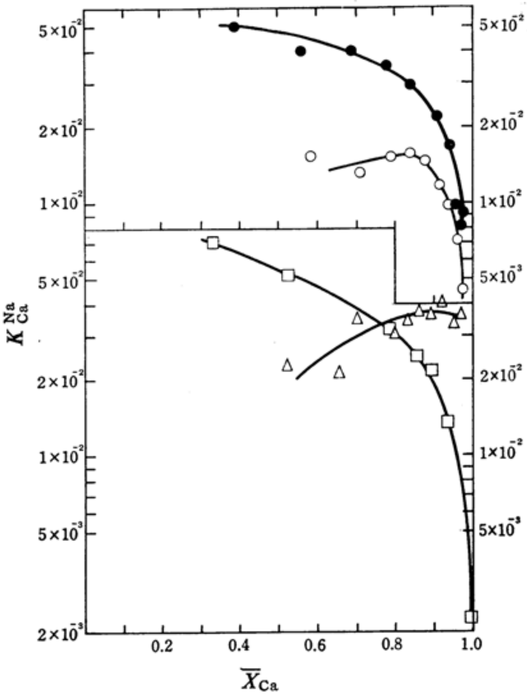

Fig. 4. Relative affinity coefficient K^{Na}_{Ca}.

● T. N. O. C-60 ○ A. C. I.
☐ Permaplex C-20 △ A. M. F. 3129 B-56

is a multifunctional resin. Högfeldt[18] has shown that both a bifunctional and a multifunctional treatment can be used to explain the same set of experimental data. Glueckauf and Watts[19,20] indicated that heterogeneous crosslinking is an important factor with respect to some other resin (or membrane) properties as well, i. e., electrolyte uptake and salt diffusion. It was also shown[21] that their approach does not lead to a quantitative theory of ion exchange equilibra.

The most remarkable feature in Fig. 4 is the strong decrease in K^{Na}_{Ca} at high $\overline{X}_{Ca}$; the more calcium is present in the resin the higher the affinity for calcium. The deviating result for the A. M. F. membrane remains unexplained.

Between $X_{Ca}=0$ and $X_{Ca}=1$ the concentration ratio term in Eq. 8 varies only by 5~10%. Changes in the external activity coefficient term can be estimated at 0.3%. There is no *a priori* reason why the internal activity coefficient term should decrease greatly at high $\overline{X}_{Ca}$. The electrical term in Eq. 8 can be assumed to remain approximately constant and the pressure-volume term should bring about a gradual decrease in K^{Na}_{Ca} with increasing $\overline{X}_{Ca}$.

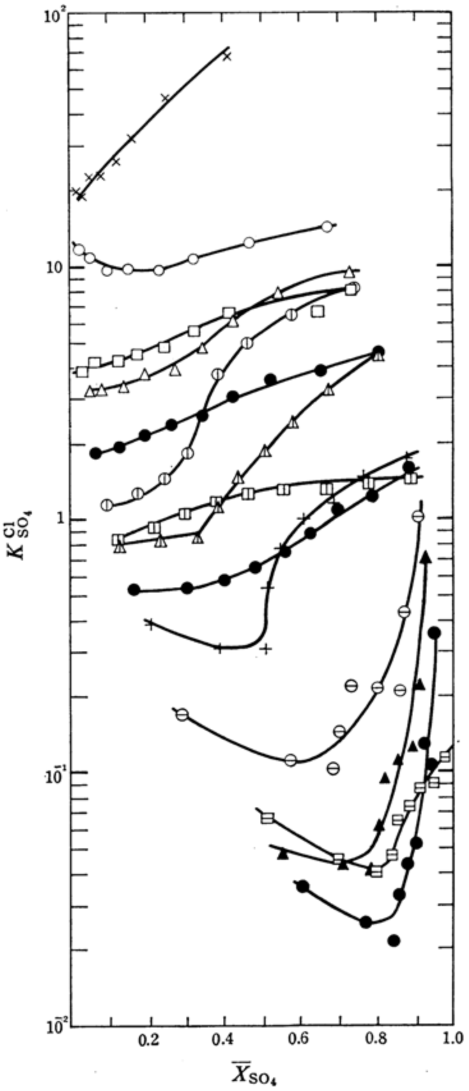

Fig. 5. Relative affinity coefficient $K^{Cl}_{SO_4}$.

Total external concn.	0.01N	0.15N	0.50N
T. N. O. A-60	●	●	●
Permaplex A-20	⊟	◫	☐
A. M. F. 3129 B-96	▲	◬	△
A. C. I.	⊖	⦶	○
C. S. I. R.-TA	+		×

If the resin is heterogeneous with respect to crosslinking, then at high $\overline{X}_{Ca}$ the few sodium ions will be situated preferentially in the areas of least crosslinking, forming islands of high swelling, which are squeezed by the elastic forces in the surrounding more crosslinked area. A serious deviation from proportionality between π and $\overline{X}_{Ca}$ may then occur. In should be noted that the strong decrease in K^{Na}_{Ca} occurs in the same range of $\overline{X}_{Ca}$ in

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[18] E. Högfeldt, *Ark. f. Kemi*, **13**, 491 (1959).
[19] E. Glueckauf and R. E. Watts, *Nature*, **191**, 904 (1961).
[20] E. Glueckauf and R. E. Watts, *Proc. Roy. Soc.*, **268A**, 339 (1962).
[21] E. Glueckauf, ibid., **268A**, 350 (1962).

which interaction with respect to conductivity was observed.

With respect to the Cl/SO$_4$ equilibria on the anion exchange resins (Fig. 5) attention is drawn to the sharp increase in affinity for chloride at high $\bar{X}_{SO_4}$ and low external concentration. This affinity is generally higher in the highly crosslinked resins (A. C. I. and C. S. I. R.-T. A.) where the sharp increase starts at $\bar{X}_{SO_4}=0.6$ and $\bar{X}_{SO_4}=0.4$ respectively, while in the other resins it starts only at approximately $\bar{X}_{SO_4}=0.75$. In the shape of the curves for higher external concentrations there is some indication that the increase is then less sharp but starts at a much lower $\bar{X}_{SO_4}$. In all casses less swelling is connected with a higher affinity for chloride.

The contribution of the concentration ratio term to $K_{SO_4}^{Cl}$ changes by 15～30% with $\bar{X}_{SO_4}$ across the ranges of $\bar{X}_{SO_4}$ investigated at each exteral concentration. The external activity coefficient term can be estimated from

$$\frac{f^2_{Cl}}{f_{SO_4}}=\frac{f^2_{Cl}\cdot f^2_{Na}}{f_{SO_4}\cdot f^2_{Na}}=\frac{\gamma^4_{NaCl^*}}{\gamma^3_{Na_2SO_4^*}} \tag{9}$$

in which γ is the mean ion activity coefficient. [At the same ionic strength $I=(1+1/2X_{SO_4})\times(m_{Cl}+2m_{SO_4})$]. Values derived from listed data[22] are given in Table II. The increase in affinity for chloride with external concentration is due not only to the concentration ratio term but also to a considerable change in the external activity coefficient ratio.

TABLE II. ESTIMATED VALUES FOR $\frac{f^2_{Cl}}{f_{SO_4}}$

External concn., N	$X_{SO_4}=0$	$X_{SO_4}=1$
0.01	1.8	2.0
0.15	5.1	6.5
0.50	10.7	16.8

In a resin with hetrogeneous crosslinking the chloride ions are preferentially situated in regions with relatively high crosslinking and, when at high $\bar{X}_{SO_4}$ the SO$_4$ ions invade these regions, pressure-volume effects increase the affinity for chloride. The influence of heterogeneity can be expected to be strongest when the resin is in its most swollen state (low external concentration or high $\bar{X}_{SO_4}$); in regions of low crosslinking the swelling changes more with external concentration than in regions of high crosslinking.[23]

The high affinity for chloride does not occur in the resins with the highest internal molality (see Table I) but in the resins with the highest degree of crosslinking. This is a strong indication that the pressure-volume term is of relative importance.

Summary

The relative affinity coefficient K_j^i is shown to be dependent on the ratio of external and internal total concentrations, the ratio of the external activity coefficients and of the internal activity coefficients, a pressure-volume term and an electrical term. K_j^i is therefore dependent on the "loading" of the resin $\bar{X}_j$.

Several cation exchange resins exhibit a very strong affinity for calcium at high calcium loading and this affinity increases sharply with $\bar{X}_{Ca}$; this effect is attributed to heterogeneity in the crosslinking of the resin and it is a strong indication that here the pressure-volume term plays a decisive rôle.

The pressure-volume term appears to be of relative importance also in the Cl/SO$_4$ equilibrium on anion exchange resins, particularly when these are highly crosslinked. Heterogeneity in the crosslinking probably causes the sharp increase in affinity for Cl at high SO$_4$ loading and low (0.01N) external concentration.

Conductivity measurements on the resins in single and mixed forms is useful to get an indication of the binding forces between counterions and fixed ions and these measurements can also reveal interactions which may have a bearing on ion exchange equilibrium.

The author wishes to express his sincere thanks to Mr. J. Venlet who carried out the experimental work and who assisted in the data evaluation.

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[22] R. Parsons, "Handbook of Electrochemical Constants," Butterworths, London (1959).

[23] R. J. Stewart and W. F. Graydon, *J. Phys. Chem.*, **61**, 164 (1957).