(15–50% aqueous KOH) was 10^{-9} sec.[13] The present experiments are more direct than this earlier work and should be more meaningful. The present data agree with very recent observations from irradiation of hydrocarbon mixtures at pressures of approximately 40 torr which indicate that *sec*-$C_4H_9^+$ abstracts a hydride ion faster than it isomerizes to *t*-$C_4H_9^+$. Indeed, no evidence was reported for isomerization of *sec*-$C_4H_9^+$ to *t*-$C_4H_9^+$,[4e] and the experiments strongly corroborate each other.

Acknowledgment. The author is grateful to Drs. F. H. Field and J. L. Franklin for helpful discussions.

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The Donnan Equilibrium in Cross-Linked Polystyrene Cation and Anion Exchangers[1]

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Abstract: Techniques utilizing a "reference compound" and high specific activity ^{22}Na, ^{36}Cl, ^{35}S, and ^{45}Ca were employed to determine the equilibrium water uptake and absorption of NaCl, Na_2SO_4, and $CaCl_2$ from dilute aqueous solutions by nominal 8% DVB cross-linked polystyrene-based cation and anion exchangers. Values of the molal distribution coefficients for electrolyte, λ_D, as small as 0.001 were measured, and the predictions of a general equation for the concentration dependence of λ_D, derived assuming a Donnan membrane equilibrium, were confirmed. The activity coefficients of electrolyte absorbed by the exchangers slowly increased as the external electrolyte concentration decreased below 0.1 *m*. It was concluded that the spherical ion exchangers employed were physically homogeneous to a high degree and that their absorption of strong electrolytes could be described quantitatively in terms of a Donnan equilibrium.

When two coexistent phases are subject to the restriction that one or several of the ionic constituents present in them cannot pass from one phase to another, a particular equilibrium, known as a Donnan equilibrium, is established. Usually the restriction is caused by a membrane which is permeable to solvent and to small ions but is impermeable to large ions; therefore, these equilibria are described as Donnan *membrane equilibria*. The presence of a membrane is not essential, however; in a gel or in an ion exchanger where there are structurally bound ions, the equilibria also are of the Donnan type.

The important aspects of the Donnan equilibrium with ion exchangers are that an unequal distribution of ions, an osmotic pressure difference, and a potential difference exist between the gel and external phases. In this paper, only the distribution of small ions and water will be considered for organic ion exchangers in which the charge density is high as with the cross-linked polystyrenesulfonate cation exchangers or polystyrene–quaternary ammonium type anion exchangers. Because of the high charge density, the Donnan equilibrium is nonideal and the thermodynamic treatment of Donnan and Guggenheim[2a] must be employed.

The equilibrium distribution of electrolytes between ion exchangers and dilute external aqueous solutions may be discussed in terms of the molal Donnan distribution coefficient, λ_D, defined by $\lambda_D = \bar{m}/m$, where $\bar{m}$ and m are the electrolyte molalities in the ion exchanger and external solution phases, respectively. A general expression for λ_D for a strong electrolyte dissociating into ν_c co-ions and ν_g counterions (or "gegenions") is[2b]

$$\lambda_D = (|z_c|m/\bar{m}_T)^{|z_c/z_g|}(\gamma_\pm/\bar{\gamma}_\pm)^{\nu/\nu_c}\exp(-\pi\bar{v}/RT) \quad (1)$$

where the total number of ions formed per mole of electrolyte, ν, is given by $\nu = \nu_c + \nu_g$; z_c and z_g are the numbers of charges on the co-ion and counterions, respectively; $\bar{m}_T$ is the total molality of the ion-exchange phase given by $\bar{m}_T = (\bar{m}_R + |z_c|\bar{m}_c)$, where $\bar{m}_R$ is the molality of ion-exchange groups and $\bar{m}_c$ that of co-ions; $\gamma_\pm$ and $\bar{\gamma}_\pm$ are the mean molal activity coefficients of electrolyte in aqueous and exchanger phases, respectively; π is the swelling pressure; and $\bar{v}$ is the partial molar volume of the electrolyte in the exchanger. The quantity $\exp(-\pi\bar{v}/RT)$ is approximately unity and constant and, henceforth, will be thus regarded.[3]

Writing eq 1 in the logarithmic form

$$\log \lambda_D = |z_c/z_g| \log (m/\bar{m}_T) - (\nu/\nu_c) \log (\gamma_\pm/\bar{\gamma}_\pm) + |z_c/z_g| \log |z_c| \quad (2)$$

The numerical value of the variation of log λ_D with log m will approach $|z_c/z_g|$, the absolute value of the ratio of the charge carried by the co-ion to that by the counterion, when the external electrolyte solution be-

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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

[2] (a) F. G. Donnan and E. A. Guggenheim, *Z. Physik. Chem.*, **A162**, 346 (1932). (b) This equation can be shown to be identical with equations (5–49) given by F. Helfferich, "Ion Exchange," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 142.

[3] Typical values for a nominal 8% divinylbenzene cross-linked polystyrenesulfonate exchanger invaded by an aqueous NaCl solution are: π = 100 atm, $\bar{v}_{NaCl} \approx$ 25 cc mole^{-1}, so that $\exp(-\pi\bar{v}_{NaCl}/RT)$ = 0.903.

comes sufficiently dilute for $\bar{m}_T = \bar{m}_R$ = constant, provided that the activity coefficient ratio $(\gamma_\pm/\bar{\gamma}_\pm)$ also becomes approximately constant. Many reports[4] on electrolyte distribution in ion exchangers have appeared, however, in which λ_D decreased much less rapidly than predicted by eq 2, and in some cases became nearly independent of *m;* yet, a Donnan equilibrium was assumed, and eq 1 was employed to compute $\bar{\gamma}_\pm$, which appeared to decrease markedly when the external electrolyte concentration became small. Recently an explanation for the surplus absorption of co-ions has been advanced based on the assumption of an extensive nonuniformity in the cross linking of ion-exchange membranes and presumably also in the more common spherical bead preparations.[5,6] It was suggested,[6] moreover, that quantitative treatments[7-12] of ion-exchange equilibria based on the Donnan law and an homogeneous ion-exchanger phase were invalid, and a detailed alternative theory was proposed.[13]

The possibility that ion-exchange materials may be either physically or chemically nonuniform, or both, cannot be dismissed readily. However, serious objections can be raised to the techniques described in all previous reports of experimental measurements of the absorption of co-ions by ion exchangers from dilute solutions, excepting possibly one very recent investigation.[14] Large, positive errors are introduced into co-ion absorption measurements if there is an incomplete phase separation of an equilibrated ion exchanger from an aqueous electrolyte solution. Further, impurities if present within an exchanger will absorb a small, virtually constant quantity of electrolyte independent of the concentration of the aqueous solution. The consequence of these errors is that λ_D tends to approach constancy independent of the concentration of the aqueous electrolyte solution as the latter becomes increasingly dilute, instead of decreasing as required by eq 1. An ingenious technique to correct for the incomplete phase separation error has been described by Glueckauf and Watts.[6] In their procedure the quantity of electrolyte released by an ion-exchange membrane was measured as a function of time, and the true amount in the membrane at equilibrium was determined by extrapolation to zero time with an equation valid for diffusion from a *homogeneous* slab. However, if the ion exchanger is not homogeneous, this equation becomes inapplicable, and conclusions about the nonuniformity of the exchanger phase derived through its employment do not appear to be justified. The techniques employed by Freeman, Patel, and Buchanan[14] appear to overcome the difficulties cited above; unfortunately, however, their measurements were not conducted with sufficiently dilute solutions for $\bar{m}_T$ to become effectively constant, so that a test of the *limiting form* of eq 2 cannot be made.

The object of this research has been to develop experimental techniques for the measurement of the invasion of ion exchangers by electrolytes which avoid the errors present in earlier experiments. An important aim was to be able to conduct measurements with aqueous electrolyte solutions sufficiently dilute to determine if the Donnan law behavior described by eq 2 was approached. Sensitive and accurate methods are required for the determination of the very small amounts of co-ion in ion exchangers in equilibrium with dilute solutions. The water content of the exchanger also must be measured accurately so that the molality of the co-ion in the exchanger can be determined as a function of its external concentration.

Experimental Section

Materials. All experiments were performed with the same preparation of Dowex 50W-X8 or of Dowex 1-X8. These materials were carefully pretreated, converted to the sodium or chloride form, respectively, air-dried, and stored in a closed container until use. The exchange capacities of the dry salt forms were 4.60 mequiv/g of the Na form and 3.84 mequiv/g of the Cl form, and their water contents when they were in equilibrium with pure water were 179.6 and 224.6 g/equiv, respectively.

Water-Content Measurements. The equivalent water content of the cation exchanger in equilibrium with pure water was determined with the "reference compound method" described by Pepper[15] wherein the increase in concentration of a dilute solution of the dyestuff, Chlorazol Sky Blue FF, was determined after a predetermined quantity of air-dried,[16] Na-form exchanger was immersed in the solution. The dye was dissolved in boiling water, and insoluble impurities were removed by filtration. Sodium acetate was added to the filtrate which was allowed to stand overnight to precipitate the dye. After redissolution in pure water, the dye was dialyzed for 24 hr to remove acetate ion and other low molecular weight contaminants. Crystals of the dye finally were vacuum dried at 100° for 3 days. Dye concentrations were determined from the optical density measured with a Cary Model 14P recording spectrophotometer. The dilute solutions were shown to obey Beer's law, and adsorption of dye by the exchanger was negligibly small. Unfortunately, adsorption occurred when electrolyte was present in solution and the method could not be used. Accordingly, recourse was made to the "settled-bed technique," wherein *ca.* 50 ml of carefully sized, spherical[17] wet exchanger was placed in a graduated, 1-cm diameter glass tube equipped with a flat bottom, and the apparent volume of the exchanger bed was measured in pure water and in various concentrations of dilute electrolyte after sedimentation equilibrium had been achieved. The attainment of equilibrium was facilitated by repetitive mechanical vibration of the glass column; final values were achieved in approximately 3 hr. The ratio of the bed volume, V, in dilute electrolyte to that in pure water, V_0, was observed to decrease linearly with electrolyte molality (Figure 1). The ratio V/V_0 was used to compute the equivalent water content of the exchanger for any concentration of salt within the range investigated, assuming that the amounts of electrolyte absorbed by the exchanger were so small that its contribution to the volume could be ignored. A plot of V/V_0 against the water activity, a_w, in the electrolyte also gave a straight line, and the points for NaCl and Na_2SO_4 fell together, as would be expected if the assumption were valid that the volume contribution of electrolyte could be neglected. A check on the "settled-bed technique" was afforded by the published value, $V/V_0 = 0.987$, for a Dowex 50-X8 cation exchanger, Na form, determined in 0.2 *m* NaCl using microscopy.[18] A short extrapolation of the curve in Figure 1 to this concentration gives $V/V_0 = 0.988$, which is considered to be in satisfactory agreement.

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[4] References to these publications have been given by R. L. Gustafson, *J. Phys. Chem.*, **67**, 2549 (1963).

[5] E. Glueckauf and R. E. Watts, *Nature*, **191**, 904 (1961).

[6] E. Glueckauf and R. E. Watts, *Proc. Roy. Soc.* (London), **A268**, 339 (1962).

[7] E. Glueckauf, *ibid.*, **A214**, 213 (1952).

[8] G. E. Boyd and B. A. Soldano, *Z. Elektrochem.*, **57**, 162 (1953).

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

[10] G. E. Boyd, S. Lindenbaum, and G. E. Myers, *ibid.*, **65**, 577 (1961).

[11] G. E. Boyd and S. Lindenbaum, *ibid.*, **69**, 2378 (1965).

[12] A. Schwarz and G. E. Boyd, *ibid.*, **69**, 4268 (1965).

[13] E. Glueckauf, *Proc. Roy. Soc.* (London), **A268**, 350 (1962).

[14] D. H. Freeman, V. C. Patel, and T. M. Buchanan, *J. Phys. Chem.*, **69**, 1477 (1965).

[15] K. W. Pepper, D. Reichenberg, and D. K. Hale, *J. Chem. Soc.*, 3129 (1952).

[16] The initial water content of the exchanger was determined by measuring the weight loss on drying an aliquot for 3 days at 95° *in vacuo* trapped with liquid nitrogen.

[17] The range in particle diameter was 125–149 μ.

[18] D. H. Freeman and G. Scatchard, *J. Phys. Chem.*, **69**, 70 (1965).

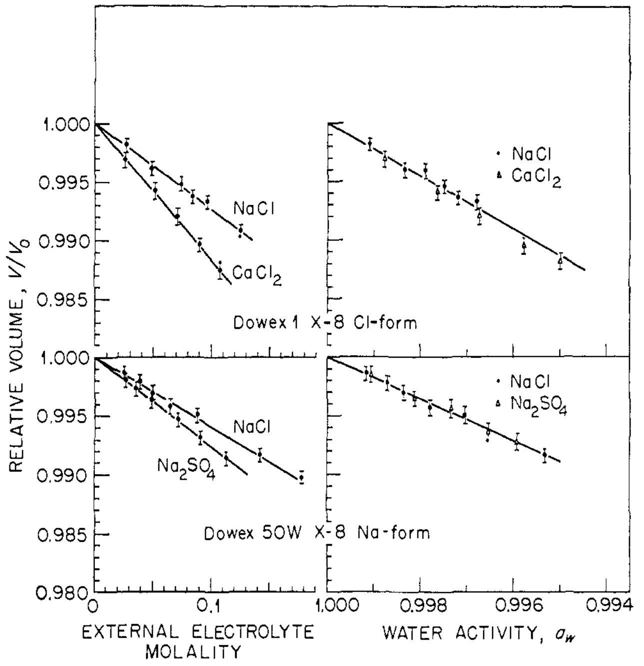

Figure 1. Concentration dependence of the relative volumes of cross-linked cation and anion exchangers.

Attempts to determine the equivalent water content of the anion exchanger, Dowex 1-X8, Cl form, in pure water with a cationic dyestuff were unsuccessful because of adsorption of the dye by the exchanger. During these experiments, however, measurements of the optical density showed that the cross-linked exchanger released linear polyelectrolyte to pure water at a rate which, after many hours, became zero and a constant concentration was established. This "soluble" polyelectrolyte was therefore employed as a "reference compound" in the following procedure: a weighed quantity of air-dried anion exchanger was brought into contact with a weighed amount of pure water, and after 48 hr an aliquot of the supernatant liquid was withdrawn and its optical density at 2240 A was measured.[19] The aliquot was returned to the supernatant together with a weighed quantity of pure water used as a wash. After reequilibration a second aliquot was withdrawn and its optical density was measured. From these measurements the equivalent water content, x_w, of the exchanger was computed. The change in x_w with increasing electrolyte concentration was estimated from the measured volume decrease using the "settled-bed technique" as with the cation exchanger. A linear decrease in V/V_0 with increasing electrolyte molality was observed (Figure 1), and a plot of V/V_0 against water activity caused the measurements with NaCl and $CaCl_2$ to fall on one straight line.[20]

Co-ion Absorption Measurements. The uptake of co-ions by the exchangers was estimated from measurements of the change in the initial electrolyte concentration when a predetermined weight of air-dried exchanger was immersed in a predetermined weight of aqueous solution of known concentration. With NaCl solutions these changes were determined with the 3.08×10^5 year ^{36}Cl and 2.60 year ^{22}Na tracers, while with Na_2SO_4 and $CaCl_2$ solutions 88.0 day ^{35}S and 165.0 day ^{45}Ca, respectively, were employed. Radioisotope preparations of the highest available specific activities were used in the appropriate chemical form. Measurements of the initial and equilibrium activities in approximately 200-λ samples weighed to 0.1 mg were conducted by liquid scintillation counting using a Packard Model 314 EX Tri-Carb liquid scintillation counting system. The counting mixture for the $Na_2{}^{35}SO_4$ and $Na^{36}Cl$ consisted of a solution of 0.8 g of 2,5-bis[2-(5-*t*-butylbenzoxazolyl)]thiophene (BBOT, Packard Instrument Co.) in 100 ml of toluene plus 100 ml of methanol. The $^{45}CaCl_2$ and $^{22}NaCl$ tracers were counted with a previously described mixture.[12] Polyethylene vials were used for all measurements to avoid the possibility of an ion-exchange reaction which might occur with glass-walled vials during the counting time. A ^{14}C standard solution was counted after each unknown to establish that there were no changes in counting efficiency with time. A sufficient number of counts were collected to give a statistical accuracy of 0.1% in each radioactivity measurement, and triplicate samples were measured. The initial concentrations of aqueous electrolyte were determined by flame spectrophotometric analysis to ±1%.

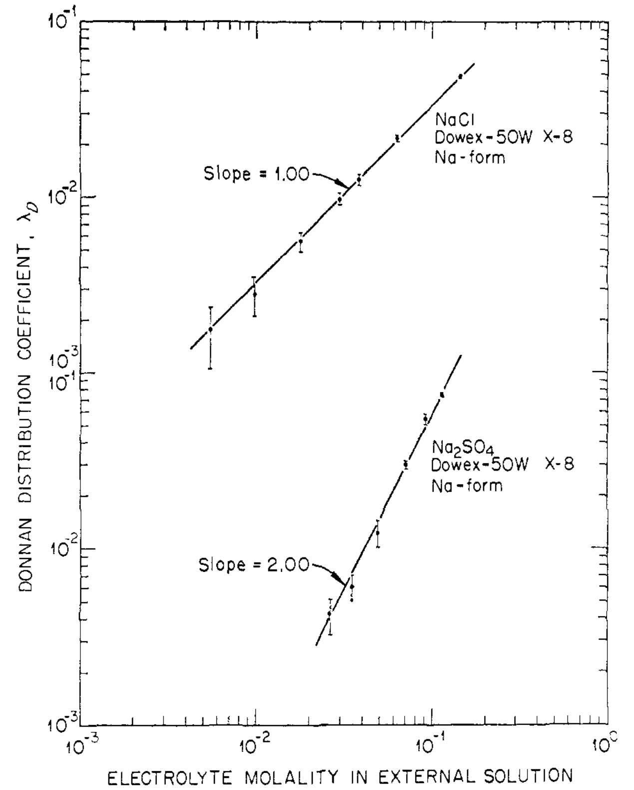

Figure 2. Electrolyte exclusion by cross-linked cation exchangers.

The employment of high specific activity radioactive tracers for the determination of electrolyte uptake and equilibrium electrolyte concentration is believed to have an important advantage over other methods, as, for example, the micropotentiometric titration of Cl^- ion with standardized $AgNO_3$ solution. Not only is the sensitivity an order of magnitude greater, but polyelectrolyte shed by the cross-linked exchanger does not interfere with the analysis as is the case in argentiometric titrations of supernatant liquids from cation and anion exchangers where it has been shown that Ag^+ also combined with linear polyelectrolyte.

Results

It is emphasized that neither the water content nor the electrolyte absorption measurement techniques described above required a separation of the ion exchanger from the aqueous electrolyte solution with which it was in equilibrium. Errors arising from incomplete phase separation, occlusion in cracks in the exchanger, etc., thus were not present. Further, the results in Table I indicate that electrolyte absorption by resin impurities was absent. Plots of these data are given in Figures 2 and 3 where the effect of the charge carried by the co-ion is made evident. The exceptionally small values of the molal distribution coefficient, λ_D, at low external electrolyte are especially interesting as they show the highly efficient electrolyte exclusion by the exchanger. The exclusion of NaCl by the strong-base anion exchanger is seen to have been nearly the same as that by the cation exchanger. The

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(19) Beer's law was shown to be valid for dilute solutions of the "reference" polyelectrolyte.

(20) Polyelectrolyte released by the sodium form of Dowex 50W-X8 exchanger was also employed as a reference compound for the estimation of its water content, and the value found with the dye stuff (*vide supra*) was confirmed.

Table I. Electrolyte Absorption by Cross-Linked Cation and Anion Exchangers

(A) System: NaR, NaCl, H_2O

m	$\gamma_\pm$	$\bar{m}_{\mathrm{NaR}}$	$\bar{m}_{\mathrm{Cl^-}}$	$\bar{\gamma}_\pm$	$\bar{\gamma}_\pm/\bar{\gamma}_\pm'$
0.0054_3	0.924	5.57_0	9.29×10^{-6}	0.698	0.700
0.0098_1	0.903	5.57_2	2.69×10^{-5}	0.724	0.728
0.0178	0.876	5.57_5	9.63×10^{-5}	0.673	0.681
0.0294	0.850	5.57_8	2.81×10^{-4}	0.632	0.644
0.0379	0.836	5.58_1	4.62×10^{-4}	0.624	0.639
0.0634	0.805	5.59_0	1.32×10^{-3}	0.594	0.619
0.1436	0.757	5.61_7	6.91×10^{-3}	0.552	0.607

(B) System: NaR, Na_2SO_4, H_2O

m	$\gamma_\pm$	$\bar{m}_{\mathrm{NaR}}$	$\bar{m}_{\mathrm{SO_4^{2-}}}$	$\bar{\gamma}_\pm$	$\bar{\gamma}_\pm/\bar{\gamma}_\pm'$
0.0263	0.610	5.58_0	1.11×10^{-4}	0.168	0.175
0.0349	0.577	5.58_3	2.08×10^{-4}	0.171	0.181
0.0489	0.537	5.58_9	5.85×10^{-4}	0.158	0.173
0.0707	0.493	5.59_9	2.05×10^{-3}	0.138	0.163
0.0908	0.463	5.60_7	4.92×10^{-3}	0.124	0.159
0.1130	0.438	5.61_7	7.96×10^{-3}	0.124	0.168

(C) System: RCl, NaCl, H_2O

m	$\gamma_\pm$	$\bar{m}_{\mathrm{RCl}}$	$\bar{m}_{\mathrm{Na^+}}$	$\bar{\gamma}_\pm$	$\bar{\gamma}_\pm/\bar{\gamma}_\pm'$
0.0083_6	0.909	4.45_4	1.95×10^{-5}	0.816	0.820
0.0128_5	0.891	4.45_6	4.65×10^{-5}	0.796	0.802
0.0241_8	0.861	4.45_9	1.91×10^{-4}	0.713	0.725
0.0546	0.814	4.46_9	1.11×10^{-3}	0.630	0.654
0.0595	0.809	4.47_1	1.17×10^{-3}	0.667	0.693
0.1005	0.777	4.48_5	3.56×10^{-3}	0.619	0.661
0.1170	0.768	4.49_0	4.79×10^{-3}	0.614	0.662

(D) System: RCl, $CaCl_2$, H_2O

m	$\gamma_\pm$	$\bar{m}_{\mathrm{RCl}}$	$\bar{m}_{\mathrm{Ca^{2+}}}$	$\bar{\gamma}_\pm$	$\bar{\gamma}_\pm/\bar{\gamma}_\pm'$
0.0232	0.650	4.46_4	6.96×10^{-5}	0.215	0.222
0.0462	0.585	4.47_6	4.38×10^{-5}	0.208	0.225
0.0630	0.557	4.48_5	1.12×10^{-3}	0.197	0.223
0.0823	0.534	4.49_5	2.93×10^{-3}	0.179	0.217
0.0896	0.527	4.49_9	3.51×10^{-3}	0.181	0.222
0.1181	0.506	4.51_4	7.20×10^{-3}	0.180	0.238

concentration dependence of λ_D was as expected from eq 2; a slope of unity was observed with NaCl when Cl^- was the co-ion (*i.e.*, in the cation exchanger) and when Na^+ was the co-ion (*i.e.*, anion exchanger). When the co-ion was doubly charged, as with SO_4^{2-} ion in the cation exchanger and with Ca^{2+} ion in the anion exchanger, the slope was 2.0. The cross-linked spherical bead ion exchangers employed in this research therefore appear to conform to the requirements for a Donnan equilibrium, and this result indicates that they are homogeneous gels with a high degree of uniformity. The practical lower limit in the magnitude of λ_D obtained with the technique employed in this research is probably *ca.* 0.001, as the co-ion absorption by the exchangers was determined as a difference between the initial and the final (equilibrium) concentration of the external aqueous electrolyte. For example, small but *negative* λ_D values were found in an experiment with NaCl (Figure 2) when the external electrolyte molality was 0.00253. Application of the method of Glueckauf and Watts[6] in which the quantity of electrolyte absorbed is determined directly should make possible the estimation of still smaller values of λ_D, particularly if high specific activity radiotracers are employed, provided that the exchangers are homogeneous.

Discussion

The nature of the interactions of the absorbed electrolyte within the ion-exchanger gel phase may be discussed in terms of its mean molal activity coefficient, $\bar{\gamma}_\pm$, which may be computed with eq 1 if a Donnan equilibrium exists. Values for the activity coefficients, $\gamma_\pm$, of electrolyte in the dilute external electrolyte solutions (column 2, Table I) and for $\bar{\gamma}_\pm'$ (column 6, Table I) were computed with equations suggested by Guggenheim.[21,22] Thus, for sodium chloride solutions more dilute than 0.1 m

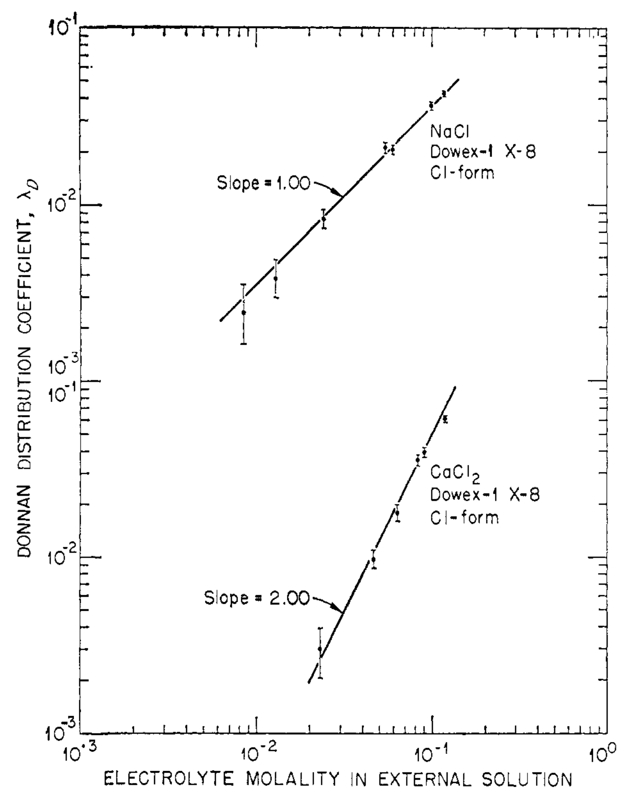

Figure 3. Electrolyte exclusion by cross-linked anion exchangers.

$$\log \gamma_\pm = -0.5085[m^{1/2}/(1 + m^{1/2})] + 0.15m \quad (3a)$$

for calcium chloride solutions

$$\log \gamma_\pm = -1.7615[m^{1/2}/(1 + 2.66m^{1/2})] + 0.169m \quad (3b)$$

and for sodium sulfate solutions

$$\log \gamma_\pm = -1.7615[m^{1/2}/(1 + 2.20m^{1/2})] - 0.165m \quad (3c)$$

The computed $\bar{\gamma}_\pm$ values are summarized in Table I, column 5, where it may be seen that the activity coefficient of the salt in the exchanger is significantly lower than in the equilibrium external solution. The magnitude of $\bar{\gamma}_\pm$ for NaCl is approximately the same in the anion as in the cation exchanger, which suggests that the forces on the diffusible ions are essentially electrical. This conclusion finds support in the much smaller $\bar{\gamma}_\pm$ values for Na_2SO_4 and $CaCl_2$ in the cation and anion exchangers, respectively, as the "screening" of the fixed charges in these exchangers by the counterions (*i.e.*, Na^+ and Cl^- ions, respectively) should be almost the same as when NaCl was the incursive electrolyte. The screening of the structurally bound charged groups by the counterions is not complete, and the activity coefficient of the co-ion is reduced significantly from the

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(21) E. A. Guggenheim and J. C. Turgeon, *Trans. Faraday Soc.*, **51**, 747 (1955).

(22) E. A. Guggenheim and R. H. Stokes, *ibid.*, **54**, 1646 (1958).

value ($\bar{\gamma}_\pm'$, column 6, Table I) it would have if present alone at the same low concentration in the exchanger.

A qualitative discussion of the consequences of the fact that the electrical potential, $\bar{\psi}$, in the exchanger is not constant throughout, as was assumed implicitly in deriving eq 1, has been given by Tye.[23] In actuality, the electrical potential changes continuously from a large value in the neighborhood of the fixed charges to a minimum in the more remote regions in the interior of the molecular network of the exchanger. Consequently, on the average in a cation exchanger, for example, the cations are at a lower potential than the anions. Replacing $\bar{\psi}$ by the unequal potentials $\bar{\psi}_+$ and $\bar{\psi}_-$ in the derivation of the Donnan equation and comparing with the equation obtained assuming $\bar{\psi}$ to be constant gives the result

$$\bar{\gamma}_\pm = \bar{\gamma}_\pm' \exp[F(z_+\nu_+\bar{\psi}_+ + z_-\nu_-\bar{\psi}_-)/(\nu_+ + \nu_-)RT] \quad (4)$$

where $\bar{\gamma}_\pm'$ is an activity coefficient which is independent of the potentials caused by the fixed ions, F is the Faraday constant, ν is the moles of ion per mole of electrolyte, and z is the charge. The quantity $\bar{\gamma}_\pm'$ will resemble the activity coefficients of the solute in simple aqueous electrolyte solutions, and it may be referred to as the Debye–Hückel mean molal coefficient. Considering NaCl, eq 4 becomes

$$\bar{\gamma}_\pm = \bar{\gamma}_\pm' \exp[F(\bar{\psi}_+ - \bar{\psi}_-)/2RT] \quad (5)$$

The potential of the anions, $\bar{\psi}_-$, is larger than that of the cations, $\bar{\psi}_+$, and the exponential term will be less than unity so that $\bar{\gamma}_\pm$ will be less than $\bar{\gamma}_\pm'$ as observed. With highly cross-linked exchangers, the exponential term will be virtually constant for small external electrolyte concentrations, and $\bar{\gamma}_\pm'$ might be expected to increase as the internal electrolyte concentration decreases. Accordingly, $\bar{\gamma}_\pm$ should increase, and this appears to be the case as may be observed in Table I where the ratio $\bar{\gamma}_\pm/\bar{\gamma}_\pm'$ is nearly constant independent of concentration. The significantly lower values of $\bar{\gamma}_\pm$ for Na_2SO_4 appear to originate in the fact that $\bar{\psi}_-$ is larger and $\bar{\psi}_+$ remains unchanged.

The models assumed by Lazare, Sundheim, and Gregor,[24] by Shone,[25] and by Mackie and Meares,[26] who applied the theory of Katchalsky and Lifson, do not appear to apply to highly cross-linked exchangers as they predict either that $\bar{\gamma}_\pm$ becomes constant or decreases. Although the potential, $\bar{\psi}_-$, of co-ions (*i.e.*, Cl^- ions in a cation exchanger) in the vicinity of the like-charged structurally bound ions on the polymer network is large, because of efficient screening of the latter by the counterions, $\bar{\psi}_-$ is relatively constant throughout the remainder of the exchanger. With lightly cross-linked exchangers which become highly swollen in dilute electrolytes, the screening of the fixed charges will be less complete, and $\bar{\gamma}_\pm$ might be expected to decrease with diminishing external concentration. However, when $\bar{\psi}_+$ and $\bar{\psi}_-$ and hence $\bar{\psi}$ are constant within the ion exchanger, the Donnan theory will be valid.

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[23] F. L. Tye, *J. Chem. Soc.*, 4784 (1961).

[24] L. B. Lazare, B. R. Sundheim, and H. P. Gregor, *J. Phys. Chem.*, 60, 641 (1956).

[25] M. G. T. Shone, *Trans. Faraday Soc.*, **58**, 805 (1962).

[26] J. S. Mackie and P. Meares, *Proc. Roy. Soc.* (London), **A232**, 485 (1955).

Dispersion of the Kerr Constant of the Acridine Orange–Polyglutamic Acid Complex

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Contribution from the IBM Research Laboratory, San Jose, California.

Received September 2, 1966

Abstract: The Kerr effect (linear electric birefringence) is generally measured in transparent regions of the spectrum and used to obtain information about the anisotropy of the polarizability. In the vicinity of an electronic absorption, the Kerr constant exhibits anomalous dispersion, and the form of this dispersion is related to the direction of the transition moment for the particular electronic transition. The origin of these effects is reviewed. Experimental work is presented on the dispersion of the Kerr constant for the acridine orange–polyglutamic acid complex in DMF. From the shape of the dispersion curve, the polarization of the absorption band for the free dye can be assigned. A structure of the dye–polymer complex compatible with these and other published data is that of a left-handed helix bound to the polymer helix so that the long axis of the dye molecule is parallel to the long axis of the polymer helix.

The study of the Kerr effect (linear electric birefringence) in both large and small molecules has been generally restricted to regions of the spectrum where the system under study does not absorb. In such transparent regions, the extensive researches of O'Konski[1] and Tinoco[2] have shown how dipole moments and polarizabilities can be obtained for macromolecules under conditions of saturation of birefringence. Information about the size and shape of

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