tration anomaly is not dependent on any particular assumption as to the cause of the sedimentation constant–concentration dependence. Though there seems to be no adequate theoretical explanation for the marked dependence observed for asymmetric particles like TMV, the viscosity contribution of the virus particles themselves is an important factor.[22,37] The results of the present investigations showing much larger effects with asymmetric molecules as the fast component as compared to the results obtained by earlier workers with more globular proteins suggests that the increase in viscosity caused by the fast component is a major factor in causing the buildup. If, as a first approximation, we were to assume that $s_{S,\text{mixt}}$ is less than s_S because of the viscosity contribution of the fast component in the mixture, we can calculate $s_{S,\text{mixt}}$ by dividing s_S by the relative viscosity derived from the fast component. Column 7 in Table II shows the buildup of the slow component calculated from equation 8 where $s_{S,\text{mixt}}$ was in turn calculated from the measured viscosities of the fast component.[43] Comparison of columns 7 and 9 show that a reasonable prediction of the buildup can be made in this way.

It should be noted that the decrease in area of the slow boundary through the cell, beyond that attributable to the geometry of the cell and the effect of the centrifugal field, implies the existence of convection in the region between the slow and fast boundaries. Since the buildup of slow component decreases throughout the run we should expect a negative density gradient due to the changing concentration of slow component immediately behind the fast boundary. This negative density gradient apparently would be greater than the positive gradient resulting from compression of the fluid in the cell. Such a negative density gradient would be unstable under the high centrifugal field and we would expect convection to occur. Since the optical patterns show two separate boundaries separated by a base line region (corresponding to a plateau of constant concentration) it would appear that convection does occur to eliminate the negative density gradient. Other examples of convective systems are being investigated in the synthetic boundary cell to study the effect of convection on the shape and movement of boundaries in the ultracentrifuge.[44]

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[43] Theoretical considerations[31,32] indicate that s varies with c partly because of the backward flow of solvent caused by the sedimenting particles. We should, therefore, expect that the buildup of slow component should be due in part to backward flow. Preliminary measurements of backward flow caused by the sedimentation of TMV indicate that the viscosity effect is a more important factor in the mixtures reported on in this paper.

[44] H. K. Schachman and W. F. Harrington (unpublished).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Studies on Ion Exchange Resins. VIII. Activity Coefficients of Diffusible Ions in Various Cation-exchange Resins

BY HARRY P. GREGOR AND MELVIN H. GOTTLIEB

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Mean ionic activity coefficients of several electrolytes in divinylbenzene–polystyrenesulfonic acid resins of different degrees of cross-linking and in equilibrium with various concentrations of electrolytic solutions were determined. With concentrated external equilibrating solutions, activity coefficients in the resin phase approached those for the solution phase Activity coefficients for all electrolytes decrease sharply with increasing dilution.

The mean activity coefficient of a diffusible electrolyte in the resin phase is an important parameter in ion-exchange reactions.[1] A previous paper in this series[2] described phase equilibria for the system: sulfonated polystyrene–divinylbenzene cation-exchange resin–aqueous electrolytic solution containing a single uni-univalent electrolyte. The resin composition varied from 2 to 17% divinylbenzene (DVB) and non-exchange electrolyte was determined for various concentrations of ammonium chloride. The mean activity coefficient of ammonium chloride in the resin phase was calculated from Gibbs–Donnan considerations, neglecting the pressure–volume term. This paper describes phase equilibria of hydrochloric acid, lithium chloride, potassium chloride, potassium acetate, potassium sulfate and ammonium chloride solutions with resins having a DVB content ranging from 0.4 to 26%. Activity coefficients for these salts in the resin phase are calculated.

Experimental

A series of sulfonated polystyrene–divinylbenzene cation-exchange resins were used; the manner of their preparation and conditioning is described in a previous paper.[2] Unless specified, the resins are not identical with those previously described. Wet weights were determined by centrifugation, non-exchange electrolyte by elution.

All of the solutions used and calculations made are on a molal (m) basis. The temperature is 24–26°. Data are expressed in the following terms: We, specific wet weight of the centrifuged resin; N.E., specific quantity in millimoles of non-exchange or diffusible electrolyte in the resin phase; m_+ and m_-, molalities of cations and movable anions in the resin phase; $\gamma^i_\pm$, mean activity coefficient of the electrolyte in the resin phase, where

$$\gamma^i_\pm = \left[\frac{\gamma^{o\nu}_\pm \, \nu_+^{\nu_+} \, \nu_-^{\nu_-} \, m^\nu}{m_+^{\nu_+} \, m_-^{\nu_-}}\right]^{\frac{1}{\nu}}$$

the superscripts i and o refer to resin and solution phases, respectively; ν_+ and ν_- are the number of cations and anions, respectively, formed on dissociation of a molecule of the neutral salt ($\nu_+ + \nu_- = \nu$). All data thus refer to a standard resin sample, namely, one gram of dry hydrogen resin.

A tabulation of the experimental values of the external molality (m), We and N.E. for resins DVB 0.4, 2, 10 and

[1] H. P. Gregor, THIS JOURNAL, 73, 642 (1951).

[2] H. P. Gregor, F. Gutoff and J. I. Bregman, *J. Coll. Sci.*, 6, 245 (1951).

TABLE I

COMPOSITION OF VARIOUS RESIN PHASES

Resin DVB	m	We, g.	N.E., milli-moles	m^i_-	m^i_+	$\gamma^i_\pm$
			Potassium chloride			
2	2.0	2.750	2.04	1.45	5.16	0.422
	1.0	3.349	1.27	0.62	3.13	.437
	0.50	3.798	0.73	.287	2.32	.399
	.10	4.792	.097	.0270	1.47	.386
	.050	5.045	.0377	.00988	1.35	.355
	.01	5.879	.0051	.0011	1.11	.26
10	2.0	1.734	.422	.815	10.2	.400
	1.0	1.767	.163	.286	8.78	.382
	0.50	1.783	.075	.126	8.30	.318
	.10	1.801	.0098	.0158	7.90	.217
	.05	1.805	.0053	.0086	7.83	.157
	.01	1.809	.0043	.0069	7.85	.039
26	2.0	1.534	.350	1.04	14.4	.298
	1.0	1.528	.147	0.426	13.5	.253
	0.50	1.540	.055	.150	12.3	.239
	.10	1.525	.0172	.0484	12.8	.0976
	.05	1.519	.0078	.022	12.9	.076
	.01	1.534	.0039	.011	12.3	.028
Dowex-50	2.0	1.662	.327	.72	11.6	.399
	1.0	1.677	.107	.221	10.4	.400
	0.50	1.685	.049	.099	10.0	.327
	.10	1.697	.0069	.0135	9.63	.213
	.05	1.698	.0028	.0055	9.58	.177
			Potassium acetate			
2	2.0	2.142	0.89	1.04	7.09	0.677
	1.0	2.979	.93	0.55	3.61	.558
	0.50	3.689	.54	.221	2.35	.520
	.10	4.801	.087	.0241	1.47	.423
	.050	5.003	.0310	.00816	1.37	.402
	.010	5.926	.014	.0030	1.09	.16
10	2.0	1.711	.321	.65	10.46	.706
	1.0	1.754	.137	.248	9.01	.527
	0.50	1.791	.062	.103	8.20	.409
	.10	1.809	.0160	.0256	7.83	.178
	.050	1.810	.0089	.014	7.79	.128
	.010	1.817	.0080	.013	7.74	.029
26	2.0	1.525	.290	.89	14.7	.508
	1.0	1.514	.149	.453	14.2	.310
	0.50	1.521	.077	.225	13.3	.217
	.10	1.525	.0239	.068	12.8	.0854
	.050	1.517	.0167	.0484	13.2	.0532
	010	1.532	.0057	.016	12.7	.022
			Hydrochloric acid			
2	2.0	3.620	3.10	1.24	3.31	1.07
	1.0	4.042	1.64	0.55	2.28	0.736
	0.48	4.442	0.78	.23	1.75	.578
	.10	5.108	.095	.023	1.28	.473
	.01	6.074	.0072	.0014	1.02	.24
10	2.0	1.787	.333	.43	6.70	1.27
	1.0	1.830	.138	.168	6.06	0.815
	0.48	1.855	.051	.059	5.76	.627
	.10	1.865	.010	.0118	5.64	.315
	.01	1.881	.0022	.0025	5.51	.077
26	2.0	1.523	.308	.600	9.35	.914
	1.0	1.517	.164	.321	9.13	.481
	0.48	1.512	.074	.146	8.96	.320
	.10	1.503	.0162	.0322	8.99	.151
	.01	1.509	.0047	.0092	8.79	.032

26 equilibrated with the various electrolytic solutions is shown in Table I. Calculated values of m_+, m_- and $\gamma^i_\pm$ are given.

A sample calculated of m_+, m_- and $\gamma_\pm$ from the experimental data for resin Dowex 50 in equilibrium with 2 m potassium chloride (Table I) is given.

Experimental.—We = 1.662 g. per dry g. in H^+ state; N.E. = 0.327 millimole of KCl per dry g. in H^+ state; capacity = 4.92 meq. per dry g. in H^+ state; $\gamma^\circ_\pm = 0.575$.

Calculations.—Dry potassium weight of resin = dry hydrogen weight − weight of hydrogen ions + weight of equivalent amount of potassium ions, or $1.187 = 1.000 - 4.92(0.001) + 4.92(0.039)$.

Weight of non-exchange KCl = number of meq. of non-exchange KCl (N.E.) multiplied by milliequivalent weight of KCl, or $W_{N\cdot E\cdot} = 0.327 \times 0.074 = 0.024$ g.

Weight of water sorbed = centrifuged weight (We) − dry K^+ weight − weight of non-exchange electrolyte, or $W_{H_2O} = 1.662 - 1.187 - 0.024 = 0.451$.

Then

$$m_+ = (4.92 + 0.327)/0.451 = 11.6$$

Also

$$m_- = 0.327/0.451 = 0.72$$

Then

$$\gamma^i_\pm = \left(\frac{\gamma^2{}_0 m_0{}^2}{m_+ m_-}\right)^{1/2} = \left(\frac{(0.575)^2 4}{11.6 \times 0.72}\right)^{1/2} = 0.399$$

The values of γ° are taken from Harned and Owen.[9] The capacities of the various resins are: DVB 0.4, 6.86; DVB 2, 5.20; DVB 10, 4.86; and DVB 26, 4.51 milliequivalents per dry gram of hydrogen resin.

Discussion

In calculating activity coefficients in the resin phase from external activities and internal molalities, the pressure–volume term is neglected.[2] Pressure–volume effects are such as to make calculated values of $\gamma^i_\pm$ high. For resins which are highly cross-linked this correction may be as high as 15–20%[1,2]; as the degree of cross-linking decreases, the pressure–volume term will also decrease. For a particular resin system, pressure–volume effects will increase as the external solution becomes more dilute. However, this term is virtually constant at external concentrations less than 0.5 m for all but the loosely cross-linked resins, where the thermodynamic osmotic pressure is small in any event.[1] Thus the observed sharp decrease of $\gamma^i_\pm$ with dilution is not due to pressure–volume effects.

The validity of calculations of mean ionic activity coefficients in the resin phase depends upon the exact separation of the resin and solution phases. The centrifugation technique may leave a thin film of solution surrounding the particle. The electrolytic content of the film would then be determined as non-exchange electrolyte. However, several considerations indicate that the solution film error is small. An absolute method for determining the solution content of the film involves measuring the rate of diffusion of a neutral molecule from the resin phase, and extrapolating to zero time to calculate the initial amount present in the resin phase. This amount can be compared with centrifugation results, as was done by Gregor, Pope and Collins.[3] The centrifuged values were on the average 3% higher than the extrapolated ones. This means that the weight of the solution film is 3% of the total solution weight.

[3] H. P. Gregor, F. C. Collins and M. Pope, *J. Coll. Sci.*, **6**, 304 (1951).

In highly concentrated solutions (> 4 m) where it is found that mean activity coefficients are the same in the resin and solution phases, the Donnan effect is swamped; both phases are equimolal with respect to diffusible electrolyte, and the presence of a solution film introduces no error. In more dilute solutions (1–2 m), where $\gamma^i_\pm$ still equals $\gamma^\circ_\pm$, Donnan effects make the concentration of non-exchange electrolyte quite low, and here the presence of the solution film introduces an error. In dilute solutions (< 0.1 m), the non-exchange electrolyte content is very much higher than would be the case if $\gamma^i_\pm = \gamma^\circ_\pm$; therefore, the presence of a 3% external solution film introduces a very small error. For example, with resin DVB 10 and ammonium chloride solutions,[2] where the weight of solution contained in a standard resin sample is 0.8 g., the values of m and N.E., respectively, are 1.44, 0.247; 0.1, 0.009; 0.01, 0.004. If the film is 3% of the solution weight, the experimental values of N.E. are calculated to be higher by 16% in 1.44 m, 26% in 0.1 m, and 6% in 0.01 m solution. Thus $\gamma^i_\pm$ values may be low by 10–15% in the more concentrated solutions; the error is but about 2% in the dilute solutions.

There are several reasons for believing that the 3% error is an upper limit. First, when resins are placed in equilibrium with water vapor at relative humidities up to 98%, the extrapolated values of the wet weights agree with ones determined by centrifugation to within 2%.[4] If the phase separation is effected by the blotting technique, where at least 10% of the solution content is removed, the non-exchange electrolyte contents are found to agree within this 10% limit. Boyd[5] has also employed the blotting technique, and reports non-exchange electrolyte contents in good agreement with ours.

The presence of a solution film is also shown by the rate of elution of non-exchange electrolyte from the resin.[6] Here the amount eluted is a linear function of the square root of time; extrapolation to zero time shows that a small amount is eluted almost instantaneously, corresponding to a solution film of about 2%.

Pepper and co-workers[7] employed a similar centrifugation technique, except that the time of centrifugation was extended to at least 30 minutes. Lower wet weights were obtained, and as a result calculated activity coefficients are higher than ours. A trend toward lower activity coefficients with dilution is evident, although their data extended only down to 0.1 N solutions.

The outstanding feature of our data is the sharp decrease in the mean activity coefficient as the external solution drops below 0.5 m. Figure 1 shows that this effect is the result of experimentally observing considerably more non-exchange electrolyte in the resin phase than would be the case if activity coefficient effects were absent. Figure 1 also emphasizes the fact that the molality of the exchange cation is very much greater than that of the movable anion.

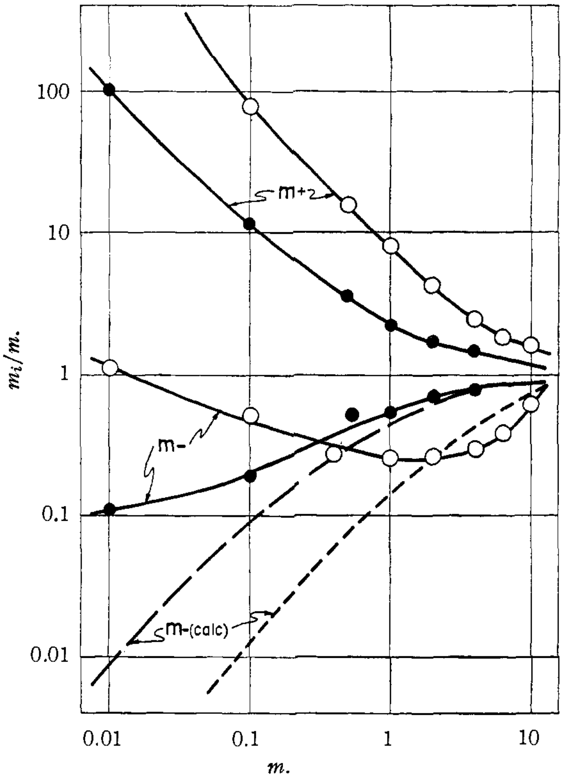

Fig. 1.—Ratio of ionic molality in the resin phase (m^i) to that in the solution phase (m) as a function of the solution molality for lithium chloride and resins DVB 26 (O) and DVB 2 (●). Calculated m^i values if $\gamma^i_\pm = \gamma^\circ_\pm$ are shown dotted.

It is possible that the observed excess of diffusible electrolyte is the result of adsorption, or ion-pair formation, or the inclusion of solution in cavities within the resin. Anionic species could be adsorbed either as the acid (hydrolytic adsorption) or as the salt.

If hydrolytic adsorption were taking place, a change in pH would be observed; such is not the case. Further, it is very unlikely that all of the different anions with their widely differing properties would show the same adsorptive effects. Also, the anion exchange resin systems studied[8] show this same effect. It is known that inorganic cations are not adsorbed to the same extent as are anions.

The possibility also exists that ion-pair formation between exchange cations and fixed anions is responsible for the observed drop in activity coefficients. For this to be the case, the degree of association would have to increase sharply as the concentration of non-exchange electrolyte decreased. This is unlikely from general considerations.

It has been suggested that surface fissures or microscopic internal cavities exist which contain the equilibrating solution. The solution volume contained in surface fissures would be included in the 3% solution film. The possibility that micro-

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(4) H. P. Gregor, K. M. Held and J. Bellin, *Anal. Chem.*, **23**, 620 (1951).

(5) G. E. Boyd, paper presented at Symposium on Complex Ions and Polyelectrolytes, Ithaca, New York, June, 1951.

(6) H. P. Gregor and M. Tetenbaum, in preparation.

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

(8) M. H. Gottlieb and H. P. Gregor, in preparation.

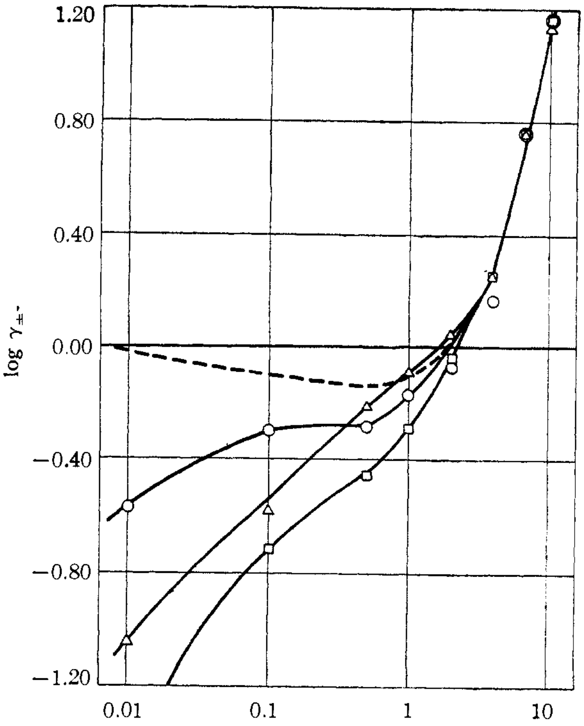

Fig. 2.—Mean activity coefficients as a function of external molality for solution (---) and resin phases; DVB 0.4, ◓; DVB 2, ○; DVB 10, △; DVB 26, □. Data are for lithium chloride.

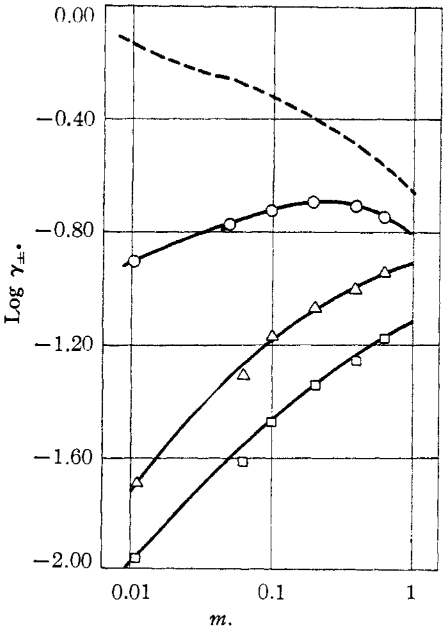

Fig. 3.—Potassium sulfate.

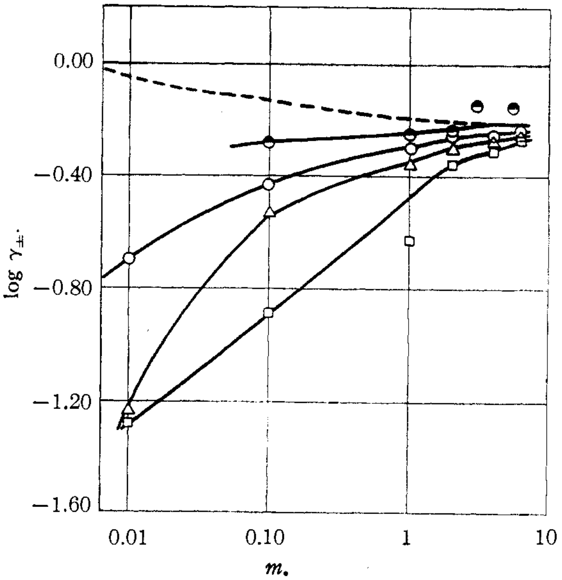

Fig. 4.—Ammonium chloride.

scopic bubbles exist is not considered likely from several points of view. First, resins prepared using the same mole per cent. of divinylbenzene, but under a wide variety of experimental conditions, and having been subjected to different wetting and drying cycles, all show nearly the same density and the same activity effects. Further, the aggregate volume of such cavities would have to be in the range 20–70% of the resin solution volume to account for the results observed, and would have to vary in an irregular manner as the concentration of the external solution increased.

From Table I and Figs. 2–4, it may be seen that for all of the electrolytes studied, $\gamma^{i}_{\pm}$ approaches or becomes equal to $\gamma^{\circ}_{\pm}$ as the concentration of the ambient solution increases above 2 *m*. At all concentrations, the ratio $\gamma^{i}_{\pm}/\gamma^{\circ}_{\pm}$ is about the same for all of the electrolytes studied with a given resin; Figs. 5 and 6 show this. One conclusion that can be drawn from all of these figures is that the interaction between the resin and the electrolyte is non-specific toward a given ion.

It should also be noted that the $\gamma^{i}_{\pm}$ values approach the $\gamma^{\circ}_{\pm}$ values when but a very small portion of the negative groups in the resin phase are movable. For example, with resin DVB 10 and lithium chloride, when *m* is 1, m_+ equals 5.8, and m_- equals 0.16; thus when the movable anionic concentration becomes only 3% of the total anionic concentration, the lithium chloride in the resin apparently becomes "the same" as in the external 1 *m* solution. At concentrations above about 0.5 *m*, it is suggested that the value $\gamma^{i}_{\pm}$ approaches the value of $\gamma^{\circ}_{\pm}$ because electrical effects due to the fixed ionic groups are reduced, and the activity coefficients of the hydrated electrolytes are determined primarily by free energies of hydration, which in turn are measured by the activity of the water in the solution. This point of view is expressed semi-quantitatively by the Bjerrum, Harned, Stokes–Robinson theory.[9] Since in these resin systems the activity of solvent is substantially the same in the resin and solution phases, except for the net pressure–volume correction for solvent and solute activities which is small, it appears reasonable that the ionic activity coefficients should be the same in both phases.

When the external solutions become increasingly dilute, it is postulated that electrical effects due to

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(9) H. S. Harned and W. B. Owen, "Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1950, p. 607.

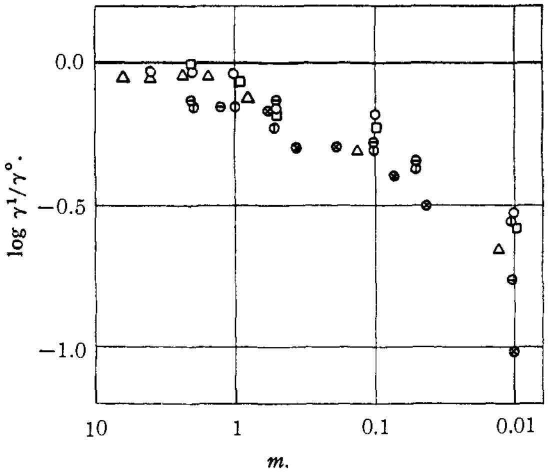

Fig. 5.—Reduced activity coefficient γ^1/γ° as a function of external molality with resin DVB 2 and hydrochloric acid (□), lithium chloride (○), potassium chloride (⦶), potassium acetate (⊖) and potassium sulfate (⊗) solutions.

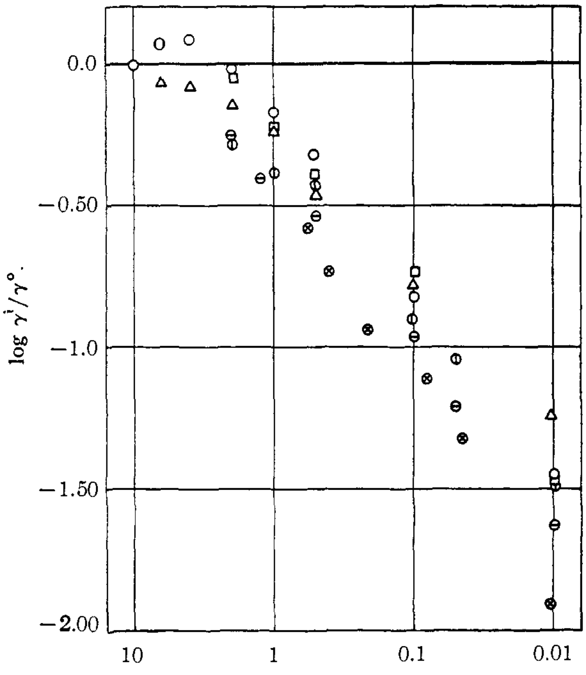

Fig. 6.—Reduced activity coefficient as a function of molality for resin DVB 26.

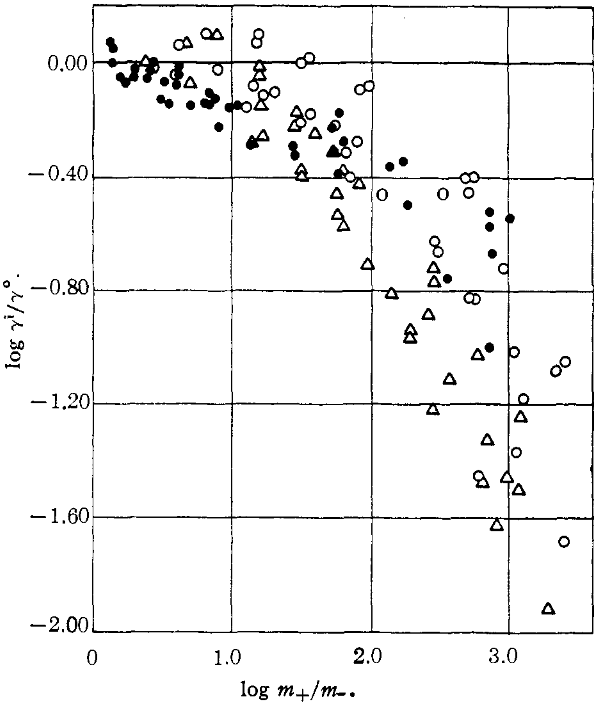

Fig. 7.—Reduced activity coefficient as a function of m_+/m_- for all electrolytes with resins DVB 2 (●), DVB 10 (○) and DVB 26 (△).

the strong potential fields of the fixed anions cause a drop in the activity coefficients of the movable cations; this phenomenon is analogous to Debye–Hückel effects. The influence of electrolytes on the free energy of a double layer has been treated by Verwey and Overbeek,[10] who show that the electric field near the charged wall decreases as the concentration of electrolyte in the bulk of the solution increases. Since the wall potential is proportional to the concentration of fixed anionic groups, and therefore to m_+, and since it varies inversely as m_-, the reduced activity coefficient γ^i/γ° would be expected to decrease with increasing values of the ratio m_+/m_-. This plot is shown in Fig. 7 for all electrolytes studied. Here it is seen that all of the data follow this relationship.

The authors wish to thank the office of Naval Research for the support given this study.

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[10] E. J. W. Verwey and J. Th. G. Overbeek, "Theory of Stability of Lyophobic Colloids," Elsevier, Amsterdam.