

slope to intercept may be somewhat higher than those calculated from molecular weights. It is possible that the differences observed in our data may indicate a slight polydispersity in the sample.

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WILMINGTON, DELAWARE

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

## Studies on Ion Exchange Resins. XI. Activity Coefficients of Diffusible Ions in a Strong Base Anion-exchange Resin

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Mean activity coefficients of the diffusible electrolyte in an anion-exchange resin were calculated from the non-exchange electrolyte and water content of the resin in equilibrium with various aqueous electrolytic solutions. The calculated activity coefficients were found to decrease sharply on dilution of the solution phase, being lowest with those electrolytes whose anions appeared to form ion-pairs with the fixed exchange cations of the resin.

A previous paper in this series<sup>2</sup> dealt with the phase equilibria of a strong acid cation exchange resin and electrolytic solutions containing the same cationic species. This paper similarly treats the equilibria between a strong base anion-exchange resin and solutions containing the exchange anion. Mean activity coefficients of potassium chloride, hydrochloric acid, potassium acetate, potassium trichloroacetate, potassium iodide, potassium thiocyanate and sodium hydroxide in the resin are calculated using the Gibbs-Donnan relationship based upon the equilibrium resin phase composition, as in the previous paper. In these calculations, the activities of the diffusible electrolyte in the resin and solution phases are set equal to one another, and the mean activity coefficient  $\gamma_{\pm}^r$  calculated from the expression

$$\gamma_{\pm}^r = (m^2 \gamma_{\pm}^s / m_+^r m_-^r)^{1/2}$$

where the molal concentrations of the diffusible cation and anion  $m_+$  and  $m_-$  are calculated from the resin-exchange capacity, the water content and the non-exchange electrolyte content. The superscript r designates the resin phase; the solution phase is not designated.

Kraus and Moore<sup>3</sup> have made a similar study with a strong base resin and hydrochloric acid solutions, using essentially similar techniques.

### Experimental

The anion-exchange resin was Dowex-2, a strong base resin prepared using 8% divinylbenzene as cross-linking agent. The exchange groups are of the benzyl-ethanol-dimethyl quaternary ammonium type; similar materials can be prepared by the chloromethylation of a styrene-divinylbenzene copolymer, followed by suitable treatment with the corresponding tertiary amine.

The equilibrations, elutions and analytical techniques were substantially the same as employed previously. Carbonate-free sodium hydroxide was used, and the eluate containing the non-exchange sodium hydroxide was analyzed for sodium flame photometrically. The detailed experi-

mental values obtained are not presented here, but are available in the thesis.<sup>1</sup>

### Discussion

The reduced mean activity coefficient  $\gamma_{\pm}^r / \gamma_{\pm}$ , hereinafter designated simply  $\gamma^r / \gamma$ , is plotted in Fig. 1 as a function of the molality of the equilibrating solution for potassium chloride, potassium acetate, potassium trichloroacetate, potassium thiocyanate and potassium iodide. In Fig. 2 the reduced activity coefficient curves are given for sodium hydroxide and hydrochloric acid.

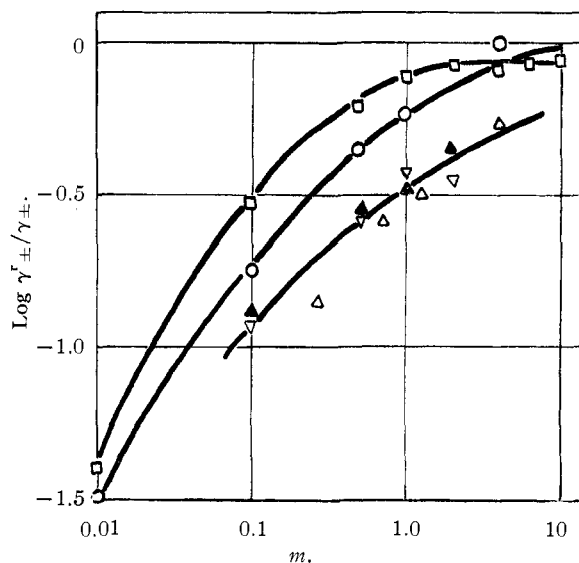


Fig. 1.—Reduced mean activity coefficient of diffusible electrolyte with DVB 8 anion-exchange resin as a function of the solution phase molality for potassium acetate ( $\square$ ), potassium chloride ( $\circ$ ), potassium thiocyanate ( $\blacktriangle$ ), potassium iodide ( $\nabla$ ) and potassium trichloroacetate ( $\triangle$ ).

In general, the data are similar to those obtained with cation exchange resin systems.<sup>2</sup> At high external concentrations  $\gamma_{\pm}^r$  approaches  $\gamma_{\pm}$ ; also,  $\gamma_{\pm}^r$  decreases sharply on dilution of the equilibrating solution. Certain significant differences are, however, observed.

(1) This paper is abstracted from the dissertation of M. H. Gottlieb, submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, Polytechnic Institute of Brooklyn, August, 1953.

(2) H. P. Gregor and M. H. Gottlieb, *THIS JOURNAL*, **75**, 3539 (1953).

(3) K. A. Kraus and G. E. Moore, *ibid.*, **75**, 1457 (1953).

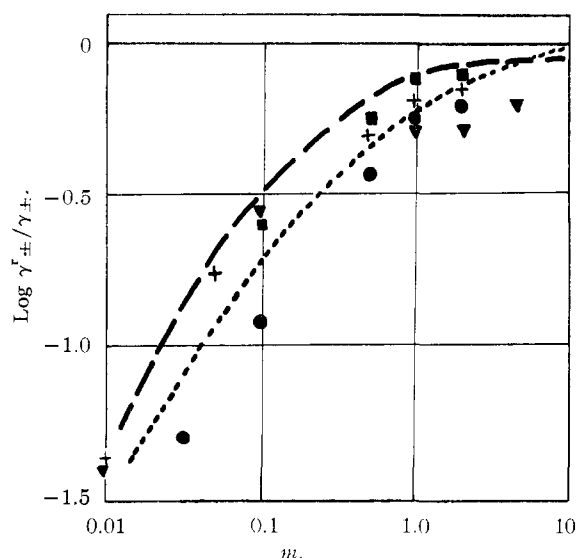


Fig. 2.—Reduced mean activity coefficient of diffusible electrolyte with DVB 8 anion-exchange resin as a function of solution phase molality for sodium hydroxide (■), hydrochloric acid (●), potassium acetate (—), and potassium chloride (---). Values for hydrochloric acid and a similar resin, taken from data of Kraus and Moore,<sup>3</sup> are shown (▼). Data for potassium chloride and a DVB 10 polystyrenesulfonic acid resin<sup>2</sup> are shown (+).

First, the acetate, chloride and hydroxide electrolytes have relatively higher values of  $\gamma^r/\gamma$ , and show the following order of reducing  $\gamma^r/\gamma$  values:  $\text{KAc} \cong \text{NaOH} > \text{KCl} > \text{HCl}$ . The iodides, thiocyanates and trichloroacetate salts show considerably lower values, all of about the same magnitude. Also included in Fig. 2 are values for potassium chloride in a polystyrenesulfonic acid resin system of comparable cross-linking<sup>2</sup>; these points are reasonably close to those for the same salt with the anion resin.

The deswelling of these resin systems with increasing concentration of the solution phase electrolyte is shown in Fig. 3, as the specific solvent weight  $W_w^r$  or water content as a function of solution phase molality. Here the values of  $W_w^r$  in dilute solutions decrease in the following order:  $\text{KAc} \cong \text{NaOH} > \text{KCl} > \text{HCl} > \text{KSCN} > \text{CCl}_3\text{COOK}$ . Also, the systems deswell as  $m$  increases with the acetate, chlorides and hydroxides, while with the iodate and thiocyanate the curve drops but slightly, and with the trichloroacetate it actually starts to rise. Again, the data obtained with potassium chloride are similar to those observed with the corresponding cation-exchange resin systems.<sup>4</sup>

The hydrochloric acid data are somewhat anomalous in relation to the potassium chloride data both as regards activity coefficients and water uptake. The activity coefficients are significantly lower than those of potassium chloride. This may be due to the effect of the species of non-exchange ion (hydrogen) on the mean activity coefficient *per se*. For example, data<sup>5</sup> on the activity coefficients of potassium nitrate in a polystyrenesulfonic acid cation-

exchange resin indicate that this electrolyte has lower activity coefficients than potassium chloride in the same resin. It is also possible that the lower hydrochloric acid activity coefficients are the result of the presence of a small amount, about 3%, of weakly basic groups. The acid adsorbed by these groups would be hydrolyzed off during the elution of non-exchange electrolyte and determined as such, making for a lower calculated value of  $\gamma_{\pm}^r$ .

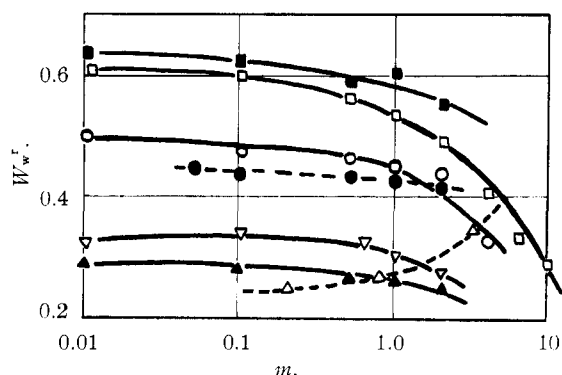


Fig. 3.—Weight of solvent (water) contained in one gram of chloride state DVB 8 anion-exchange resin, converted to various states, as a function of solution phase molality. Anionic state and solution phase electrolyte are: sodium hydroxide (■); potassium acetate (□); potassium chloride (○); hydrochloric acid (●); potassium iodide (▽); potassium thiocyanate (▲); potassium trichloroacetate (Δ).

A more serious difficulty lies in the water content data. Figure 3 indicates that substantially less water is taken up by the chloride form of the resin from dilute hydrochloric acid solutions than from potassium chloride solutions, although the external solution solvent activities are very nearly equal, and the non-exchange electrolyte content is very small. Further, the resin in this case does not show typical deswelling characteristics with increasing acid concentrations. Kraus and Moore<sup>3</sup> also observed no deswelling of a Dowex-1 resin under similar circumstances.

With the exception of hydrochloric acid, the differences between the various ions appear to be explained by ion-pair formation between the fixed quaternary group and the exchange anion. Gregor, Belle and Marcus<sup>6</sup> have correlated the swelled volumes and solvent contents of a similar resin with ion-pair formation. A subsequent paper<sup>7</sup> calculates ion-pair formation constants, which can be evaluated from selectivity coefficient data.<sup>8</sup> Selectivity coefficients for a series of anions, measured against the acetate ion when the latter is present as a micro-component, are as follows<sup>7</sup>: hydroxide, 1.3; chloride, 6.8; iodide, 85; trichloroacetate, 130; thiocyanate, 136. The order of ion-pair formation constants is the same as the order of selectivity coefficients given above.

When an ion-pair is thus formed, the activity of the movable exchange anions is greatly decreased, with a corresponding drop in the mean activity co-

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efficient. While there is simultaneously a decrease in the effective concentrations of fixed charges, which in itself would make for higher  $\gamma^r/\gamma$  values, the lowered activity of the *average* exchange anion more than compensates for this effect. Therefore, it is to be expected that an increasing degree of ion-pair formation will make for a lowered value of  $\gamma^r/\gamma$  as well as a small value of  $W_w^r$ .

The observed decrease in the mean activity coefficient of the diffusible or non-exchange electrolyte in ion-exchange resin systems with increasing dilution of the solution phase appears to be contrary to the normal behavior of simple electrolytes. Part of this difficulty lies in the manner in which the resin data are presented. If the mean activity coefficient of the diffusible electrolyte were plotted against the molality of the polyelectrolyte or of the resinate, curves of more normal appearance result. In Fig. 4 the reduced activity coefficient of ammonium chloride<sup>2</sup> is plotted against the molality of the corresponding ammonium resinate for three different solution phase concentrations. Here it is seen that more "normal" behavior is encountered. While it is impossible to vary the resinate concentration by dilution, the use of the same polymer having varying degrees of cross-linking accomplishes substantially the same effect. The reduced activity coefficients are depressed when  $m^r_{\text{NH}_4\text{Cl}} \ll m^r_{\text{NH}_4\text{R}}$ , and approaches normal behavior as  $m^r_{\text{NH}_4\text{Cl}} \rightarrow m^r_{\text{NH}_4\text{R}}$ , where  $\text{NH}_4\text{R}$  refers to the resinate species. However, in all instances  $\gamma^r/\gamma$  approaches unity as  $m^r_{\text{NH}_4\text{R}}$  approaches zero.

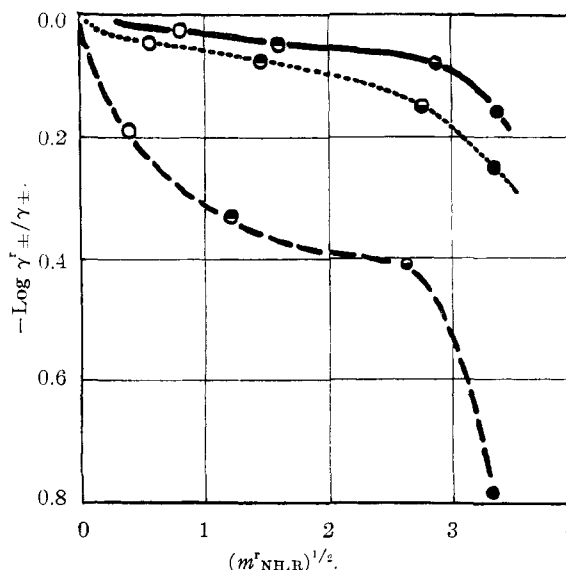


Fig. 4.—Reduced mean activity coefficients of ammonium chloride in polystyrenesulfonic acid cation exchange resins DVB 0.4 (○), DVB 2 (●), DVB 10 (◐), and DVB 26 (◑) as a function of the square root of the fixed group concentration at various solution phase concentrations:  $m = 0.1$  (---);  $m = 1$  (- - -);  $m = 2$  (—).

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[CONTRIBUTION NO. 1194 FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

## Diffusion Coefficients for the System Biphenyl in Benzene

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The diffusion coefficients, densities, viscosities and molar refractive increments for solutions of biphenyl in benzene have been determined at 25 and 35° in the concentration region 0–3 molar. Attention has been called to the significance of the overlapping of the plots of  $D\eta/T$  against  $\bar{v}$  at the two temperatures. A simple and useful deviation function has been proposed for the description of this type system. The activation energies for the viscous and diffusion processes have been compared. The suggestion has been made that the data, in particular at 25°, constitute reliable standards for calibration purposes.

Recent advances in experimental techniques permit the precise determination of diffusion coefficients in the liquid state.<sup>1–3</sup> In this communication one of the methods, Gouy diffusometry, has been applied to a non-aqueous system. Benzene solutions have been the subject of extensive thermodynamic studies. It was felt that biphenyl in benzene would form a particularly simple binary system for investigation being well suited to a ready correlation of its transport properties. The use of this particular system offers other advantages. Acceptable experimental materials are readily available using simple purification procedures. More important is the considerable accumulation of self-consistent vapor pressure data which are available

for the system over a wide range of concentrations and temperatures.<sup>4–6</sup> These vapor pressure studies were stimulated largely by the theoretical considerations of Orr and Guggenheim,<sup>7</sup> and the agreement between the predicted values for the activity coefficients and the experimental values is quite good.

In anticipation of further work on benzene solutions an effort was made to develop a satisfactory technique for work at 35°. Much of the useful vapor pressure work has been obtained at that temperature and even when possible it might not be desirable to compute activity data at temperatures widely dif-

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