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Anion-exchange Studies. XXIII.[1,2] Activity Coefficients of Some Electrolytes in the Resin Phase

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Ratios Γ of activity coefficients of a number of electrolytes in the resin ($\gamma_{\pm(r)}$) to those in the aqueous phase ($\gamma_{\pm}$) are evaluated from water and electrolyte uptake data. At high concentrations $\Gamma = \gamma_{\pm(r)}/\gamma_{\pm}$ is remarkably constant but it varies substantially at low concentrations. Activity coefficients of HCl in the resin determined as a function of HCl activity and of cross-linking can be correlated by a concentrated electrolyte model of the exchanger with the assumption that Harned's rule of the linear variation of $\log \gamma_{\pm}$ with composition holds at constant total molality. Similar considerations, with Harned's rule generalized to higher multi-component systems, permits at least semi-quantitative evaluation of $\log \gamma_{\pm \mathrm{HCl(r)}}$ for HCl–LiCl mixtures where Γ_{HCl} is comparatively small. Because of the relatively low activity coefficients of HCl in the resin phase, separation of HCl from concentrated halide solutions is possible. The separations are illustrated with several HCl–LiCl mixtures. Adsorption of sulfuric acid by the sulfate form of the exchanger is discussed and evaluation of the concentration quotient of the acid constant is attempted for the bisulfate ion in the resin phase.

In earlier publications we have endeavored to demonstrate that anion-exchange resins are extremely useful for separation of metals. However, as pointed out repeatedly, ion-exchange adsorption data obtained as a function of solution composition not only permit selection of optimum adsorption and elution conditions for separations, but also permit elucidation of equilibria in the aqueous and resin phases.

Such analysis of ion-exchange data requires assumptions or data regarding activity coefficients of distributable components (or activity coefficient ratios for ions) for both the resin and aqueous phases. For dilute electrolyte solutions reasonable estimates may be made of the activity coefficients $\gamma_{\pm}$ in the aqueous phase and it is customary, though not well established, to assume that the activity coefficients $\gamma_{\pm(r)}$ in the resin are constant. Actually rather large changes of $\gamma_{\pm(r)}$ have been reported[3,4] for dilute electrolyte solutions, though presumably activity coefficient ratios do not vary much in the resin phase as long as invasion of the resin by the supporting electrolyte is small.[5]

For concentrated electrolyte solutions, where most anion-exchange studies of metal complexes have been carried out, reliable assumptions regarding activity coefficients in the aqueous phase are difficult to obtain and further, it is not safe to assume that for the resin activity coefficients of distributable components and activity coefficient ratios of ions are independent of electrolyte concentration. Thus before anion-exchange measurements in concentrated electrolyte solutions can be used with confidence for elucidation of properties of the aqueous (or solution) phase, considerably more information regarding the resin phase must be available, particularly information on composition of the resin (electrolyte invasion) and on activity coefficients of the pertinent components.

Activity coefficients in the resin phase may be determined[3] from data on electrolyte invasion with the relationship

$$a_J = a_{J(r)} \quad (1)$$

where a is the activity of the distributable component J. Subscript (r) denotes the resin phase and no subscript the aqueous phase. Equation 1 implies that the same standard states are selected for J in the resin and aqueous phases; otherwise a proportionality constant K would appear in equation 1. With our definition of standard states the difference in standard free energies is zero and hence $K = 1$.

If J is an electrolyte with formula $M_{\nu^+}X_{\nu^-}$, where ν_+ and ν_- are the number of positive ions (M) and negative ions (X), equation 1 may be written in the form

$$a_J = m_M{}^{\nu^+} m_X{}^{\nu^-} \gamma_{\pm}{}^{\nu} = m_{M(r)}{}^{\nu^+} m_{X(r)}{}^{\nu^-} \gamma^{\nu}{}_{\pm(r)} \quad (2)$$

where m is the stoichiometric concentration of the ions indicated as subscripts, $\gamma_{\pm}$ the mean activity coefficients of the components and $\nu = \nu_+ + \nu_-$. Thus, determination of the stoichiometric concentrations of the ions in the resin phase as a function of their concentration in the aqueous phase permits computation of the activity coefficient quotient $\Gamma_J = \gamma_{\pm(r)}/\gamma_{\pm}$. If these are combined with known activity coefficients for the aqueous phase or, equivalently, if the measurements are carried out as a function of the activity of the electrolyte, computation of $\gamma_{\pm(r)}$ becomes possible. To simplify comparison of the activity coefficients in the two phases, it is convenient to express concentrations in similar units. We have chosen molalities for the aqueous phase and moles per kg. of imbibed water for the resin.

This method was used by us to determine activity coefficients $\gamma_{\pm(r)}$ for HCl,[3] and by Gottlieb and Gregor[4] for determination of $\gamma_{\pm(r)}$ of various electrolytes in anion exchangers. A number of authors determined in this manner activity coefficients of electrolytes in cation exchangers.[6] While the general conclusion seems to be that Γ_J is close to unity at high electrolyte concentrations and considerably below unity at low concentrations, detailed confirmation for other media of interest in

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[1] This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] Previous papers: XXI. K. A. Kraus, G. E. Moore and F. Nelson, THIS JOURNAL, **78**, 2692 (1956); XXII. K. A. Kraus and F. Nelson, Metal Separations by Anion-exchange in Symposium on Ion Exchange and Chromatography in Analytical Chemistry (June 1956), Am. Soc. for Testing Materials, Special Technical Publication No. 195.

[3] K. A. Kraus and G. E. Moore, THIS JOURNAL, **75**, 1457 (1953).

[4] M. H. Gottlieb and H. B. Gregor, *ibid.*, **76**, 4639 (1954).

[5] K. A. Kraus and F. Nelson, Proceedings of the International Conference on the Peaceful Uses of Atomic Energy (Geneva, 1955), **7**, 113, 131, United Nations 1956.

[6] See *e.g.*, D. Reichenberg in "Ion Exchangers in Organic and Biochemistry," C. Calmon and T. R. E. Kressman, editors, Interscience Publishers, Inc., New York, N. Y., 1957, p. 73.

studies of metal complexes was desirable. Further, since a remarkable difference was found in the adsorbabilities of certain metal chloride complexes from HCl and LiCl solutions,[5,7] it was of special interest to investigate whether this difference is reflected in the activity coefficients of these electrolytes in the resin phase.

Experimental

1. **Method.**—The composition of the exchangers in equilibrium with various electrolyte solutions was determined by modification of the method of Pepper, Reichenberg and Hale.[8] Resin samples (0.2 to 1 g.) in small columns were treated with solutions of known composition. After equilibration the columns were centrifuged to constant weight in a "clinical" centrifuge at approximately 2000 r.p.m. From the weighings and the weight of "dry" resin the sum of the weights of imbibed water and electrolyte can be determined if a correction is made for the small amount of liquid which adheres to the beads after centrifugation. This correction was assumed to equal 0.033 liter per liter of bed, the value found earlier for the volume of retained liquid in columns of glass beads of similar mesh size[3] and confirmed in the present study.

The amount of electrolyte imbibed by the exchanger was determined by standard analytical or radiometric techniques. In the former, the exchanger, after centrifuging, is washed with sufficient water to remove the imbibed electrolyte which may then be determined. For HCl, H_2SO_4 and LiCl we have used acid–base and argentometric titrations. For $(NH_4)_2SO_4$ the NH_4^+ ion concentration was determined by first passing the solutions through cation exchangers in the hydrogen form and then titrating the amount of hydrogen ions released. The washed resin beds were frequently centrifuged to check reproducibility of the "water-washed" weights. In general, successive weighings agreed to better than ±1%. Through combination of the titrations and weighings a complete stoichiometric description of the resin is possible in terms of moles of electrolyte and kilograms of water per kg. of dry resin.

In the radiometric method radioactive tracers are added to the electrolyte solutions and the counting rate per mole of electrolyte established. After equilibration, centrifugation and weighing the resin beds were counted in a well-type scintillation counter to determine the amount of retained electrolyte. This technique greatly simplifies the analytical problem and is adaptable to routine determination of activity coefficients in the resin phase. It is particularly useful for dilute electrolyte solutions where the extent of electrolyte adsorption is small and difficult to establish accurately by more standard analytical techniques.

2. **Materials.**—Most experiments were carried out with portions of the same batch of quaternary amine polystyrene divinylbenzene exchanger (Dowex-1, *ca.* 10% D.V.B. 170–230 mesh) which has been used in most of our other studies. The capacity was 3.52 moles of sites per kg. of dry chloride form resin which is slightly less than the value found earlier.[3] While the resins were used in air-dry form, all weighings, as well as capacities, refer to resin dried to constant weight in a vacuum desiccator at 60° over the dehydrating agent "Anhydrone."

For a few experiments resins of the same type but different cross-linking (1 to 16% D. V. B.) were used. Their capacities were 4.13, 4.22, 4.01, 3.26 and 2.65 moles of sites per kg. dry chloride form resin for the 1, 2, 4, 8 and 16% D.V.B. resins, respectively. Some experiments were carried out with a new "high porosity" Dow resin (type 21K) which seems to have properties similar to a low cross-linked exchanger and, according to the manufacturer, has a network similar to Dowex-1 and the same functional group (trimethylammonium ion). Its capacity was 4.40 moles per kg. dry resin (chloride form).

C.P. reagents were used throughout. Concentrated HCl and LiCl stock solutions were passed through anion-exchange beds to purify them from "adsorbable" impurities. The radioactive tracers (Na^{24}, $T_{1/2}$ = 15 hr.; Ba^{133}, $T_{1/2}$ = 8 yr.; Co^{60}, $T_{1/2}$ = 5.2 yr.) were used as obtained from the Radioisotopes Division of ORNL since according to their analyses they were of satisfactory purity. All measurements were carried out in an air-conditioned room at 25 ± 1°.

Results and Discussion

1. **Activity Coefficients in the Resin Phase.**—The main purpose of this study was determination of activity coefficients in the resin phase for electrolytes which are frequently supporting media in anion-exchange studies of metal complexes and the present paper summarizes our results for LiCl, HCl, $(NH_4)_2SO_4$, H_2SO_4 and HCl–LiCl mixtures. The HCl data are a recheck at high concentrations of those reported[3] since the present (weight) method is more accurate than the volume method used previously. We shall also report our studies with NaCl, $BaCl_2$ and $CoCl_2$ which were carried out by the tracer method.

The results for the various electrolytes, all obtained with the 10% D.V.B. resin, are summarized in Table I, which lists the analytical data (molality of electrolyte J in the aqueous phase (m_J) and in the resin phase ($m_{J(r)}$), anion concentration $m_{X(r)}$ in the resin, water content), the activity coefficient ratio $\Gamma_J = \gamma_{\pm(r)}/\gamma_{\pm}$ and the activity coefficients $\gamma_{\pm(r)}$ for the resin phase. The latter were computed from Γ_J with the values of $\gamma_{\pm}$ for the aqueous phase summarized by Harned and Owen,[9] and Robinson and Stokes.[10]

It is apparent from examination of Table I that Γ_J is surprisingly constant at high electrolyte concentrations and is not far from unity. Indeed, Γ_{LiCl} varies only from *ca.* 0.7 to 0.8 as m_{LiCl} changes from 2 to 20 and $\gamma_{\pm(r)}$ from 0.7 to 50. The ratio Γ_{NaCl} varies from 1 to 1.1 for $0.9 \leqslant m_{NaCl} \leqslant 5.9$ but drops off rapidly at lower concentrations. The ratio Γ_{HCl} is considerably lower and lies between 0.5 and 0.6 for $m_{HCl} > 2$.

The values of $\Gamma_{(NH_4)_2SO_4}$ are also remarkably constant in the molality range 0.8 to 5.8 but are substantially higher than unity (*ca.* 2). While $\Gamma_{H_2SO_4}$ is reasonably constant (*ca.* 0.4) at high concentrations it decreases rapidly for $m_{H_2SO_4} < 3$, presumably because most of the adsorbed H_2SO_4 reacts with the $SO_4^=$ ions of the exchanger to form HSO_4^- ions[11] (see also section 5).

The values of Γ_{CoCl_2} and Γ_{BaCl_2} are almost the same at low molalities. Near $m_J = 2$, Γ_{BaCl_2} is considerably larger than Γ_{CoCl_2} which appears to go through a shallow maximum near $m = 1$. The decrease in Γ_{CoCl_2} is paralleled by intense blue coloration of the exchanger. In this region adsorption of Co(II) presumably as negatively charged complexes becomes important. Such adsorption has been demonstrated earlier for Co(II) in HCl solutions.[12]

In summary, present results are consistent with those reported earlier for other electrolytes.[3,4,6] At low imbibed electrolyte concentrations activity coefficients in the resin phase tend to be consider-

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[7] K. A. Kraus, F. Nelson, F. B. Clough and R. C. Carlston, THIS JOURNAL, **77**, 1391 (1955).

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

[9] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 2nd edition, 1950.

[10] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths Scientific Publications, London, 1955.

[11] (a) K. A. Kraus, F. Nelson and J. F. Baxter, THIS JOURNAL, **75**, 2768 (1953); (b) R. E. Anderson, W. C. Bauman and D. F. Harrington, *Ind. Eng. Chem.*, **47**, 1620 (1955).

[12] K. A. Kraus and G. E. Moore, THIS JOURNAL, **75**, 1460 (1953).

ably lower than in the aqueous phase for reasons which are still obscure. At high concentrations, and over a wide concentration range, activity coefficients in the resin of "strong" electrolytes do not differ markedly from those in the aqueous phase which further supports the now widely accepted hypothesis that these organic ion exchangers may be likened to concentrated electrolytes and that it is convenient to consider these imbibed electrolytes "completely" dissociated in the resin.[13] In general, interaction of the imbibed electrolyte with the "resin-electrolyte" is relatively small though, as in the adsorption of acids, there are notable exceptions.

TABLE I

ACTIVITY COEFFICIENTS OF SOME ELECTROLYTES IN THE RESIN PHASE (DOWEX-1 × 10)

m	$m_{J(r)}$	$m_{X(r)}$	kg_{H_2O}/kg_{res}	$r_J = \gamma_{\pm(r)}/\gamma_{\pm}$	$\gamma_{\pm(r)}$
A. Lithium chloride					
0	0	6.40	0.550	..	..
2.07	1.09	7.59	.542	0.72	0.67
4.10	3.03	9.80	.520	.75	1.16
6.03	5.15	12.3	.492	.76	2.1
8.03	7.46	15.0	.467	.76	3.9
9.82	8.63	16.6	.442	.82	7.3
12.8	11.9	20.4	.414	.82	16.2
17.4	17.1	26.5	.376	.82	38
18.5	18.2	27.6	.374	.82	44
19.8	20.0	29.7	.363	.81	50
B. Hydrochloric acid					
2.13	1.94	8.64	0.525	0.52	0.51
4.45	5.18	12.2	.502	.56	1.12
6.90	8.50	15.8	.483	.60	2.5
9.68	12.3	20.0	.457	.62	5.9
12.5	16.8	25.2	.419	.61	12.1
14.6	20.0	28.6	.410	.61	19
16.0	23.2	32.5	.379	.58	24
C. Sodium chloride					
0.0021	0.0003	6.40	0.550	0.048	0.046
.010	.0015	6.40	.550	.104	.094
.050	.0035	6.40	.550	.357	.29
.100	.0061	6.43	.548	.507	.39
.25	.0187	6.46	.546	.72	.52
.91	.114	6.89	.519	1.03	.68
2.24	.507	7.63	.494	1.18	.73
5.90	2.62	10.72	.434	1.11	1.08
D. Ammonium sulfate					
0	0	2.62	0.645	..	..
0.82	.12	2.86	.614	2.37	0.51
1.07	.17	2.92	.613	2.44	.46
2.30	.59	3.47	.585	2.16	.31
2.98	.84	3.81	.567	2.14	.28
4.70	1.14	4.37	.522	2.63	.29
5.80	1.65	5.00	.503	2.43	.27
E. Sulfuric acid					
0.0015	0.080	2.71	0.642	0.0058	0.0046
.0025	.142	2.79	.636	.0066	.0048
.0050	.259	2.96	.624	.0086	.0055
.0110	.585	3.41	.598	.0105	.0055
.0150	.739	3.62	.585	.0120	.0059
.0235	1.00	4.01	.560	.0148	.0064
.0285	1.16	4.28	.540	.0159	.0065
.099	2.17	5.63	.487	.0332	.0088
.242	2.88	6.48	.468	.0641	.013
.515	3.54	7.34	.443	.113	.017
1.04	4.23	8.22	.422	.196	.025
2.24	5.84	10.2	.391	.320	.041
3.47	7.86	12.5	.364	.378	.058
4.94	10.4	15.4	.338	.416	.087
7.46	14.9	20.4	.308	.451	.162
F. Cobalt chloride					
0.002	0.0012	6.40	0.550	0.0087	0.007
.02	.0010	6.45	.546	.092	.06
.05	.0017	6.45	.546	.192	.11
.20	.0108	6.55	.539	.41	.20
.61	.121	6.89	.529	.54	.25
1.03	.413	7.61	.520	.57	.30
2.09	2.20	12.1	.460	.49	0.44
4.09	9.72	32.6	.267	.45	1.01
G. Barium chloride					
0.02	0.0012	6.40	0.550	0.09	0.06
0.20	.0098	6.45	.548	.43	.19
1.775	.630	8.29	.501	.80	.36

The difference between $\gamma_{\pm HCl(r)}$ and $\gamma_{\pm LiCl(r)}$ is small if compared with the marked differences in the adsorbabilities of complex ions in these media.[5,7] However, considerable interaction of the acid with the resin is implied, which becomes apparent if the number of moles of electrolyte taken up per kg. of resin are compared. The excess uptake of HCl compared with LiCl is much too large to result from acid–base reactions with lower amines which may be present as impurities in the exchanger, although this mechanism may be responsible for the extremely low values of $\gamma_{\pm HCl(r)}$ which occur in very dilute solutions.[3] The difference in HCl and LiCl uptake may result from other acid–base reactions with the resin, *e.g.*, with its aromatic groups or, it may result from a more general effect of the resin on the activity coefficients of electrolytes dissolved in it, *i.e.*, from differences in the "salting effects" of the resin on these electrolytes.

2. **Water Content.**—The water content of the resin decreases with increasing electrolyte invasion and the extent is markedly different for each electrolyte. Figure 1 gives a summary of the data for the 10% D.V.B. resin in the form of plots of moles of water in the resin *vs.* moles of imbibed electrolyte, both computed per mole of exchange sites. The slopes of these functions give the number of moles of water displaced from the exchanger per mole of imbibed electrolyte. These are *ca.* 1.0, 1.5 and 5.0 for the 1:1 electrolytes HCl, LiCl and NaCl, respectively. For $(NH_4)_2SO_4$, the value is 15, *i.e.*, much larger than for the 1:1 electrolytes. For sulfuric acid the number of moles of water displaced per mole of electrolyte adsorbed is initially 9.2 and decreases to *ca.* 3.2 at large values of imbibed H_2SO_4. The larger figure presumably applies when acid uptake is paralleled by the neutralization reaction $H_2SO_4 + SO_4{}^{=}{}_{(r)} \rightarrow 2HSO_4{}^{-}{}_{(r)}$. The water content curves for $CoCl_2$ also show a change in slope. At low $CoCl_2$ uptake, approximately 3.6 moles of H_2O are displaced per mole of imbibed $CoCl_2$, which is only slightly less than for $BaCl_2$. At high $CoCl_2$ concentrations the amount of wa-

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(13) K. A. Kraus and F. Nelson, THIS JOURNAL, **76**, 984 (1954).

ter displaced becomes considerably larger. The change in slope presumably reflects the change in type of ion adsorbed which, at high $CoCl_2$ concentrations, presumably is a negatively charged complex.

To evaluate the importance of shrinkage, or expansion, in various electrolytes, densities, ρ, of the swollen resin were determined in water and, in concentrated HCl and LiCl solutions. In water, ρ was obtained by direct pycnometry. For HCl and LiCl solutions an attempt was made to find that electrolyte concentration where the resin just began to float. Though the resin was too inhomogeneous to give a clear-cut "flotation point," because over a moderate range of electrolyte concentrations part of the resin tended to float and part to settle, the following densities are considered good average values: H_2O, $\rho = 1.097$; $m_{HCl} = 12.7$, $\rho = 1.158$; $m_{LiCl} = 8.23$, $\rho = 1.151$. From these densities and the known weights of imbibed water and electrolyte the volumes v of swollen resin per gram of dry resin chloride were found to be: $v_{H_2O} = 1.41$; $v_{HCl} = 1.44$; $v_{LiCl} = 1.39$. This (10% D.V.B.) resin thus does not shrink appreciably and indeed might as a first approximation be considered a cage with constant volume. On this basis the amount of water displaced per mole of imbibed electrolyte is expected to be related to the apparent molal volumes of the electrolytes. The pertinent volumes should be those which apply to the concentrated electrolyte mixture (resin chloride–imbibed salts) which seems to be the most successful model of the resin. Although these volumes are not known, it is of interest that the apparent molal volumes of the electrolytes in binary mixtures (see ref. 9, page 253) seem to increase in the same order as the values of water displaced from the resin by these electrolytes.

3. Activity Coefficients of HCl as a Function of Cross-linking.—Activity coefficients $\gamma_{\pm HCl(r)}$ were determined (Table II) for Dowex-1 resins with different D.V.B. content at constant HCl activity ($m_{HCl} = 12.7$). As cross-linking increases from 1 to 16% D.V.B., Γ_{HCl} and hence $\gamma_{\pm HCl(r)}$ decreases by almost a factor of two. Further, Γ_{HCl} is almost unity for the 1% D.V.B. resin.

Activity coefficients $\gamma_{\pm HCl(r)}$ were also determined for the apparently low cross-linked ("high porosity") quaternary amine resin (Dowex-21K) as a function of HCl activity ($0.02 \leqslant m_{HCl} \leqslant 16$, Table III). Values of Γ_{HCl} tend to be larger than those for the 10% D.V.B. resin (Table I) but otherwise are very similar.

Comparison of the data in Tables I, II and III shows that $\gamma_{\pm HCl(r)}$, though generally less than $\gamma_{\pm HCl}$, does not differ from it widely at any given activity of HCl. Plots of log $\gamma_{\pm HCl(r)}$ *vs.* $m_{HCl(r)}$ also are very similar to those of log $\gamma_{\pm HCl}$ *vs.* m_{HCl}, as was demonstrated earlier.[3] The values of $\gamma_{\pm HCl(r)}$ plotted in this manner lie in a narrow region below those of $\gamma_{\pm HCl}$.

TABLE II

ADSORPTION OF HCl AS A FUNCTION OF CROSS-LINKING (Dowex-1, $m_{HCl} = 12.7$)

% D.V.B	$m_{HCl(r}$	$m_{Cl(r)}$	kg_{H_2O}/kg_{res}	$\Gamma = \gamma_{\pm(r)}/\gamma_{\pm}$	$\gamma_{\pm}(r)$
1	13.2	14.8	2.58	0.91	19.0
2	13.8	16.3	1.69	.85	17.8
4	14.6	18.8	0.95	.77	16.1
8	15.6	22.2	.498	.68	14.2
10	17.1	25.5	.420	.61	12.7
16	18.5	31.3	.207	.53	11.1

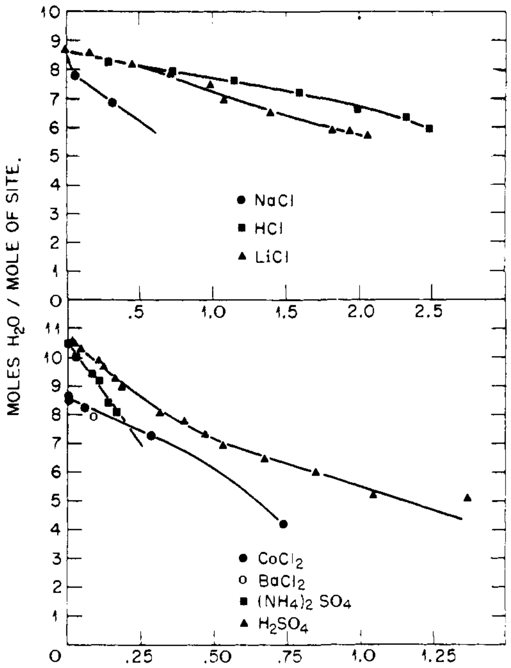

Fig. 1.—Water content of an anion exchanger in various media.

TABLE III

ADSORPTION OF HCl BY A LOW CROSS-LINKED ANION EXCHANGER (Dowex-21K)

m_{HCl}	$m_{HCl(r)}$	$m_{Cl(r)}$	kg_{H_2O}/kg_{res}	$\Gamma_{HCl} = \gamma_{\pm(r)}/\gamma_{\pm}$	$\gamma_{\pm(r)}$
0.02	0.0036	3.11	1.423	0.19	0.17
.10	.0135	3.16	1.403	.48	.38
.501	.237	3.72	1.287	.53	.40
1.03	0.737	4.37	1.217	.58	.47
2.10	2.08	5.81	1.200	.59	.60
4.44	4.89	8.65	1.176	.68	1.37
9.65	11.0	15.1	1.093	.75	7.1
16.0	19.5	24.3	0.940	.74	30.5

Such comparison of activity coefficients in the resin and aqueous phases, though useful for estimation of Γ_{HCl} and $\gamma_{\pm HCl(r)}$ does not focus attention on the intrinsically high electrolyte concentration of the resins. Since from many points of view the resin phase with its imbibed electrolyte might profitably be considered a mixed concentrated electrolyte solution, an alternate method of correlation, based on application of Harned's rule (see ref. 9, Chapter 14), has been chosen.

We shall assume that the resin network together with its counterions behaves like a concentrated electrolyte solution with molality m_{RCl} which is given by the number of moles of sites per 1000 grams of imbibed water. On imbibing a 1:1 electrolyte, J, the total electrolyte concentration of the resin, $m_{t(r)}$, is given by

$$m_{t(r)} = m_{RCl} + m_{J(r)} \qquad (3)$$

At constant $m_{t(r)}$ and if J is a chloride, $\gamma_{\pm J(r)}$ should be given by

$$\log \gamma_{\pm J(r)} = \log \gamma_{\pm J(J)} - \alpha m_{RCl} \qquad (4)$$

where α is a constant and $\gamma_{\pm J(J)}$ is the activity coefficient of J in a binary aqueous solution of concentration $m_{t(r)}$.

To test applicability of this expression, values of α for HCl were calculated from the data of Tables I, II and III. Since $m_{t(r)}$ becomes considerably larger than 16, the highest concentration for which values of $\gamma_{\pm HCl}$ are recorded,[9,10] an extrapolation method was used for their estimation. The values of $\gamma_{\pm HCl}$ in the region $10 < m_{HCl} < 16$ were fitted to the quadratic expression

$$\log \gamma_{\pm HCl} = A_{HCl} + B_{HCl}\, m_{HCl} + C_{HCl} m^2_{HCl} \quad (5)$$

and the computed constants $A_{HCl} = -0.30$, $B_{HCl} = 0.156$, $C_{HCl} = -0.00225$ were assumed to hold at higher concentration. The computed values of α could be approximated by the linear expression $\alpha = 0.21 - 0.0032 m_{t(r)}$. Thus, although α is not independent of ionic strength, Harned's rule seems to apply because approximately the same values of α are obtained for resins of different cross-linking, immersed in different HCl solutions provided $m_{t(r)}$ is the same.

An alternate, though equivalent, method for demonstrating the applicability of Harned's rule is illustrated in Fig. 2. One may use the activity coefficients $\gamma_{\pm HCl(r)}$ and the values of $\gamma_{\pm HCl}$ (or $\gamma_{\pm HCl(HCl)}$) observed or estimated at the same $m_{t(r)}$ for the binary HCl solutions and compute point by point, activity coefficients of a trace amount of HCl in the resin phase ($\gamma_{\pm HCl(RCl)}$) assuming that the linear variation of log γ with m holds, *i.e.*, that

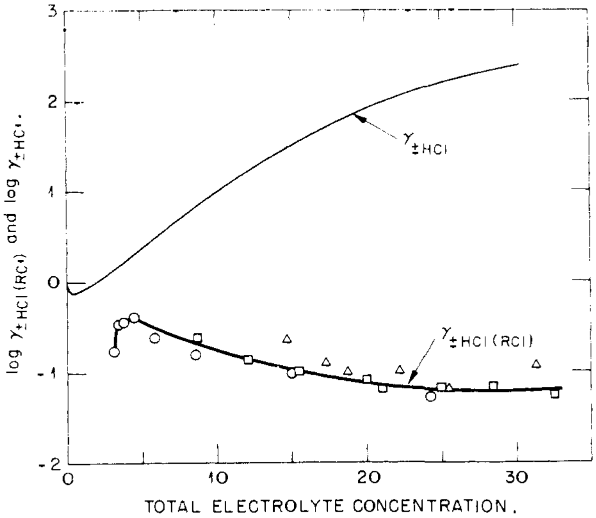

Fig. 2.—Computed activity coefficients $\gamma_{\pm HCl(RCl)}$ of trace HCl in various anion exchangers: □, Dowex-1 × 10 (Table I); △, Dowex-1, Variable DVB (Table II); ○, Dowex 21K (Table III).

$$\log \gamma_{\pm HCl(RCl)} = \log \gamma_{\pm HCl(r)} + (m_{HCl(r)}/m_{RCl}) \log (\gamma_{\pm HCl(r)}/\gamma_{\pm HCl(HCl)}) \quad (6)$$

These values of log $\gamma_{\pm HCl(RCl)}$ decrease regularly and with reasonable scatter from *ca.* -0.44 at $m_{t(r)} = 5$ to -1.2 at $m_{t(r)} = 32$ and are approximately the same for high cross-linked and low cross-linked resins at the same $m_{t(r)}$. If this concentrated electrolyte model of the resin is generally applicable, one expects that activity coefficients approximately equal to $\gamma_{\pm HCl(RCl)}$ would be found for aqueous solutions containing small amounts of HCl and a high concentration of the equivalent monomer of the resin, *e.g.*, benzyltrimethylammonium chloride. Such activity coefficients could be obtained through measurement of the activity of HCl in such mixtures and the comparison would be most interesting.

The activity coefficients of trace LiCl in the resin ($\gamma_{\pm LiCl(RCl)}$) were computed from the data of Table I by an equation analogous to (6). For high LiCl concentrations $\gamma_{\pm LiCl}$ was estimated from a quadratic equation analogous to (5) with the constants $A_{LiCl} = -0.37$, $B_{LiCl} = 0.165$ and $C_{LiCl} = -0.0028$ which were obtained by fitting the known values[9] of $\gamma_{\pm LiCl}$ in the region $16 < m_{LiCl} < 20$. The computed values of log $\gamma_{\pm LiCl(RCl)}$ (Fig. 3) increase from *ca.* -0.5 at $m_{t(r)} = 8$ to 1.0 at $m_{t(r)} = 30$. The rapid divergence of $\gamma_{\pm LiCl(RCl)}$ and $\gamma_{\pm HCl(RCl)}$ with increasing $m_{t(r)}$ dramatically illustrates the large differences in the interaction of LiCl and HCl with the resin and the importance of ionic strength for enhancing this difference.

4. **Activity Coefficients in LiCl–HCl Mixtures. Separation of HCl from Concentrated Chloride Solutions.**—Activity coefficient ratios Γ_{HCl} and Γ_{LiCl} were determined for HCl–LiCl mixtures of constant total molality $m_t = m_{HCl} + m_{LiCl} = 9.9$ and the results are summarized in Table IV.

TABLE IV

ADSORPTION OF HCl AND LiCl FROM MIXTURES

($m_{HCl} + m_{LiCl} = 9.90$; Dowex-1 × 10)

m_{HCl}	$m_{HCl(r)}$	$m_{LiCl(r)}$	$m_{Cl(r)}$	D_{HCl}[a]	kg_{H_2O}/kg_{resin}	Γ_{HCl}	Γ_{LiC}
0.00704	0.187	9.26	17.78	14	0.424	0.15	0.77
.0157	0.339	9.14	17.95	11	.413	.16	.77
.115	1.35	8.54	18.49	6	.408	.21	.78
.411	3.58	6.90	19.20	4.2	.403	.24	.84
1.99	7.72	4.02	20.71	1.9	.394	.35	.97
3.97	9.81	2.74	21.27	1.2	.405	.43	1.01
5.95	11.1	1.71	21.28	1.0	.417	.50	1.04
7.92	12.2	0.81	21.25	0.8	.428	.55	1.07
9.90	13.0	0	20.97	0.7	.442	.60	1.09[b]

[a] In units: moles HCl per kg. dry resin/moles HCl per liter of solution. [b] Extrapolated.

As the medium changes from essentially pure LiCl to pure HCl, Γ_{LiCl} rises moderately from 0.77 to 1.07. The values of Γ_{HCl} are much lower, particularly for $m_{HCl} \ll m_{LiCl}$ ($\Gamma_{HCl} = 0.14$ at $m_{HCl} = 0.007$; $\Gamma_{HCl} = 0.60$ at $m_{HCl} = 9.9$) which implies that HCl can be removed by anion exchangers in the chloride form from concentrated LiCl solutions. The extent of this adsorbability is described in Table IV by the distribution coefficients of HCl, D_{HCl} which were computed, after conversion to the usual units (moles per kg. of dry resin/moles per liter of solution) from the equation

$$D_{HCl} = \frac{m_{H(r)}}{m_H} = \frac{m_{Cl}}{m_{Cl(r)}} \frac{\gamma^2_{\pm HCl}}{\gamma^2_{\pm HCl(r)}} = \frac{m_{Cl}}{m_{Cl(r)}} \frac{1}{\Gamma^2_{HCl}} \quad (7)$$

which follows directly from equation 1.

Typical separations of HCl ($M = 0.1$) from LiCl solutions (m = 5, 10 and 16) are illustrated in Fig. 4 in the form of "break-through curves." While

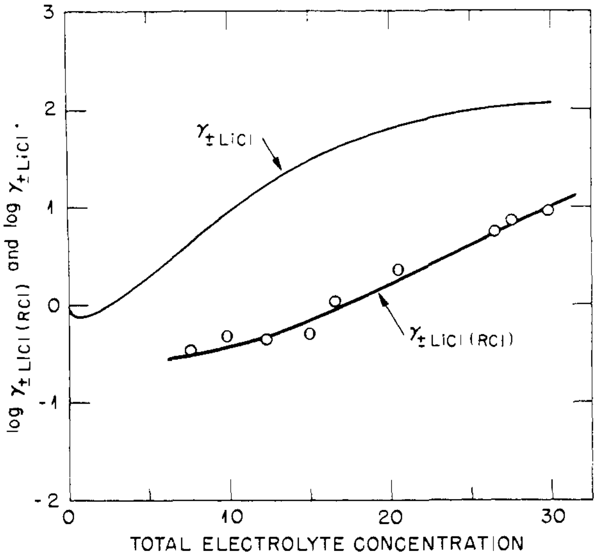

Fig. 3.—Computed activity coefficients $\gamma_{\pm \text{LiCl(RCl)}}$ of trace LiCl in Dowex-1 × 10.

the retardation of HCl is only moderately large for $m_{\text{LiCl}} = 5$, it amounts to more than 8 column volumes for $m_{\text{LiCl}} = 16$. Removal of the adsorbed HCl may be achieved within *ca.* 1 column volume on washing with water. In similar experiments with magnesium chloride solutions ($m_{\text{MgCl}_2} = 5$, $m_{\text{HCl}} = 0.12$) 50% break-through of the acid occurred at 3.8 column volumes, illustrating that low activity coefficients of HCl in the resin are found in other concentrated chloride solutions, not only in LiCl–HCl mixtures.

While a detailed explanation of the effect of concentrated electrolytes on the activity coefficients of HCl in the resin is not feasible at this time, the following considerations may illustrate the various relationships involved and supply at least a semi-quantitative interpretation. Harned's rule of the linear variation of the logarithm of the activity coefficients in mixtures of constant total concentration (or ionic strength) may be generalized for a system of n one-one electrolytes as[14]

$$\log \gamma_{\text{J}} = \sum_{i=1}^{n} F_{\text{i}} \log \gamma_{\text{J(i)}} \qquad (8)$$

Here $\gamma_{\text{J(i)}}$ is the activity coefficient of a trace amount of J in electrolyte i and $F_{\text{i}} = m_{\text{i}}/\Sigma m_{\text{i}} = m_{\text{i}}/m_{\text{t}}$ where m_{t} is the total (constant) electrolyte concentration. For a resin system with 3 electrolytes[15] (HCl, LiCl and RCl) equation (8) becomes

$$\log \gamma_{\text{HCl(r)}} = F_{\text{HCl(r)}} \log \gamma_{\text{HCl(HCl)}} + F_{\text{LiCl(r)}} \log \gamma_{\text{HCl(LiCl)}} + F_{\text{RCl}} \log \gamma_{\text{HCl(RCl)}} \qquad (9)$$

Similar equations may be written for $\gamma_{\text{LiCl(r)}}$ and γ_{RCl}. On the basis of equation 9 log $\gamma_{\text{HCl(r)}}$ is determined by the fractions F of HCl, LiCl and RCl in the resin phase and by the activity coefficients of pure HCl ($\gamma_{\text{HCl(HCl)}}$), of trace HCl in RCl ($\gamma_{\text{HCl(RCl)}}$) and of trace HCl in LiCl ($\gamma_{\text{HCl(LiCl)}}$) with all activity coefficients determined at the same electrolyte concentration which is given here by $m_{\text{Cl(r)}}$.

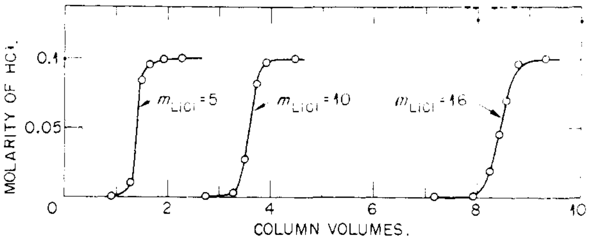

Fig. 4.—Adsorption of HCl from concentrated LiCl solutions (Dowex-1 × 10, $M_{\text{HCl}} = 0.1$).

By combining equations 7 and 8 an expression can be obtained which relates D to the (experimental) values of F and the various "limiting" activity coefficients. For mixtures containing a small amount of HCl in a large excess of LiCl, *i.e.*, when the terms involving F_{HCl} and $F_{\text{HCl(r)}}$ vanish, this expression becomes

$$\log D_{\text{HCl}} = \log \frac{m_{\text{Cl}}}{m_{\text{Cl(r)}}} + 2 \log \gamma_{\pm\text{HCl}} - 2 \log \gamma_{\pm\text{HCl(r)}} = \log \frac{m_{\text{Cl}}}{m_{\text{Cl(r)}}} + 2 \log \gamma'_{\pm\text{HCl(LiCl)}} - 2\, F_{\text{LiCl(r)}} \log \gamma_{\pm\text{HCl(LiCl)}} - 2\, F_{\text{RCl}} \log \gamma_{\pm\text{HCl(RCl)}} \qquad (10)$$

The activity coefficient for the aqueous phase carries a prime as a reminder that it needs to be evaluated at a different total electrolyte concentration than the equivalent term for the resin.

Calculations of D_{HCl} with equation 10 and the data of Table I are summarized in Table V. Since values of $\gamma_{\pm\text{HCl(LiCl)}}$ are not available except for $m_{\text{LiCl}} < 6$ (ref. 9, p. 467) we have approximated D_{HCl} by substituting $\gamma_{\pm\text{HCl(HCl)}}$ for $\gamma_{\pm\text{HCl(LiCl)}}$. This is equivalent to writing

$$\begin{aligned} \log \gamma'_{\pm\text{HCl(LiCl)}} &= \log \gamma'_{\pm\text{HCl(HCl)}} + \beta' \\ \log \gamma_{\pm\text{HCl(LiCl)}} &= \log \gamma_{\pm\text{HCl(HCl)}} + \beta \end{aligned} \qquad (11)$$

and then setting

$$\beta' - \beta F_{\text{LiCl(r)}} = 0 \qquad (12)$$

Though β and β' are functions of the total chloride concentration and though β' is probably a small negative quantity for $m_{\text{LiCl}} < 4$ (ref. 9, p. 467), at high chloride concentrations β and β' are probably positive and $\beta > \beta'$ which tends to make $\beta' - \beta F_{\text{LiCl(r)}}$ small since $F_{\text{LiCl(r)}} < 1$.

Thus though equation 12 cannot be considered more than a first approximation, computations based on it should be qualitatively correct. Table V demonstrates the relative magnitudes of the various terms and that the computed values of D_{HCl} rise with m_{LiCl}, as observed. The term log $m_{\text{Cl}}/m_{\text{Cl(r)}}$ which is approximately constant at high m_{LiCl} becomes a large negative quantity at very low m_{LiCl} and then is dominant in making D_{HCl} small. Since log $\gamma_{\pm\text{HCl(RCl)}}$ is always negative (see Fig. 2) the last term of equation 10 will always favor adsorption. While $\gamma'_{\pm\text{HCl(HCl)}}$ rises more rapidly than $\gamma'_{\pm\text{HCl(HCl)}}$ because it is evaluated at a higher total molality, the difference between the second and third term of equation 10 is positive because the third term contains $F_{\text{LiCl(r)}}$, which is substantially less than unity.

An attempt was made to apply these considerations to computation of Γ_{HCL} for the HCl–LiCl

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(14) We are indebted to Professor George Scatchard for pointing out to us this extension of Harned's rule.

(15) For 2 electrolytes, *e.g.*, HCl and RCl, equation 8 becomes log $\gamma_{\text{HCl(r)}} = F_{\text{HCl(r)}} \log \gamma_{\text{HCl(HCl)}} + F_{\text{RCl}} \log \gamma_{\text{HCl(RCl)}}$ which may also be obtained by rearrangement of equation 6.

TABLE V

ESTIMATION OF D_{HCl} FOR TRACE AMOUNTS OF HCl IN LiCl SOLUTIONS

(Based on data of Table I)

m_{LiCl}	$\log \frac{m_{Cl}}{m_{Cl(r)}}$	$\log \gamma'_{HCl(HCl)}$[a]	$\log \gamma_{HCl(HCl)}$[b]	$F_{LiCl(r)} \times \log \gamma_{HCl(HCl)}$	$\log \gamma_{HCl(RCl)}$[b]	$F_{RCl} \times \log \gamma_{HCl(RCl)}$	$\log D_{HCl}$[c]
2.07	−0.44	0.01	0.72	0.10	−0.63	−0.30	−0.02
4.10	− .38	.25	.99	.31	− .75	− .35	.20
6.03	− .31	.51	1.28	.54	− .87	− .41	.45
8.03	− .27	.77	1.55	.77	− .96	− .44	.61
9.82	− .23	1.00	1.67	.87	−1.02	− .44	.91
12.8	− .20	1.33	1.95	1.14	−1.13	− .46	1.10
17.4	− .18	1.73	2.25	1.45	−1.20	− .48	1.34
18.5	− .17	1.82	2.29	1.51	−1.21	− .47	1.39
19.8	− .18	1.91	2.35	1.58	−1.21	− .46	1.40

[a] Evaluated for solution phase at $m_t = m_{LiCl}$. [b] Evaluated for resin phase at $m_{t(r)} = m_{Cl(r)}$. [c] Computed from equation $\log D_{HCl} = \log \frac{m_{Cl}}{m_{Cl(r)}} + 2 \log \gamma'_{HCl(HCl)} + 2\beta' - 2F_{LiCl(r)} \log \gamma_{HCl(HCl)} - 2F_{LiCl(r)}\,\beta - 2F_{RCl} \log \gamma_{HCl(RCl)}$ setting $2\beta' - 2F_{LiCl(r)}\,\beta = 0$.

TABLE VI

COMPUTATION OF Γ_{HCl} FOR HCl–LiCl MIXTURES

(Data from Table IV)

m_{HCl}	$\log \gamma'_{HCl(HCl)}$	$(F_{HCl(r)} + F_{LiCl(r)}) \times \log \gamma_{HCl(HCl)}$	$F_{RCl} \log \gamma_{HCl(RCl)}$	$\log \Gamma_{HCl}$ (calcd.)	$\log \Gamma_{HCl}$ (obsd.)
0.00704	1.02	0.94	−0.50	−0.58	−0.82
.0157	1.02	.94	− .51	− .59	− .80
.115	1.02	.97	− .50	− .55	− .68
.411	1.02	1.02	− .50	− .50	− .62
1.99	1.02	1.12	− .49	− .39	− .46
3.97	1.02	1.18	− .47	− .31	− .37
5.95	1.02	1.20	− .46	− .28	− .30
7.92	1.02	1.22	− .45	− .25	− .26
9.90	1.02	1.23	− .44	− .23	− .22

mixtures of Table IV. Applying Harned's rule to both $\log \gamma_{HCl(r)}$ and $\log \gamma_{HCl}$, one obtains

$$\log \Gamma = \log \frac{\gamma_{HCl(r)}}{\gamma_{HCl}} = F_{HCl(r)} \log \gamma_{HCl(HCl)} + F_{LiCl(r)} \log \gamma_{HCl(LiCl)} + F_{RCl} \log \gamma_{HCl(RCl)} - F_{HCl} \log \gamma'_{HCl(HCl)} - F_{LiCl} \log \gamma'_{HCl(LiCl)} \quad (13)$$

This equation simplifies to

$$\log \Gamma = (F_{HCl(r)} + F_{LiCl(r)}) \log \gamma_{HCl(HCl)} + F_{RCl} \log \gamma_{HCl(RCl)} - \log \gamma'_{HCl(HCl)} + F_{LiCl(r)}\,\beta - F_{LiCl}\beta' \quad (14)$$

if we apply equation 11. If one assumes again that as a first approximation $F_{LiCl(r)}\beta - F_{LiCl}\,\beta' = 0$, log Γ may be computed and the results are summarized in Table VI. While agreement between calculated and observed values of Γ_{HCl} is satisfactory and indeed better than expected at high HCl concentrations, the observed values are consistently smaller at low HCl concentrations. This is not surprising if one recalls[3] that presence of small amounts of lower amine groups as impurities in the resin can substantially lower $\gamma_{\pm HCl(r)}$.

5. The Sulfate–Bisulfate Equilibrium in the Resin Phase.—The strong adsorption of sulfuric acid by the sulfate form of the anion exchanger which is reflected in the low values of $\Gamma_{H_2SO_4}$ and $\gamma_{\pm H_2SO_4(r)}$ (Table I) presumably results from the acid–base reaction

$$HSO_4^-{}_{(r)} \rightleftharpoons SO_4^={}_{(r)} + H^+{}_{(r)} \quad (15)$$

with an equilibrium constant

$$k_{a(r)} = \frac{(SO_4^=)_{(r)}(H^+)_{(r)}}{(HSO_4^-)_{(r)}} \frac{g_{SO_4(r)}g_{H(r)}}{g_{HSO_4(r)}} = k_a{}^0{}_{(r)}G_{a(r)} \quad (16)$$

where parentheses indicate concentrations of species, g their activity coefficients, $k_a{}^0{}_{(r)}$ the concentration quotient and $G_{a(r)}$ the species activity coefficient quotient. With our choice of standard states, *i.e.*, that they are the same for distributable components in both phases, the equilibrium constant in the resin phase $k_{a(r)}$ is identical to that in the aqueous phase and $k_{a(r)} = k_a = 0.0104$.[10] The concentration quotients and the activity coefficient quotients of course differ for the two phases, *i.e.*, $k_a{}^0{}_{(r)} \neq k_a{}^0$; $G_{a(r)} \neq G_a$. While evaluation of $k_a{}^0{}_{(r)}$ or $G_{a(r)}$ is difficult because simultaneous determination of the concentrations of the species $SO_4^=$, HSO_4^- and H^+ in the resin is implied, other concentration and activity coefficient quotients may be determined from the following relationships after making some simplifying assumptions

$$a_{H_2SO_4} = (H^+)^2(SO_4^=)g^2{}_H g_{SO_4} = (H^+)^2{}_{(r)}(SO_4^=)_{(r)}g^2{}_{H(r)}g_{SO_4(r)} = k_a(H^+)(HSO_4^-)g_H g_{HSO_4} = k_a(H^+)_{(r)}(HSO_4^-)_{(r)}g_{H(r)}g_{HSO_4(r)} \quad (17)$$

$$a^{1/2}{}_{H_2SO_4} = k_a \frac{(HSO_4^-)g_{HSO_4}}{(SO_4^=)^{1/2}g^{1/2}{}_{SO_4}} = k_a \frac{(HSO_4^-)_{(r)}}{(SO_4^=)^{1/2}{}_{(r)}} \frac{g_{HSO_4(r)}}{g^{1/2}{}_{SO_4(r)}} \quad (18)$$

At low sulfuric acid invasion where the free hydrogen ion concentration, $(H^+)_{(r)}$, in the resin is presumably small, the sulfate and bisulfate concentrations may be approximated by the relationships $(HSO_4^-)_{(r)} = 2m_{H_2SO_4(r)}$ and $(SO_4^=)_{(r)} = C_{SO_4} - m_{H_2SO_4(r)}$ where C_{SO_4} is the sulfate capacity of the resin in the units moles per kg. water. Thus the species activity coefficient quotient $g_{HSO_4(r)}/g^{1/2}{}_{SO_4(r)}$ may be computed. This ratio varies (Table VII) from approximately 0.08 to 0.3 as $m_{H_2SO_4(r)}$ increases from 0.08 to 3.5 where *ca.* 90% of the $SO_4^=$ in the resin is converted to HSO_4^-. A plot of $\log (g_{HSO_4(r)}/g^{1/2}{}_{SO_4(r)})$ *vs.* $m_{H_2SO_4}$ is approximated by the linear equation

$$\log (g_{HSO_4(r)}/g^{1/2}{}_{SO_4(r)}) = -1.05 + 0.178\, m_{H_2SO_4(r)}$$

If the ratio $g_{HSO_4(r)}/g^{1/2}{}_{SO_4(r)}$ is combined with estimates of the sulfate and bisulfate concentrations in the aqueous phase, the activity coefficient quotient

$$G = \frac{g_{HSO_4(r)}g^{1/2}{}_{SO_4}}{g_{HSO_4}g^{1/2}{}_{SO_4(r)}}$$

for the ion exchange equilibrium

$$^1/_2(SO_4^=)_{(r)} + HSO_4^- \rightleftarrows (HSO_4^-)_{(r)} + {}^1/_2(SO_4^=) \quad (19)$$

may be computed with equation 18. Table VII includes values of this quotient obtained by estimating (HSO_4^-) and $(SO_4^=)$ at low concentrations ($m_{H_2SO_4} < 0.05$) from the data of Sherrill and Noyes[16] and at high concentrations from the Raman data of Maranville, Smith and Young.[17] The activity coefficient quotient for the sulfate–bisulfate exchange equilibrium varies remarkably little in the concentration range $0.001 < m_{H_2SO_4} < 0.5$, while the activity coefficients in each phase vary considerably. Further, G is considerably smaller than unity which implies that at a given sulfuric acid concentration bisulfate formation in the resin phase is more favored than in the aqueous phase, a fact which is of course also apparent from the observation that $g_{HSO_4(r)}/g^{1/2}{}_{SO_4} \ll 1$.

It is thus probably safe to assume that at high sulfuric acid invasion the principal species in the resin phase are hydrogen and bisulfate ions with concentrations $(H^+)_{(r)} \approx m_{H_2SO_4(r)} - C/2$ and $(HSO_4^-)_{(r)} \approx m_{H_2SO_4(r)} + C/2$ where C is the capacity of the exchanger in the units moles of sites per kg. imbibed water. The activity coefficient products $g_{H(r)}g_{HSO_4(r)}$ thus computed with equation 17 are listed in Table VIIB. As shown in Fig. 5, a plot of log $g_{H(r)}g_{HSO_4(r)}$ at high values of $m_{H_2SO_4(r)}$ is approximated by the linear equation log $g_{H(r)}$·$g_{HSO_4(r)} = -1.42 + 0.203m_{H_2SO_4(r)}$.

TABLE VII

THE SULFATE–BISULFATE EQUILIBRIUM IN THE RESIN PHASE

(Computations based on data of Table I)

A. Low H_2SO_4 invasion

$m_{H_2SO_4}$	$(HSO_4^-)_{(r)}$	$(SO_4^=)_{(r)}$	$\frac{g_{HSO_4(r)}}{g^{1/2}{}_{SO_4(r)}}$	$\frac{g_{HSO_4(r)}g^{1/2}{}_{SO_4}}{g_{HSO_4}g^{1/2}{}_{SO_4(r)}}$
0.0015	0.160	2.55	0.078	0.067
.00253	.284	2.51	.085	.068
.0050	.518	2.44	.105	.086
.011	1.17	2.24	.110	.083
.015	1.48	2.14	.120	.088
.0235	2.00	2.01	.141	.095
.0285	2.32	1.94	.146	.094
.099	4.34	1.29	.214	.104
.242	5.76	0.72	.296	.101
.515	7.08	0.26	(.303)	(.068)

B. High H_2SO_4 invasion

$m_{H_2SO_4}$	$(HSO_4^-)_{(r)}$	$(H^+)_{(r)}$	$g_{H(r)}g_{HSO_4(r)}$	$\frac{g_{\pm H,HSO_4(r)}}{g_{\pm H,HSO_4}}$
1.04	8.22	0.24	0.47	0.71
2.24	10.2	1.53	0.56	.54
3.47	12.5	3.23	1.43	.52
4.94	15.4	5.43	4.99	.51
7.46	20.4	9.43	38.7	.51

The activity coefficient quotient $G_{a(r)}$ (equation 16) which is needed to represent the sulfate–bisulfate equilibrium in the resin can be obtained from $g_{HSO_4(r)}/g^{1/2}{}_{SO_4(r)}$ and $g_{H(r)}$ $g_{HSO_4(r)}$. Unfortunately, these products are determinable only one at a time at the extremes of the sulfuric acid concentration range while they are needed over the entire concentration range. To make some estimate of $G_{a(r)}$ we shall assume that the straight line variation of the logarithms of these products with $m_{H_2SO_4(r)}$ holds throughout the H_2SO_4 concentration range although, of course there is no assurance that this procedure is reliable. Nevertheless, it should permit a preliminary estimation of the magnitude of $G_{a(r)}$.

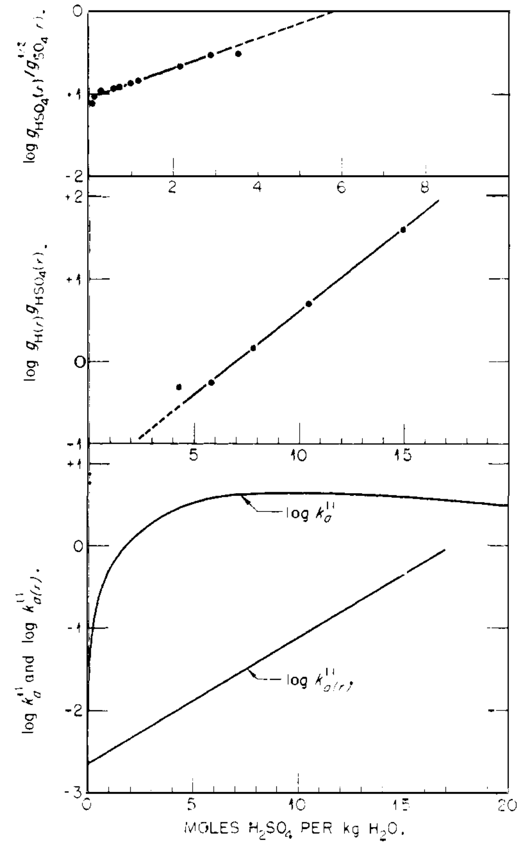

Fig. 5.—The sulfate–bisulfate equilibrium in the resin phase.

On the basis of the assumptions made, log $G_{a(r)}$ may be represented by the linear equation log $G_{a(r)} = 0.68 - 0.153m_{H_2SO_4(r)}$ and log $k^0{}_{a(r)}$ hence increases linearly with $m_{H_2SO_4(r)}$. A comparison of $k^0{}_a$ and $k^0{}_{a(r)}$ (Fig. 5) shows that the bisulfate ion is a very much weaker acid in the resin phase than in the aqueous phase, a fact which presumably is responsible for the high selectivity of the sulfate form of the resin for sulfuric acid.

Acknowledgment.—We are indebted to Mrs. Donna Michelson and Dr. R. M. Rush for permission to include previously unpublished measurements on the uptake of hydrochloric acid and lithium chloride.

OAK RIDGE, TENN.

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(16) M. S. Sherrill and A. A. Noyes, THIS JOURNAL, **48**, 1861 (1926).

(17) We are indebted to Professor T. F. Young for making these data available to us in tabular form.