

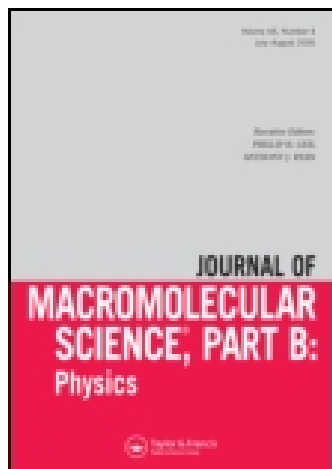
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## **Ion-Exchange Selectivity Coefficients in the Exchange of Calcium, Strontium, Cobalt, Nickel, Zinc, and Cadmium Ions with Hydrogen Ion in Variously Cross-Linked Polystyrene Sulfonate Cation Exchangers at 25°C\***

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### Summary

The ion-exchange selectivity parameters for the exchange of trace calcium, strontium, cobalt, nickel, zinc, and cadmium ions with hydrogen ion in cross-linked polystyrene-sulfonic acid cation exchangers have been determined from equilibrium ionic distribution measurements at 25°C in dilute solutions of perchloric acid and polystyrene-sulfonic acid. The selectivity behavior in perchloric acid solutions shows that the divalent ion is always preferred by the resin phase. The selectivity coefficients are a smooth function of resin phase concentration, increasing with concentration for  $\text{Sr}^{2+}$  more than for  $\text{Ca}^{2+}$  and  $\text{Cd}^{2+}$  and being practically independent of resin phase concentration for  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$ . The selectivity coefficients measured in salt-free solutions of polystyrene-sulfonic acid

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show a marked dependence on the polyelectrolyte concentration, the divalent ion being preferred by the aqueous phase. This preference diminishes with the concentration of polyelectrolyte. These results are interpreted by resort to the Gibbs-Duhem equation. This thermodynamic analysis has been facilitated by the availability of osmotic coefficient data for the pure polyelectrolyte ion forms over a large concentration range. Ion-exchange selectivity predictions by using this approach accurately reflect the observed ion-exchange selectivity behavior.

## INTRODUCTION

Ion-exchange selectivity in uni-univalent systems has been extensively investigated for many years [1,2]. The more complicated uni-divalent systems have received much less attention [3-9]. It was the objective of this research to focus attention to this relatively neglected area of research. A second objective was the prediction for these systems of the ion-exchange equilibria through purely thermodynamic considerations. Successful interpretation of such selectivity data was expected to facilitate meaningful insight with regard to the factors important in the uni-divalent selectivity behavior of ion-exchange resins and membranes [10]. For example, electrostatic interaction between polyion and counterions is considered to be a dominant factor influencing the enhanced selectivity of multivalent ions [2] beyond the obvious influence of valence appearing as exponents in the equation for selectivity coefficient. It has also been suggested that specific ion interactions, such as ion-pair formation, influence most strongly the observed selectivity in polystyrene-sulfonic acid ion exchangers [11,12]. With the availability of a valid interpretation of the selectivity phenomenon, the opportunity for quantitative assessment of mass transport in ion-exchange membranes is expected to be improved as well [13,14].

Divalent ion preference for the exchanger phase depends strongly upon the nature of the repeating functional unit of the exchanger. If the functional unit of the exchanger is weakly acidic, the relative distribution of uni- and divalent ions between exchanger and solution phases is a primary function of the pH of the system. Preference of divalent ion over univalent ion is much enhanced at high pH, such enhancement being remarkably magnified when complexation of the divalent ion by the ionized functional unit occurs [15,16].

In this investigation, consideration of the distribution of uni- and divalent pairs of ions between solution and exchanger phases has been limited to the strongly acidic divinylbenzene polystyrene-sulfonic acid copolymer. Earlier equilibrium distribution measurements of such systems had shown that in the exchange with hydrogen

ion the divalent ion is always favored by the resin phase [5,7,8]. For the  $\text{Zn}^{2+}$ - $\text{Na}^+$  exchange, preference for the divalent ion is a function of resin cross-linking [3]. In the case of the  $\text{Mg}^{2+}$ - $\text{K}^+$  exchange, however,  $\text{K}^+$  ion is favored by the resin, the selectivity coefficient being independent of solution concentration and resin loading [9]. Since the dependence of selectivity on resin phase concentration and the identity of the divalent ion has not been reported in detail, measurements were initiated to determine the ion-exchange selectivity parameters for trace quantities of  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Cd}^{2+}$  exchanging with hydrogen ion, when equilibrated with polystyrene-sulfonic acid or perchloric acid.

To elucidate further the nature of univalent-divalent ion-exchange selectivity equilibrium, ionic distribution measurements of the various divalent ions, between dilute perchloric acid or polystyrene-sulfonic acid solutions and six different cross-linked polystyrene-sulfonic acid cation exchangers, were determined at 25°C. Electrolyte imbibement and water contents of the ion exchangers were measured to facilitate expression of resin phase concentrations in molality units. The resin phase concentration range, 1.24-6.91 m, was determined by the nominal percent divinylbenzene (DVB) content of the polystyrene-sulfonic acid ion exchanger.

Numerous attempts to predict ion-exchange equilibria have been reported, and a rather complete discussion of the spectrum of theoretical approaches and models that have been employed has been presented by Helfferich [2]. One of the most successful of these uses osmotic coefficient measurements of  $\leq 0.5\%$  cross-linked resins in the Gibbs-Duhem equation to compute ion-activity coefficient ratios in the resin phase [17-23]. However, because of the unavailability of osmotic data for the polyion forms at low-concentration values, assumptions that are necessary with respect to osmotic behavior in the dilute concentration region negate the utility of this approach. This deficiency is eliminated by the availability of osmotic data obtained with the linear polyelectrolyte analog of the cross-linked exchanger for the various ion forms employed in this experimental study [24]. It is possible to employ the Gibbs-Duhem equation in a more meaningful way as a consequence of the availability of these osmotic data.

## EXPERIMENTAL DETAILS

### Materials

Polystyrene-sulfonic acid was prepared by passing a solution of sodium polystyrene sulfonate (mol wt 40,000; lot CP 522-13-118; kindly supplied by Dr. Brodof of the Dow Chemical Co., Midland,

Michigan) through an ion-exchange column ( $H^+$  ion form). The resulting solution was passed through a mixed bed ion-exchange column and finally dialyzed against distilled deionized water for 1 week. The polystyrene-sulfonic acid prepared in this manner was shown to be free of impurities by ultraviolet absorption [25], equivalent weight, and osmotic coefficient measurements [26].

Reagent grade perchloric acid and distilled deionized water were used in all experiments. Acid concentrations were determined by titration with standard base. The polystyrene-sulfonic acid ion exchanger was a Dowex 50 type of high uniformity and quality (purchased from the Bio-Rad Company). The ion-exchange resins were conditioned before use by several exchange cycles. After conditioning, all resins were washed free of imbibed electrolyte, filtered, and stored in sealed dark glass bottles for use in the ion-exchange distribution experiments.

The ion-exchange resin equivalent content, water content at each ionic strength, and imbibed electrolyte concentration were determined using standard techniques [2]. The equivalent capacities of the ion-exchange resins used in the selectivity measurements are given in Table 1.

TABLE 1  
Equivalent Capacity of Ion-Exchange Resins Used  
in Selectivity Measurements

	Nominal divinylbenzene content:					
	1%	2%	4%	8%	12%	16%
Equivalent capacity (meq $H^+$ /g dry HR)	5.38	5.49	5.26	5.15	5.07	4.94

Water contents of ion-exchange resins equilibrated with 0.168 m  $HClO_4$  were determined using a centrifugation technique [2] and are expressed as grams of water per gram of dry hydrogen resin (HR) in Table 2.

Imbibed perchloric acid concentration was determined using a similar centrifugation procedure, and the results are expressed in Table 3 as milliequivalents of perchloric acid per gram of water in the ion exchanger.

The experimental ion-exchange resin equivalent capacity (meq  $H^+$ /g dry HR), given in Table 1, water capacity (g  $H_2O$ /g dry HR), given in Table 2, as well as dry resin content of stock hydrogen form ion-exchange resin (g dry HR/g stock HR) are mean values. The

TABLE 2  
Water Content of Ion-Exchange Resin Equilibrated with  
0.168 m Perchloric Acid

	Nominal divinylbenzene content:					
	1%	2%	4%	8%	12%	16%
Water content (g water/g dry HR)	4.52	3.09	1.80	1.20	0.887	0.715

TABLE 3  
Imbided Perchloric Acid Concentration of Ion-Exchange Resin  
with 0.168 m Perchloric Acid

	Nominal divinylbenzene content:			
	1%	2%	4%	8%
Imbided perchloric acid concentration (imbided meq/g resin phase water)	0.045	0.029	0.016	0.015

average mean deviation of each quantity for the six resin DVB contents is 0.8, 0.9, and 0.2%, respectively.

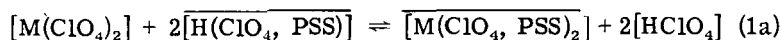
Procedure

Selectivity studies were carried out using the batch equilibration method [2]. The equilibrating samples were shaken for at least 2 days at  $25 \pm 1^\circ\text{C}$ . After equilibrium had been reached the samples were stored in a thermostatically controlled bath at  $25 \pm 0.1^\circ\text{C}$  for 1 hr prior to their activity measurement. All samples were filtered through a microporous filter into vials employed in the counter assembly. The radioactivity in the samples was assayed in one of two ways, depending on the isotope used in the experiment. Gamma counting was used for  $^{60}\text{Co}$  and  $^{65}\text{Zn}$  isotopes; the measurements were made using a Packard automatic gamma counter. Liquid scintillation counting [27] was used to measure the activity in solutions containing  $^{45}\text{Ca}$ ,  $^{63}\text{Ni}$ ,  $^{90}\text{Sr}$ , and  $^{109}\text{Cd}$  radionuclides. Several measurements were made to determine the extent to which efficiency changes would interfere with the liquid scintillation radioactivity measurements. This work demonstrated that the liquid scintillation

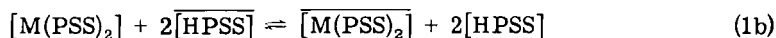
counting efficiency is constant in the region where the selectivity experiment measurements were made. All radioactivity measurements were performed at least twice on each sample, total net counts being greater than 50,000. The average precision of the radioactivity measurements was found to be 0.5%.

## RESULTS

The ion-exchange reaction that occurs when trace divalent metal exchanges with  $H^+$  ion in the resin and solution phases as encountered in this study may be represented by



where  $[\overline{H^+}] = [\overline{ClO_4}] + [\overline{PSS}]$  neglecting trace concentrations and  $[\overline{PSS}] \gg [\overline{ClO_4}]$ , and



Species within a squared bracket represent molal concentrations. Barred brackets refer to resin phase molal concentrations. The selectivity terms  $K_D$ ,  $K_{EX}$ , and  $K_{AC}$  used in this paper are expressed as

$$K_D = \frac{[\overline{M^{2+}}]}{[M^{2+}]} \quad (2)$$

$$K_{EX} = \frac{[\overline{M^{2+}}]}{[M^{2+}]} \left( \frac{[H^+]}{[\overline{H^+}]} \right)^2 \quad (3)$$

$$K_{AC} = \frac{[\overline{M^{2+}}]}{[M^{2+}]} \left( \frac{[H^+]}{[\overline{H^+}]} \right)^2 \frac{\gamma_{\pm HClO_4}^4}{\gamma_{(0)\pm Ca(ClO_4)_2}^3} \quad (4)$$

all anion concentrations canceling. In these equations  $\gamma_{\pm HClO_4}$  is the mean molal activity coefficient of perchloric acid and  $\gamma_{(0)\pm Ca(ClO_4)_2}$  is the mean molal activity coefficient of trace  $Ca(ClO_4)_2$  at the ionic strength of the perchloric acid. Both activity coefficients are from the literature [28,29]. The  $\gamma_{(0)\pm}$  of  $Ca(ClO_4)_2$  is used in the absence of mean molal activity coefficient data for the other divalent perchlorate salts used in the experimental program. The activity coefficient of hydrochloric acid is used for the perchloric acid activity coefficient at 0.016 m. The terms  $K_D$ ,  $K_{EX}$ , and  $K_{AC}$  are determined from measured quantities with the following expressions:



$$K_D = \frac{D_o - D_e}{D_e} \times \left\{ \frac{\text{ml of solution}}{\left( \frac{\text{g of}}{\text{(stock HR)}} \right)_{\% \text{DVB}} \left( \frac{\text{g dry HR}}{\text{g stock HR}} \right)_{\% \text{DVB}} \left( \frac{\text{g H}_2\text{O}}{\text{g dry HR}} \right)_{\% \text{DVB}} m_{\text{HClO}_4}} \right\} \quad (5)$$

$$K_{EX} = K_D \times \left[ \frac{(\text{meq H}^+/\text{g H}_2\text{O})}{\left( \frac{(\text{meq H}^+/\text{g dry HR})_{\% \text{DVB}}}{(\text{g H}_2\text{O}/\text{g dry HR})_{\% \text{DVB}}} \right) m_{\text{HClO}_4}} \right] \quad (6)$$

$$K_{AC} = K_{EX} \left( \frac{\gamma_{\pm \text{HClO}_4}^4}{\gamma_{(0)\pm \text{Ca}(\text{ClO}_4)_2}^3} \right)_{m_{\text{HClO}_4}} \quad (7)$$

where  $D$  represents the counts per minute per gram of solution before and after equilibration (subscripts 0 and e) and all other terms have their usual meaning.

The selectivity terms given in Table 4 show the distribution coefficient  $K_D$  for the hydrogen, trace divalent ion exchange rapidly increasing with resin phase concentration. For all the exchange reactions the selectivity coefficient  $K_{EX}$  and the modified selectivity coefficient  $K_{AC}$  are larger than unity. The divalent ion is always favored by the resin phase.

From the graphical representation of the selectivity data in Fig. 1 the dependence of  $K_{EX}$  on resin phase molality and the identity of the divalent ion is most readily apparent. The selectivity coefficients are a smooth function of resin phase concentration, suggesting that the resins used in this experimental program are homogeneous. Four distinct selectivity coefficient trends are observed. Selectivity coefficients for the  $\text{Sr}^{2+}$ - $\text{H}^+$  exchange reaction increase rapidly with resin phase concentration, whereas those for the  $\text{Ca}^{2+}$ - $\text{H}^+$  exchange reaction increase less rapidly. For the  $\text{Cd}^{2+}$ -,  $\text{Co}^{2+}$ -,  $\text{Ni}^{2+}$ -, and  $\text{Zn}^{2+}$ - $\text{H}^+$  ion-exchange reactions at low resin phase concentrations, the selectivity coefficients are practically independent of resin phase concentration. At high resin phase concentrations the selectivity coefficient for the  $\text{Cd}^{2+}$ - $\text{H}^+$  exchange reaction increases, whereas those for  $\text{Co}^{2+}$ -,  $\text{Ni}^{2+}$ -, and  $\text{Zn}^{2+}$ - $\text{H}^+$  exchange reactions decrease with increasing resin concentration. For  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$ ,  $K_{EX}$  behaves in a similar fashion over the entire resin phase concentration range.

TABLE 4  
Selectivity Terms for Trace  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  
 $\text{Zn}^{2+}$ , and  $\text{Cd}^{2+}$  with Hydrogen Ion-Exchange Resin  
in 0.168 m Perchloric Acid

$\% \text{ DVB}$	$\bar{m}_{\text{H}^+}$	$K_D$	$K_{\text{EX}}$	$K_{\text{AC}}$
Trace $\text{Ca}^{2+}$				
1	1.236	113	2.09	3.97
2	1.808	298	2.59	4.91
4	2.95	916	2.97	5.67
8	4.62	2960	3.92	7.45
12	5.72	6950	6.01	11.40
16	6.91	12200	7.26	13.80
Trace $\text{Sr}^{2+}$				
1	1.236	173	3.21	6.09
2	1.808	413	3.59	6.80
4	2.95	1320	4.30	8.17
8	4.62	4940	6.52	12.38
12	5.72	12580	10.88	20.7
16	6.91	22100	13.13	24.9
Trace $\text{Co}^{2+}$				
1	1.236	105	1.94	3.68
2	1.808	215	1.87	3.54
4	2.95	559	1.82	3.46
8	4.62	1342	1.78	3.37
12	5.72	2030	1.76	3.34
16	6.91	2570	1.52	2.89
Trace $\text{Ni}^{2+}$				
1	1.236	101	1.87	3.54
2	1.808	202	1.75	3.32
4	2.95	534	1.74	3.30
8	4.62	1325	1.75	3.33
12	5.72	1974	1.71	3.24
16	6.91	2600	1.54	2.93
Trace $\text{Zn}^{2+}$				
1	1.236	92.4	1.71	3.26
2	1.808	202	1.75	3.32
4	2.95	515	1.68	3.19
8	4.62	1302	1.72	3.27

TABLE 4 (continued)

% DVB	$\bar{m}_{H^+}$	$K_D$	$K_{EX}$	$K_{AC}$
12	5.72	1918	1.66	3.15
16	6.91	2530	1.50	2.85
Trace $Cd^{2+}$				
1	1.236	98	1.82	3.45
2	1.808	218	1.89	3.59
4	2.95	601	1.97	3.72
8	4.62	1651	2.19	4.15
12	5.72	2930	2.54	4.82
16	6.91	4460	2.65	5.03

The variation of the distribution coefficient for the  $Zn^{2+}$ - $H^+$  ion exchange reaction with the ratio of solution molality to resin phase molality is shown in Fig. 2. The slope of this log-log plot is 2.05 compared with a slope of 2.00 predicted from the mass action expression. This result is expected since  $K_{EX}$  is essentially independent of solution and resin phase concentrations for this system, as seen from Fig. 1.

Table 5 presents the selectivity terms determined at various perchloric acid concentrations for the  $Co^{2+}$ - and  $Zn^{2+}$ - $H^+$  ion-exchange reactions. The modified selectivity coefficient  $K_{AC}$  does not appear to be independent of external perchloric acid concentration. This result is undoubtedly a consequence of the inability to estimate accurately the changes introduced in aqueous activity coefficient ratios at the different acid concentrations since the selectivity coefficient is insensitive to the small variations in resin phase concentration with external solution concentration. The constancy of the ratio of  $K_{EX}$  for the  $Zn^{2+}$ - $H^+$  system in 0.168 and 0.016 m  $HClO_4$  over the complete resin concentration range [ $K_{EX}(0.168)/K_{EX}(0.016) = 1.27, 1.14, 1.15, 1.13, 1.18, 1.24$ ] is supportive of this estimate of the situation. Failure of the attempt to demonstrate the expected constancy of  $K_{AC}$  by identifying the variation of  $\gamma_{(o) \pm M^{2+}(ClO_4)_2}$  with that of  $Ca(ClO_4)_2$  in the different acid concentrations is very likely due to this oversimplification.

The selectivity terms for the  $Zn^{2+}$ - $H^+$  ion exchange reaction in 0.010 m polystyrene-sulfonic acid and for the  $Ca^{2+}$ - $H^+$  ion-exchange reaction in 0.040 m polystyrene-sulfonic acid are given in Tables 6 and 7, respectively. Figure 3 shows the variation of the selectivity coefficient with resin phase concentration for the  $Zn^{2+}$ - and  $Ca^{2+}$ - $H^+$

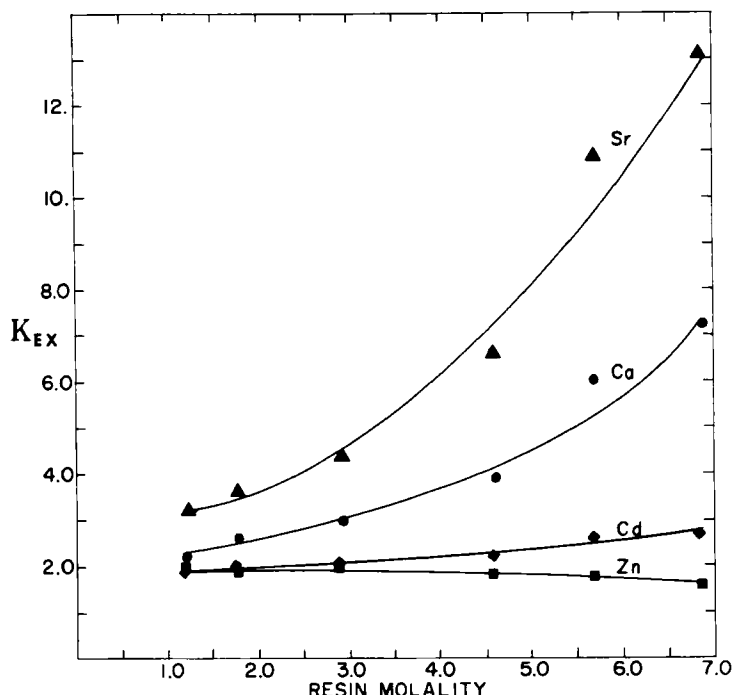


FIG. 1. Resin phase concentration dependence of the molal selectivity coefficient,  $K_{EX}$ , for several trace divalent ion, hydrogen ion, ion exchanges (using polystyrene-sulfonic acid cross-linked with divinylbenzene as the ion exchanger in 0.168 m perchloric acid).

ion-exchange reactions in polystyrene-sulfonic acid. The relative change in selectivity coefficient with resin phase concentration is the same as that observed in the perchloric acid selectivity studies as is to be expected.

Table 8 presents the selectivity terms for the divalent, hydrogen ion exchanges in 0.01 m polystyrene-sulfonic acid. The selectivity coefficients given in Table 8 show similar behavior to those measured in perchloric acid; i.e., the order of decreasing selectivity is  $Sr^{2+} > Ca^{2+} > Cd^{2+} \sim Co^{2+} \sim Ni^{2+} \sim Zn^{2+}$ , as was observed in Fig. 1.

The selectivity terms for the  $Co^{2+}$ - $H^+$  ion-exchange reaction with 8% DVB ion-exchange resin in polystyrene-sulfonic acid are given in Table 9. The dependence of the selectivity coefficient on the solution phase concentration for the  $Co^{2+}$ - and  $Zn^{2+}$ - $H^+$  ion-exchange reaction with 8% DVB ion-exchange resin in perchloric acid and

TABLE 5

Selectivity Terms for Trace  $\text{Zn}^{2+}$  and  $\text{Co}^{2+}$  with  
Hydrogen Ion-Exchange Resin in 0.168, 0.016, and  
0.001 m Perchloric Acid

% DVB	$\bar{m}_{\text{H}^+}$	$K_{\text{D}}$	$K_{\text{EX}}$	$K_{\text{AC}}$
Trace $\text{Zn}^{2+}$ ; Selectivity Terms in 0.168 m Perchloric Acid				
1	1.236	92	1.71	3.26
2	1.808	202	1.75	3.32
4	2.95	515	1.68	3.19
8	4.62	1302	1.72	3.27
12	5.72	1918	1.66	3.15
16	6.91	2530	1.50	2.85
Trace $\text{Zn}^{2+}$ ; Selectivity Terms in 0.016 m Perchloric Acid				
1	1.012	8261	2.16	2.88
2	1.604	19044	1.99	2.65
4	2.80	56610	1.94	2.59
8	4.50	142400	1.88	2.51
12	5.61	230800	1.96	2.60
16	6.64	375000	1.87	2.49
Trace $\text{Co}^{2+}$ ; Selectivity Terms in Perchloric Acid <sup>a</sup>				
$m_{\text{HClO}_4}$	$\bar{m}$	$K_{\text{D}}$	$K_{\text{EX}}$	$K_{\text{AC}}$
0.168	4.62	1342	1.78	3.37
0.1086	4.58	3016	1.69	2.97
0.1114	4.58	2859	1.68	2.93
0.0630	4.54	9271	1.77	2.75
0.0672	4.54	7548	1.64	2.58
0.0413	4.52	22800	1.89	2.79
0.0406	4.52	23700	1.90	2.82

<sup>a</sup> 8% DVB HR.

polystyrene-sulfonic acid is compared in Fig. 4. The selectivity coefficient in perchloric acid as was pointed out earlier is practically independent of solution phase concentration. In salt-free polystyrene-sulfonic acid, however, it is markedly lower than that measured in perchloric acid solutions and is a remarkably strong function of polyelectrolyte concentration, decreasing rapidly with decreasing

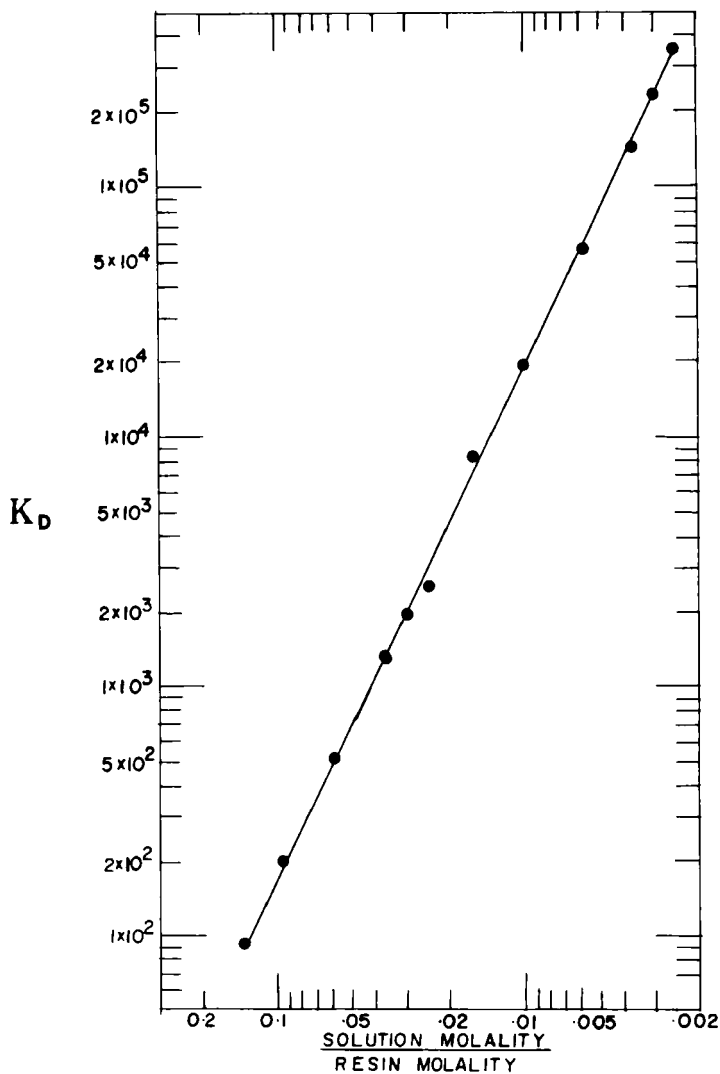


FIG. 2. Variation of the ion-exchange distribution coefficient,  $K_D$ , with the ratio of the solution molality to the resin molality for trace zinc ion, hydrogen ion, ion exchange (using polystyrene-sulfonic acid ion-exchange resins of variable cross-linkage in aqueous perchloric acid).

polyelectrolyte concentration. Furthermore, at low polyelectrolyte concentrations,  $\log K_{EX}$  decreases linearly with  $\log m_{HPSS}$ .

The average mean deviation in  $K_D$  for six  $M^{2+}-H^+$  ion-exchange

TABLE 6  
Selectivity Terms for Trace  $\text{Zn}^{2+}$  with  
Hydrogen Ion-Exchange Resin in 0.01 m  
Polystyrene-Sulfonic Acid

% DVB	$\bar{m}_{\text{H}^+}$	$K_{\text{D}}$	$K_{\text{EX}}$
1	1.012	513	0.050
2	1.604	1020	0.039
4	2.80	2730	0.035
8	4.50	6180	0.030
12	5.61	8280	0.026
16	6.64	12270	0.027

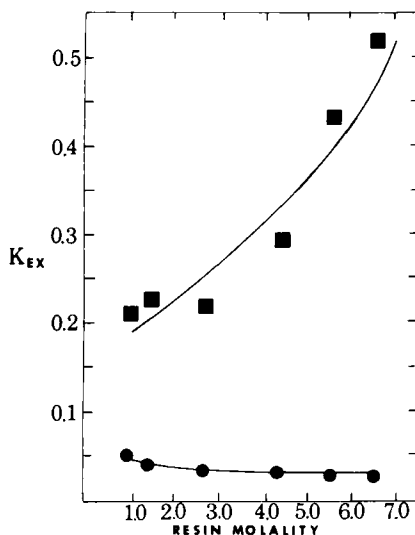


FIG. 3. Variation of the molal selectivity coefficient,  $K_{\text{EX}}$ , with resin phase concentration for the trace  $\text{Zn}^{2+}$  ion (●), hydrogen ion, ion exchange in 0.01 m polystyrene-sulfonic acid and the trace  $\text{Ca}^{2+}$  ion (■), hydrogen ion, ion exchange in 0.04 m polystyrene-sulfonic acid (using polystyrene-sulfonic acid cross-linked with divinylbenzene as the ion exchanger).

reactions with six differently cross-linked ion-exchange resins in 0.168 m  $\text{HClO}_4$  is 1.7%. Values calculated for  $K_{\text{EX}}$  and  $K_{\text{AC}}$  in this system have an estimated accuracy of 3%.

TABLE 7

Selectivity Terms for Trace  $\text{Ca}^{2+}$  with  
Hydrogen Ion-Exchange Resin in 0.04 m  
Polystyrene-Sulfonic Acid

% DVB	$\bar{m}_{\text{H}^+}$	$K_{\text{D}}$	$K_{\text{EX}}$
1	1.012	134	0.21
2	1.604	363	0.22
4	2.80	1056	0.21
8	4.50	3750	0.29
12	5.61	8580	0.43
16	6.64	14470	0.52

TABLE 8

Selectivity Terms for Trace  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Co}^{2+}$ ,  
 $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Cd}^{2+}$  with Hydrogen Ion-Exchange Resin  
in 0.01 m Polystyrene-Sulfonic Acid

% DVB	Trace $\text{M}^{2+}$	$m_{\text{H}^+}$	$K_{\text{D}}$	$K_{\text{EX}}$
1	$\text{Ca}^{2+}$	1.012	570	0.055
2	$\text{Ca}^{2+}$	1.604	1390	0.053
4	$\text{Ca}^{2+}$	2.80	4162	0.053
1	$\text{Sr}^{2+}$	1.012	551	0.053
2	$\text{Sr}^{2+}$	1.604	1478	0.057
4	$\text{Sr}^{2+}$	2.80	5073	0.064
1	$\text{Co}^{2+}$	1.012	500	0.048
2	$\text{Co}^{2+}$	1.604	1117	0.043
4	$\text{Co}^{2+}$	2.80	3226	0.041
1	$\text{Ni}^{2+}$	1.012	540	0.052
2	$\text{Ni}^{2+}$	1.604	1245	0.048
4	$\text{Ni}^{2+}$	2.80	3571	0.045
1	$\text{Zn}^{2+}$	1.012	513	0.050
2	$\text{Zn}^{2+}$	1.604	1020	0.039
4	$\text{Zn}^{2+}$	2.80	2734	0.035
1	$\text{Cd}^{2+}$	1.012	473	0.045
2	$\text{Cd}^{2+}$	1.604	1007	0.039
4	$\text{Cd}^{2+}$	2.80	3134	0.039



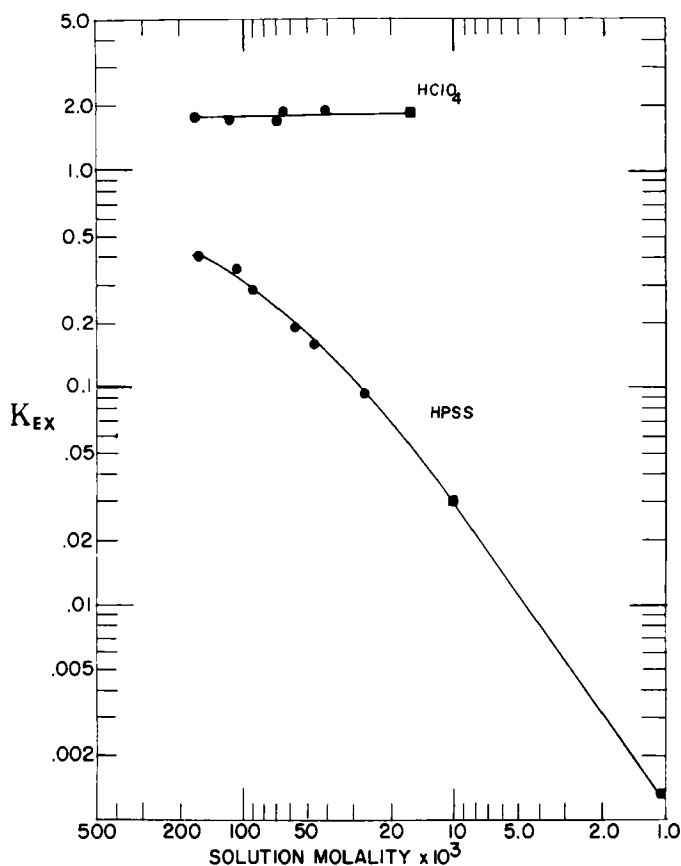


FIG. 4. Variation of the selectivity coefficient,  $K_{EX}$ , with solution phase concentration for trace cobalt (●) and zinc (■) ion, hydrogen ion, ion exchanges (using polystyrene-sulfonic acid ion exchanger cross-linked with 8% divinylbenzene equilibrated in perchloric or polystyrene-sulfonic acid solutions).

## DISCUSSION

The results obtained in this study and listed above satisfy the first objective of this research program. They provide the more extensive examination of uni- and divalent ion exchange that was sought. The second objective, a more fundamental and quantitative

TABLE 9

Selectivity Terms for Trace Cobalt-Hydrogen  
Ion Exchange with 8% DVB Polystyrene-Sulfonic Acid  
Ion-Exchange Resin in Solutions of  
Polystyrene-Sulfonic Acid

$m_{\text{HPSS}}$	$\bar{m}_{\text{HR}}$	$K_{\text{D}}$	$K_{\text{EX}}$
$0.973 \times 10^{-3}$	4.42	27060	$1.312 \times 10^{-3}$
$0.978 \times 10^{-3}$	4.42	26567	$1.298 \times 10^{-3}$
$2.41 \times 10^{-2}$	4.425	3277	$9.74 \times 10^{-2}$
$2.42 \times 10^{-2}$	4.425	2991	$8.97 \times 10^{-2}$
$4.61 \times 10^{-2}$	4.44	1494	$1.61 \times 10^{-1}$
$5.82 \times 10^{-2}$	4.45	1098	$1.88 \times 10^{-1}$
$1.060 \times 10^{-1}$	4.47	643	$3.61 \times 10^{-1}$
$0.910 \times 10^{-1}$	4.46	650	$2.86 \times 10^{-1}$
$1.628 \times 10^{-1}$	4.49	318	$4.14 \times 10^{-1}$
$1.666 \times 10^{-1}$	4.49	299	$4.12 \times 10^{-1}$

understanding of the selectivity patterns that evolve from these and other related studies, is more difficult to achieve.

Reasonably accurate corrections for deviations from ideality of the mixed simple electrolyte of the aqueous phase in the ion-exchange equilibrium studies permit computation of qualitatively meaningful  $K_{\text{AC}}$  values. The preference of divalent ion for the resin phase that is observed in the ion-exchange resin-simple electrolyte systems at every resin phase concentration studied is thus attributable to its stronger interaction with the macroion.

This interpretation is consistent with the analysis of ion-exchange selectivity patterns observed in uni-univalent anion exchange studies. A careful thermodynamic analysis of such systems showed that resin phase activity coefficients were predominantly responsible for the preferred behavior of one anion over another [2,21].

With the cations studied in this research program the interaction of counter- and macroion is believed to be exclusively electrostatic in nature. As a consequence the preference for one ion over another by the resin phase should be influenced only by the relative sizes of the competing ions. To test this estimate of the situation, in Table 10 the ionic charge-to-bare ion radius ratio,  $q/r$ , is compared with the order of the observed selectivity coefficients. The selectivity order is exactly opposite to that predicted, decreasing with increasing charge to radius ratio. This result can be rationalized only by assuming that ion exchange in polystyrene sulfonate-based ion

TABLE 10  
Order of Selectivity Coefficient Compared  
with Ionic Charge-to-Radius Ratio

Ion	Ionic radius <sup>a</sup> (in Å)	q/r	Order of selectivity
Sr <sup>2+</sup>	1.12	1.78	1 (highest K <sub>EX</sub> )
Ca <sup>2+</sup>	0.99	2.02	2
Cd <sup>2+</sup>	0.97	2.06	3
Co <sup>2+</sup>	0.72	2.78	4
Ni <sup>2+</sup>	0.69	2.90	5
Zn <sup>2+</sup>	0.74	2.70	6 (lowest K )

<sup>a</sup>M. J. Sienko and R. A. Plane, *Physical Inorganic Chemistry*, W. A. Benjamin, New York, 1963, p. 68, Table 2-4.

exchangers is controlled by hydrated cation-polyion interactions, as deduced by many earlier investigators [1].

Since macroion-counterion interactions are dominant in determining selectivity patterns the desired achievement of a more quantitative and fundamental analysis of the ion-exchange selectivity data compiled in this study requires meaningful evaluation of the thermodynamic properties of the various ion forms of the copolymer itself. Osmotic coefficient data, obtained in this laboratory for the salt-free polystyrene-sulfonic acid and its divalent salt forms over a large concentration range, are available for this purpose [24]. These data are presented in Fig. 5. At low concentrations the osmotic coefficient values of all conforms are much lower than unity. This is a characteristic property of highly charged polyelectrolytes [30]. In the case of the divalent ion forms the osmotic coefficient reaches a constant low value which is unaffected by further dilution. At high concentration the osmotic coefficient of all ion forms increases with concentration paralleling the rise in osmotic coefficient that characterizes simple electrolytes [28]. This rapid increase in the value of the osmotic coefficient of simple electrolyte is a consequence of ion-solvent interactions [31] and is undoubtedly the dominant contributing factor in the enhancement of osmotic coefficient values in the polyelectrolyte systems as well [1]. This confirmation of sizable ion-solvent interaction is consistent with the earlier correlation of selectivity order with hydrate ion size.

The osmotic coefficient data that were obtained for the polystyrene-

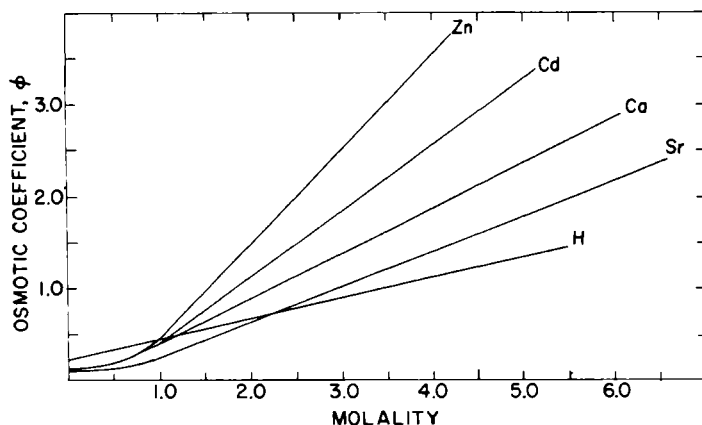


FIG. 5. Concentration dependence of the molal osmotic coefficient,  $\phi$ , for polystyrene-sulfonic acid and several of its divalent metal salts in aqueous solution.

sulfonic acid are independent of molecular weight. Values obtained with samples having an average molecular weight of 40,000 and 500,000, respectively, were the same within the small experimental error range of the measurements. In addition, the two sets of osmotic coefficient values essentially converge with osmotic data obtained over the higher concentration range in an earlier study using a <0.5% DVB copolymer of polystyrene-sulfonic acid [18]. These facts combined with the estimate of resin phase homogeneity, deduced from the regular selectivity trends that are observed (see Fig. 1), justify the use of the Gibbs-Duhem equation for estimate of thermodynamic parameters for each of the various ion forms of the linear and cross-linked polyelectrolytes.

By assigning the same standard state to each component in the two phases at equilibrium the thermodynamic equilibrium distribution constant for each component is unity and

$$\ln K_{AC} = \ln \frac{\bar{\gamma}_{\pm}^2 H^+ (HClO_4)}{\bar{\gamma}_{\pm M^{2+}} (M (ClO_4)_2)} \quad (8)$$

for the ion-exchange resin, simple electrolyte equilibrium, whereas

$$\ln K_{EX} = \ln \frac{(\bar{\gamma}_{\pm H^+})^2 (\gamma_{\pm M^{2+}})}{(\bar{\gamma}_{\pm M^{2+}}) (\bar{\gamma}_{\pm H^+})^2} \quad (9)$$

for the ion-exchange resin, linear polyelectrolyte equilibrium.

In the ion-exchange resin-simple electrolyte system the term  $\gamma_{\pm}^2 \text{ClO}_4 (\text{HClO}_4) / \gamma_{\pm}^2 \text{ClO}_4 (\text{M} (\text{ClO}_4)_2)$  is common to both components and cancels. Since in the experimental program  $\text{PSS} \gg \text{ClO}_4$ , the effect of  $\text{ClO}_4$  on the chemical potential of the polyelectrolyte is negligible. The deviation from ideal behavior of the exchanging cations is then related to their unavailable single ion activity coefficients by the ratio of the mean molal activity coefficients of the pure components since

$$(\gamma_{\text{M}}^Z \gamma_{\text{P}})^{1/(Z+1)} = \gamma_{\pm} \approx \gamma_{\text{M}}$$

where  $Z$  is the degree of polymerization and is much greater than unity.

A differential form of the Gibbs-Duhem equation [28],

$$(d\phi/d \ln m) + (\phi - 1) = (d \ln \gamma/d \ln m) \quad (10)$$

has been used first with the osmotic coefficient data to interpret the selectivity measurements made using the 8% DVB-PSS copolymer ion-exchange resin in salt-free polystyrene-sulfonic acid solutions. By using one resin form while varying the concentration of polyelectrolyte the resin phase activity coefficients [32] are held constant. The observed change in selectivity coefficient then reflects the changes in the solution activity coefficients with concentration. At the low polyelectrolyte concentrations used for the selectivity measurements the osmotic coefficient of the various ion forms of the polyelectrolyte is essentially constant (see Fig. 5). The differential form of the Gibbs-Duhem equation which evolves for this situation is

$$\frac{d \ln K_{\text{EX}}}{d \ln m_{\text{PSS}}} = (\phi_{\text{M}^{2+}} - 1) - 2(\phi_{\text{H}^+} - 1) \quad (11)$$

and the linear decrease in  $\ln K$  with  $\ln m_{\text{PSS}}$  that is observed in Fig. 4 is predicted. The calculated slope (0.66) does not agree with the experimental value (1.32). This result is undoubtedly a consequence of the influence of the potential determining  $\text{H}^+$  ion on the "condensation" of the trace metal ion at low polyelectrolyte concentrations. As the polyelectrolyte concentration increases the calculated slope approaches the experimental value suggesting that the  $\text{M}^{2+}$ - $\text{H}^+$  interactions occurring in dilute polyelectrolyte solutions are effectively screened at the high polyelectrolyte concentrations encountered in the ion-exchange resin. If this is the case the integrated form of the Gibbs-Duhem equation, given below, should be useful for prediction of the trace, divalent hydrogen ion-exchange equilibria:

$$\ln \frac{\gamma_{\pm m}}{\gamma_{\pm m \text{ ref}}} = \phi_m - \phi_{m \text{ ref}} + \int_{m \text{ ref}}^m (\phi - 1) d \ln m \quad (12)$$

Evaluation of the integral in this equation has been accomplished graphically by using a polar planimeter. Results of this calculation give  $\gamma_m/\gamma_{m \text{ ref}}$ , the resin phase activity coefficient at the concentration of the ion exchanger divided by the activity coefficient at the reference concentration. The term  $\gamma_{\pm m \text{ ref}}^2 (H^+)/\gamma_{\pm m \text{ ref}} (M^{2+})$  that is needed to complete the computation is unavailable because of the unattainability of osmotic data at lower polyelectrolyte concentrations. At some very low concentration the value of  $\phi$  must rise and approach unity at infinite dilution [33].\* This term has been estimated from the observed modified selectivity coefficient obtained with the 1% DVB cross-linked ion-exchange resin, and the modified selectivity coefficients, calculated for the divalent hydrogen ion-exchange equilibria, are compared in Table 11 with the experimental values. Selectivity trends are, indeed, predictable from this analysis, and the good correlation between the experimental and calculated  $K_{AC}$  values justifies the use of the polyelectrolyte analog for estimate of the thermodynamic properties of ion-exchange resins and their equilibria.

## CONCLUSION

The results of this investigation, both experimental and correlative, suggest that the ion-exchange resins employed in this study were essentially homogeneous. Selectivity coefficients (in perchloric

\*There is divided opinion with regard to the correctness of this statement. However, since the Gibbs-Duhem equation is proven to apply to polyelectrolytes in this study, the persistence of low  $\phi$  values with increasingly dilute systems suggests an infinitely small activity coefficient at infinite dilution implying minute activity coefficients at finite concentration. The effect of polyelectrolyte on the colligative properties of their aqueous solutions does not correspond to this estimate of the situation suggesting that osmotic coefficients must eventually rise at concentrations unaccessible to experiment. In addition, theoretical models (e.g., the rigid cylindrical rod) must break down in very dilute systems because the rod is never infinitely long and the actual length must eventually be much less than the distance between strands. As a consequence, predictions based on the cylindrical model are not valid. Eventually at sufficient dilution a spherical model is most appropriate and the Debye-Hückel formalization most likely applies. One can expect as a consequence the standard result.

TABLE 11  
Calculated and Experimental Values of the Modified  
Molal Selectivity Coefficient for Trace Divalent Ion,  
Hydrogen Ion, Ion-Exchange Reactions  
in 0.168 m Perchloric Acid

% DVB	$\overline{m}_{H^+}$	$(\gamma_{H^+}/\gamma_{H^+ \text{ ref}})^2$	$\gamma_{H^{2+}}$	K <sub>AC</sub>
		$\gamma_{M^{2+}}/\gamma_{M^{2+} \text{ ref}}$	$\gamma_{H^{2+}}$	
Trace Sr <sup>2+</sup>				
1	1.236	0.288	6.09	6.09
2	1.808	0.300	6.35	6.80
4	2.95	0.354	7.48	8.17
8	4.62	0.655	13.80	12.38
12	5.72	0.926	19.56	20.7
16	6.91	1.425	30.0	24.9
Trace Ca <sup>2+</sup>				
1	1.236	0.275	3.97	3.97
2	1.808	0.324	4.67	4.91
4	2.95	0.404	5.82	5.67
8	4.62	0.642	9.25	7.45
12	5.72	0.894	12.9	11.40
16	6.91	1.159	16.7	13.80
Trace Zn <sup>2+</sup>				
1	1.236	0.192	3.26	3.26
2	1.808	0.250	4.24	3.32
4	2.95	0.216	3.66	3.19
8	4.62	0.184	3.12	3.27
12	5.72	0.153	2.70	3.15
16	6.91	0.125	2.12	2.85
Trace Cd <sup>2+</sup>				
1	1.236	0.261	3.45	3.45
2	1.808	0.307	4.06	3.59
4	2.95	0.334	4.32	3.72
8	4.62	0.400	5.30	4.15
12	5.72	0.414	5.87	4.82
16	6.91	0.473	6.25	5.03

acid solutions) for the divalent, hydrogen ion exchange are only slightly dependent on external solution concentration because of

changes in activity coefficient ratios in the aqueous phase. Several different selectivity trends with increasing resin phase concentration are observed with the different divalent ions, resin phase activity coefficients being controlled by hydrated cation-polyion interactions. The effect of such interaction in producing these trends can be estimated by a thermodynamic analysis that employs osmotic data for the polyelectrolyte analog of the ion exchanger in the Gibbs-Duhem equation. The experimental selectivity coefficient trends for six different divalent metal ions have been accurately predicted by this approach over a large resin phase concentration range.

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### REFERENCES

- [1] J. A. Marinsky, ed., *Ion Exchange*, Vol. 1, Dekker, New York, 1966.
- [2] F. Helfferich, *Ion Exchange*, McGraw-Hill, New York, 1962.
- [3] G. E. Boyd, F. Vaslow, and S. Lindenbaum, *J. Phys. Chem.*, **71**, 2214 (1967).
- [4] T. R. E. Kressman and J. A. Kitchener, *J. Chem. Soc.*, p. 1201 (1949).
- [5] O. D. Bonner and F. L. Livingston, *J. Phys. Chem.*, **60**, 530 (1956).
- [6] O. D. Bonner and L. L. Smith, *J. Phys. Chem.*, **61**, 326 (1957).
- [7] O. D. Bonner and L. L. Smith, *J. Phys. Chem.*, **61**, 1614 (1957).
- [8] K. A. Kraus and R. J. Raridon, *J. Phys. Chem.*, **63**, 1901 (1959).
- [9] H. P. Gregor, O. R. Abolafia, and M. H. Gottlieb, *J. Phys. Chem.*, **58**, 984 (1954).
- [10] A. S. Tombalakian, C. Y. Yeh, and W. F. Graydon, *J. Phys. Chem.*, **71**, 435 (1967).
- [11] S. A. Rice and F. E. Harris, *Z. Physik. Chem. (Frankfurt)*, [N.F.] **8**, 207 (1956).
- [12] E. H. Cruickshank and P. Meares, *Trans. Faraday Soc.*, **53**, 1289 (1957).
- [13] J. H. B. George and R. A. Courant, *J. Phys. Chem.*, **71**, 246 (1967).
- [14] A. E. Lagos and J. A. Kitchener, *Trans. Faraday Soc.*, **56**, 1245 (1960).



- [15] C. Eger, W. M. Anspach, and J. A. Marinsky, *J. Inorg. Nucl. Chem.*, **30**, 1899 (1968).
- [16] C. Eger, J. A. Marinsky, and W. M. Anspach, *J. Inorg. Nucl. Chem.*, **30**, 1911 (1968).
- [17] B. Soldano and Q. V. Larson, *J. Am. Chem. Soc.*, **77**, 1331 (1955).
- [18] B. Soldano and D. Chesnut, *J. Am. Chem. Soc.*, **77**, 1334 (1955).
- [19] B. Soldano, Q. V. Larson, and G. E. Myers, *J. Am. Chem. Soc.*, **77**, 1339 (1955).
- [20] G. E. Myers and G. E. Boyd, *J. Phys. Chem.*, **60**, 521 (1956).
- [21] G. E. Boyd, S. Lindenbaum, and G. E. Myers, *J. Phys. Chem.*, **65**, 577 (1961).
- [22] E. Glueckauf, *Proc. Roy. Soc. (London)*, **A214**, 207 (1952).
- [23] J. F. Duncan, *Australian J. Chem.*, **8**, 293 (1955).
- [24] M. M. Reddy, J. A. Marinsky, and A. Sakar, *J. Phys. Chem.*, **74**, 3891 (1970).
- [25] J. A. V. Butler, A. B. Robins, and K. V. Shooter, *Proc. Roy. Soc. (London)*, **A241**, 299 (1957).
- [26] M. M. Reddy and J. A. Marinsky, *J. Phys. Chem.*, **74**, 3884 (1970).
- [27] M. S. Patterson and R. C. Greene, *Anal. Chem.*, **37**, 854 (1965).
- [28] R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, 2nd Revised Ed., Butterworth, London, 1965.
- [29] J. M. Stokes and R. H. Stokes, *J. Phys. Chem.*, **67**, 2442 (1963).
- [30] S. A. Rice and M. Nagasawa, *Polyelectrolyte Solutions*, Academic, New York, 1961, Chap. 8.
- [31] R. H. Stokes and R. A. Robinson, *J. Am. Chem. Soc.*, **70**, 1870 (1948).
- [32] H. P. Gregor, *J. Am. Chem. Soc.*, **73**, 642 (1951).
- [33] F. Oosawa, *J. Polymer Sci.*, **23**, 421 (1957).

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