

with carbon disulfide<sup>21</sup> is tetrafluoromethane, also the result of cleavage of both carbon-sulfur bonds of the carbon disulfide molecule. It is only in the electrochemical fluorination of carbon disulfide in anhydrous hydrogen fluoride<sup>17</sup> and in the fluorination of carbon disulfide with nitrogen-diluted fluorine gas<sup>18</sup> that perfluoroalkyl molecules with both carbon-sulfur bonds intact are produced, *e.g.*,  $\text{CF}_2(\text{SF}_6)_2$ ,  $\text{CF}_2(\text{SF}_3)_2$ , and  $\text{SF}_3\text{CF}_2\text{SF}_5$ .

In a comparison of the reactions of cobalt trifluoride and fluorine with ketones, Holub and Bigelow<sup>22</sup> found that the two fluorinating agents differed with respect to the type of compounds produced. The products of reaction with cobalt trifluoride were all formed by cleavage of the ketone molecule, whereas some of the products of reaction with fluorine were not formed by

cleavage. In this respect the reaction of fluorinating agents with ketones is similar to the reaction of fluorinating agents with carbon disulfide. Holub and Bigelow<sup>22</sup> explained their results on the basis of a difference between the fluorination mechanisms of cobalt trifluoride and of fluorine. Although perfluoroalkyl molecules with both carbon-sulfur bonds intact are not the predominant products of the reaction of fluorine with carbon disulfide, their formation indicates that the mechanism of the fluorination of carbon disulfide with fluorine probably differs fundamentally from the mechanism of the fluorination of carbon disulfide with covalent fluorides.

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(21) R. Wagner, W. Shinn, and W. Gunther, U. S. Atomic Energy Comm., ANL-6687, Chemical Engineering Division Summary Report, Jan.-Mar., 1963.

(22) F. F. Holub and L. A. Bigelow, *J. Am. Chem. Soc.*, **72**, 4879 (1950).

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## Ion-Exchange Studies in Concentrated Solutions. I. The Alkali Cations with a Sulfonic and a Carboxylic Acid Resin<sup>1</sup>

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An investigation of the cation-exchange behavior on Dowex-50W (sulfonic acid type) and Bio-Rex 70 (carboxylic acid type) resins of Na, Rb, and Cs tracers in 0.1 *M* to saturated solutions of  $\text{LiClO}_4$ ,  $\text{LiCl}$ ,  $\text{LiNO}_3$ ,  $\text{LiC}_2\text{H}_3\text{O}_2$ , and of the corresponding acids and of  $\text{CsCl}$  on Dowex-50W, has been made. The exchange in dilute solutions is discussed in terms of the competition for solvation of the cation between water and the resin anionic groups. As the aqueous phase concentration rises, deviations from the simple mass-action law behavior occur; these deviations are explained in terms of the decreasing water activity, increasing cation-anion interactions in both the resin and aqueous phases, and resin invasion by nonexchange aqueous electrolyte. Individual differences among the various salts and acids are related to the different water activities and extent of anion-cation interactions present in the aqueous phase, and the variation of resin selectivity with the nature of the exchange group is treated in terms of the varying complexing ability for cations shown by the different resin anions.

### Introduction

The selectivity of a moderately cross-linked sulfonic (strong) acid type cation-exchange resin for alkali and hydrogen ions in dilute aqueous solution is  $\text{Li}^+ < \text{H}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$ ; a discussion of the various models which have been advanced to explain this order is given in a recent book by Helfferich.<sup>2</sup> It has been noted, however, that in concentrated solutions of strong acids,  $\text{HCl}$ ,<sup>3,4</sup>  $\text{HBr}$ ,<sup>4</sup> and  $\text{HClO}_4$ ,<sup>4</sup> this order becomes reversed, and a reversal has been reported for 13 *M*  $\text{LiCl}$ ,<sup>5,6</sup> also. In the original discussion of the reversal of the elution order in concentrated  $\text{HCl}$  solutions<sup>3</sup> it was suggested that disruption of the solvation shell of

the ions, that is, ion dehydration, was the principal reason for the inversion, with the invasion of the resin by nonexchange electrolyte, the shrinkage of the resin, and possible interaction with the chloride anions playing secondary roles.

In order to investigate more fully the effects of the water activity and of the nature of the anion on this reversal, a study of the distribution of sodium and cesium, and in some cases rubidium, tracers between a strong (sulfonic) acid resin and solutions of  $\text{HClO}_4$ ,  $\text{HNO}_3$ ,  $\text{HCl}$ , and  $\text{HC}_2\text{H}_3\text{O}_2$ , as well as of their corresponding lithium salts, and of  $\text{CsCl}$ , has been performed and is reported upon herein. During the course of this work, studies of the  $\text{HClO}_4$ <sup>4</sup> and of the  $\text{LiCl}$ <sup>5</sup> systems appeared in the literature, and the results are in general agreement with the present work, although we believe more definite conclusions can be drawn from the wider scope of this paper.

Another factor which influences the selectivity of the

(1) This work was supported by the U. S. Atomic Energy Commission.

(2) F. Helfferich, "Ion Exchange," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(3) R. M. Diamond, *J. Am. Chem. Soc.*, **77**, 2978 (1955).

(4) G. R. Choppin and R. H. Dinius, *Inorg. Chem.*, **1**, 140 (1962).

(5) W. A. Platek and J. A. Marinsky, *J. Phys. Chem.*, **65**, 2113 (1961).

(6) H. Kakihana, N. Maruichi, and N. Namasaki, *ibid.*, **60**, 36 (1956).

resin for various cations is the nature of the anionic group affixed to the resin matrix. To illustrate the magnitude of this effect, the Li salts described above were used to elute Na and Cs tracers from a polyvinyl carboxylic acid resin and the results compared with those obtained for the sulfonic acid resin and with previously reported work using other weak acid exchangers.

### Experimental

**Reagents.**—The cation-exchange resins were Dowex AG 50W-X12, 50–100 mesh, a styrene-based sulfonic acid exchanger, and Bio-Rex 70 (refined Duolite CS-101), 50–100 mesh, a polyvinyl carboxylic acid exchanger, both obtained from Bio-Rad Laboratories, Richmond, Calif. The capacity of the Dowex-50W was 5.2 mequiv./g. of dry resin, and its water uptake was 0.75 g. of water/g. of dry resin; the Bio-Rex 70 figures were 10.0 and 1.00, respectively. The salt and acid solutions were prepared by volumetric dilution of accurately analyzed concentrated solutions of reagent grade material [except CsCl, which was 95% CsCl + 5% (RbCl + KCl)] with distilled H<sub>2</sub>O. The Na<sup>22</sup> tracer (as carrier-free NaCl) was purchased from Nuclear Science and Engineering Corp., Pittsburgh, Pa.; the Na<sup>24</sup> (as NaHCO<sub>3</sub>) and Rb<sup>86</sup> (as RbNO<sub>3</sub>) tracers were produced in the Livermore pool-type reactor, Lawrence Radiation Laboratory, Livermore, California; and the Cs<sup>137</sup> (carrier-free) tracer was obtained from the Lawrence Radiation Laboratory Health Chemistry Source Preparation Department.

**Procedure.**—Batch measurements were made by placing 0.1000 g. of Dowex-50W resin and 10.00 ml. of a salt or acid solution of known tracer concentration in a 30-ml. polyethylene bottle with a polyethylene screw top and shaking for 4 hr. Two 2.00-ml. samples were removed through fritted glass filters and  $\gamma$ -counted using a well-type Na(Tl)I scintillation crystal and a single-channel pulse-height analyzer. The distribution ratio was calculated as

$$D = \frac{(\text{vol. of equilibrated soln.})}{(\text{wt. of dry resin})} \times \frac{(\text{counts/min./ml. of init. soln.} - \text{counts/min./ml. of equil. soln.})}{(\text{counts/min./ml. of equil. soln.})} \quad (1)$$

where the solution volume is in milliliters and the resin weight is in grams. The resin used in the batch experiments had been previously washed with HCl and distilled water and dried over Mg(ClO<sub>4</sub>)<sub>2</sub>. Variation of the shaking time over the period 1–24 hr. showed no appreciable difference in *D*, establishing that equilibrium had been attained.

For the Dowex-50W column determinations several adjustable-head ion-exchange columns were prepared. Elution volumes from these different columns were normalized to one standard column, and the normalization factors agreed in all cases with the weights of resin used. The standard column was 31.4 cm. in length, 0.42 cm. in diameter, and contained 2.64 g. of (dry) resin. Each column was washed first with >20 column volumes of 6 *M* HClO<sub>4</sub> and then with >20 column volumes of the salt or acid solution under investigation in order to convert it to the desired ionic form. In order to minimize swelling and shrinking differences in the resin column as the solution concentration was changed, a relatively high (X12) cross-linked resin was used, and pre-shrinking with 6 *M* HClO<sub>4</sub> eliminated any significant further shrinkage at higher solution concentrations. A glass wool plug was used to prevent flotation of the resin in concentrated solutions and to keep the total volume of the column constant.

The Bio-Rex 70 determinations were all done on one column, similar to the standard column described above and containing 1.07 g. of (dry) resin. The resin was first washed with 8 *M* LiCl to convert it from the Na to the Li form and was loaded into

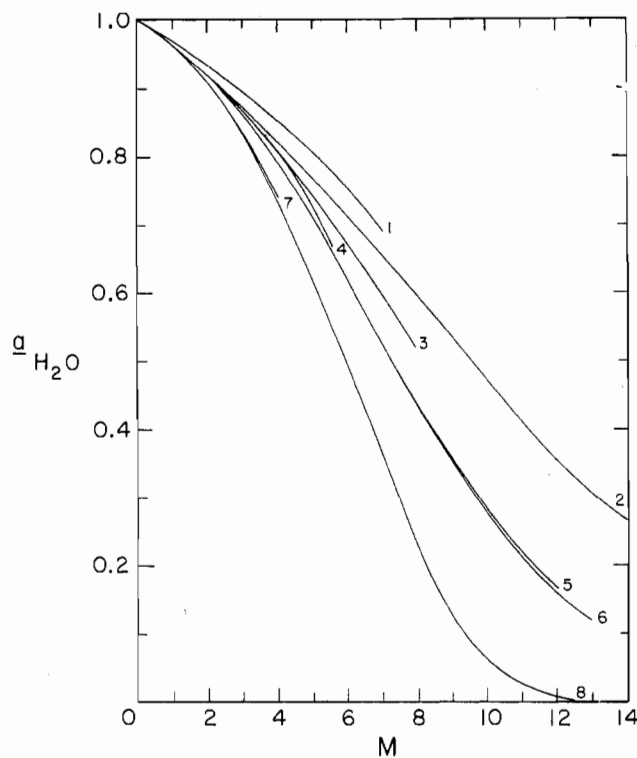


Fig. 1.—Variations of water activity with aqueous molarity (R. A. Robinson and R. M. Stokes, "Electrolyte Solutions," Butterworth Scientific Publications, London, 1955) of: 1, CsCl; 2, HNO<sub>3</sub> ("Landolt-Börnstein Tables," Springer-Verlag Berlin, 1923, Supplement 3, Part 3, p. 2145); 3, LiNO<sub>3</sub>; 4, LiOAc; 5, HCl; 6, LiCl; 7, LiClO<sub>4</sub>; 8, HClO<sub>4</sub>.

the column with 8 *M* LiCl. Glass wool plugs were placed above and below the resin bed.

The volume of solution necessary to elute a tracer ion from the column was determined by placing 10  $\mu$ l. of the tracer ion solution on the glass wool plug, allowing it to sink into the plug, and immediately beginning the elution of the tracer at a flow rate of <1 drop/min. The elution volume was observed to be independent of the flow rate under these conditions, indicating that equilibrium conditions were being closely approximated. Successive fractions were collected through the use of a photoelectric drop counter and  $\gamma$ -counted as in the batch determinations; the fraction with the highest number of counts corresponds to the peak elution volume.

Most of the column determinations were made using two or three tracers at the same time in order to keep the conditions for the different tracers as alike as possible, especially in the cases where the elution volumes for two tracers were very similar. Two or more determinations were made in almost every case for each tracer in each solution. The ratios of the *D* values for Na<sup>+</sup> and Cs<sup>+</sup> obtained with 0.1 *M* solutions by the batch and the column methods were the same, indicating the equivalence of the procedures.

All experimental work was done at room temperature, 23  $\pm$  2°.

### Results

The variation of peak elution volume (as ml. of solution) with molarity of the salt or acid solution for Na, Rb, and Cs tracers is shown in Fig. 2–13. These volumes have an amount subtracted corresponding to the volume of solution in the column system external to the resin phase, that is, to the interstitial column volume. For the standard Dowex-50W column this

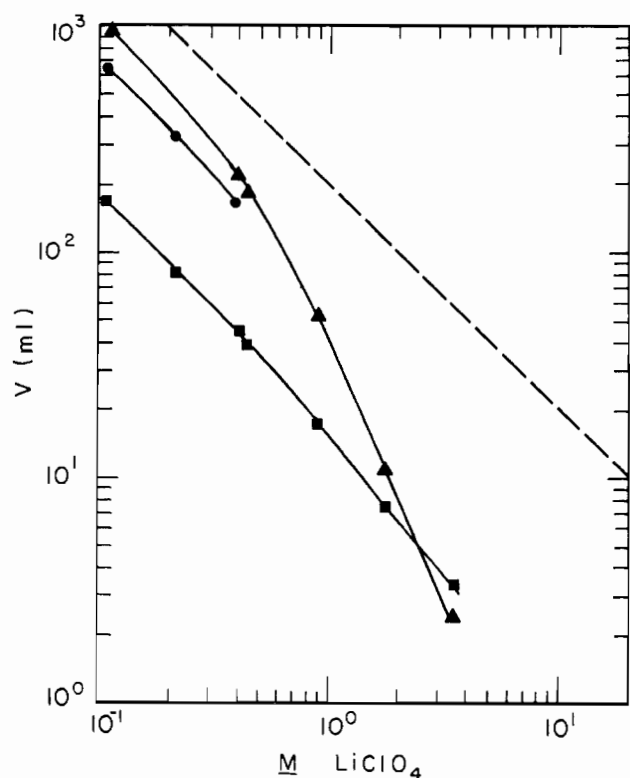


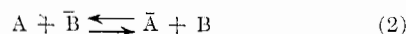
Fig. 2.—Corrected peak elution volume,  $V$  (ml.) on Dowex-50W vs.  $\text{LiClO}_4$  molarity for alkali tracers: ■, Na; ●, Rb; ▲, Cs; — — —, slope  $-1.0$ .

interstitial volume ranged from 1.31 ml. in 0.1  $M$  solution (as determined by the elution of  $\text{I}^-$  tracer) to 1.6 ml. in 10  $M$   $\text{HClO}_4$  (asymptotic value for  $\text{Cs}^+$  tracer elution), while for the Bio-Rex 70 column the value ranged from 1.65 ml. in 0.1  $M$   $\text{LiClO}_4$  to 2.70 ml. in concentrated  $\text{LiClO}_4$ ,  $\text{LiNO}_3$ , and  $\text{LiCl}$ . The reproducibility in the column runs was  $\pm 0.1$  ml. or  $\pm 5\%$ , whichever was the larger.

Distribution ratios from the batch experiments on Dowex-50W have been converted to peak elution volumes for the standard column by multiplying by the factor 2.64 (the weight, in grams, of dry resin in the column). This number agreed with the factor obtained by directly comparing several batch distribution ratios and column elutions at the same aqueous phase concentration; in general, batch methods were used whenever the elution volume exceeded 200 ml.

### Discussion

The equation for the exchange of an alkali ion,  $\text{A}^+$ , with a monovalent cation,  $\text{B}^+$ , on an ion-exchange resin may be written



where charges and ion hydration have been omitted for simplicity and the superscript bar denotes the resin phase. The corresponding equilibrium constant is

$$K = \frac{(\bar{\text{A}})(\text{B})}{(\text{A})(\bar{\text{B}})} = \frac{[\bar{\text{A}}][\text{B}]\gamma_{\text{A}}\gamma_{\text{B}}}{[\text{A}][\bar{\text{B}}]\gamma_{\text{A}}\gamma_{\text{B}}} \quad (3)$$

where parentheses denote activity, brackets indicate

concentration in arbitrary units, and  $\gamma$  is the corresponding species activity coefficient.

For dilute aqueous solutions (below 0.1  $M$ ) and when the alkali ion is present in only tracer quantities, it is possible to make two simplifying assumptions concerning eq. 3. The first is that the ratio of the activity coefficients in the aqueous phase,  $\gamma_{\text{B}}/\gamma_{\text{A}}$ , will remain constant over the dilute concentration range of B employed. The second is that there is negligible change in the water activity and negligible resin invasion with the dilute electrolyte solutions, that is, negligible non-exchange electrolyte enters the resin phase, so that  $[\bar{\text{B}}]$  remains constant. This implies that the activity coefficient ratio in the resin phase also remains constant, since for constant  $[\bar{\text{B}}]$ ,  $\bar{\gamma}_{\text{B}}$  is constant, and  $\bar{\gamma}_{\text{A}}$  has a characteristic constant value as long as  $[\bar{\text{A}}]$  is in tracer concentration (Harned's rule).

We may now choose our concentration units for the resin phase as millimoles (or counts) per g. of (dry) resin, and for the aqueous phase as millimoles (or counts) per ml. of solution, or molarity. Then

$$K[\bar{\text{B}}] \frac{\bar{\gamma}_{\text{A}}\gamma_{\text{B}}}{\gamma_{\text{A}}\bar{\gamma}_{\text{B}}} = C^{\text{dil}} = \frac{[\bar{\text{A}}][\text{B}]}{[\text{A}]} \quad (4)$$

where  $C^{\text{dil}}$  is a constant under our dilute aqueous phase assumptions. From the plate theory of Mayer and Tompkins<sup>7</sup> the distribution ratio,  $D$ , can be related to column elution behavior, that is, to the corrected peak elution volume, by the relationship

$$D = \frac{[\bar{\text{A}}]}{[\text{A}]} = \frac{\text{ml. of soln. in corrected peak elution vol.}}{\text{g. of (dry) resin in column}} \quad (5)$$

which when substituted in eq. 4 yields

$$C^{\text{dil}} = D[\text{B}] = \frac{\text{ml. of soln. in corrected peak elution vol.}}{\text{g. of (dry) resin in column}} [\text{B}] \quad (6)$$

For a particular column (weight of resin), and abbreviating the corrected peak elution volume to  $V$  (ml.), this reduces to

$$\text{constant} = [\text{B}]V \text{ (ml.)} \quad (7)$$

and taking logarithms and rearranging

$$\log V \text{ (ml.)} = -\log [\text{B}] + \log \text{constant} \quad (8)$$

As shown in Fig. 2-13, the log-log plots of corrected peak elution volume,  $V$  (ml.), vs. solution molarity,  $[\text{B}]$ , for each of the tracers with each of the solutions used (with the exception of  $\text{HAc}$ ) either has or approaches a slope of  $-1.0$  at the lowest solution concentration employed (0.1  $M$ ), as required by eq. 8. This result is an example of the familiar mass-action effect in dilute solution exchange. However, it may be noted that as the concentration increases, each of these lines sooner or later deviates from slope  $-1.0$ , indicating the breakdown of one or both of the assumptions used in deriving eq. 4. Since the assumptions were made specifically for dilute solutions, it is not surprising that they should become invalid. In fact, it is probably more surprising that in some cases the slope of  $-1.0$  holds up to con-

(7) S. W. Mayer and E. R. Tompkins, *J. Am. Chem. Soc.*, **69**, 2866 (1947).

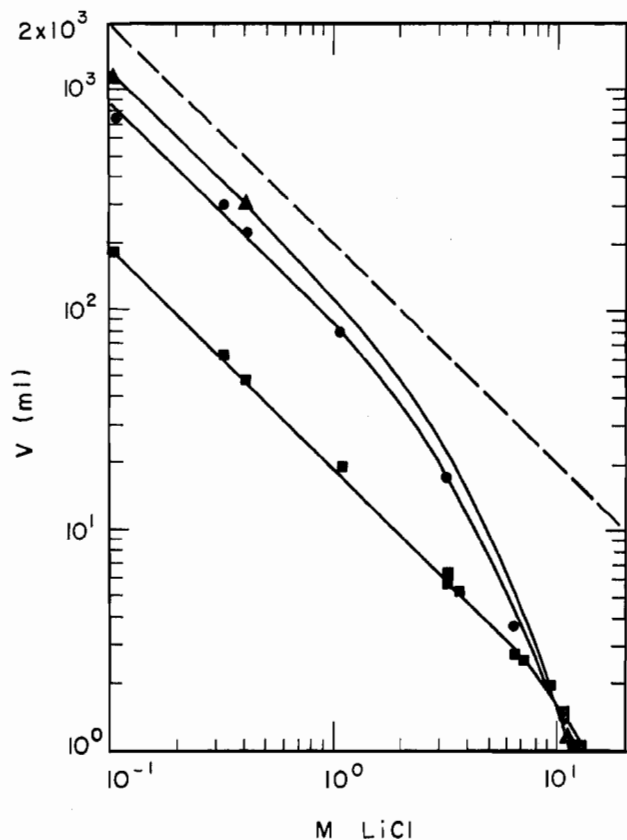


Fig. 3.—Corrected peak elution volume  $V$  (ml.) on Dowex-50W vs. LiCl molarity for alkali tracers: ■, Na; ●, Rb; ▲, Cs; — — —, slope  $-1.0$ .

concentrations as high as several molar. For moderately cross-linked resins, resin invasion is known to become appreciable when the external aqueous solution is at concentrations above 1  $M$  and may even lead, for concentrated solutions, to a nonexchange electrolyte concentration in the resin phase comparable to that of the resin sites themselves. Also, aqueous activity coefficients begin to diverge appreciably from each other above 1  $M$  concentration, causing the activity coefficient ratios to deviate increasingly from a constant value. It thus becomes necessary to modify the description of ion exchange used in the dilute solution case and to consider the additional types of interactions present in concentrated solutions which can contribute to a deviation from the mass-action law.

Since the aqueous solution behavior of even simple binary electrolytes at high concentrations still defies quantitative interpretation, it is obvious that the more complicated two-phase ion-exchange systems can only be discussed in qualitative terms at this stage in our knowledge. Nevertheless, as will be seen in this and succeeding papers, a few ideas suffice to explain the gross behavior of ion-exchange resin systems with concentrated solutions, at least when involving simple, inert-gas-core ions such as those of the alkalis, alkaline and rare earths, and halides.

Our starting point is to consider the possible interactions involving a cation in an aqueous solution. Because of its positive charge, the cation will tend to surround itself with a negatively charged atmosphere or

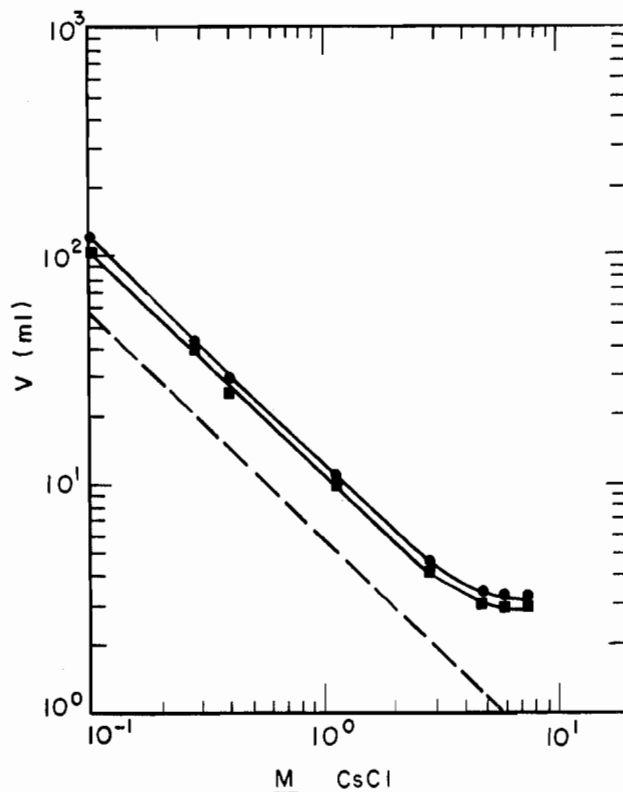


Fig. 4.—Corrected peak elution volume  $V$  (ml.) on Dowex-50W vs. CsCl molarity for alkali tracers: ■, Na; ●, Rb; — — —, slope  $-1.0$ .

the negative ends of polar molecules, *i.e.*, to solvate itself with electron-rich species. To do this, it can interact with the water molecules (ion hydration) or with the anions present (complex formation) or both. The effect of the water-water interactions, that is, of the hydrogen-bonded water structure, will be relatively unimportant when dealing with ions for which ion hydration is significant, as is the case with the alkali ions and is certainly true for more highly charged species, and so will be neglected in this paper. (This last factor becomes important for large, poorly hydrated ions such as the tetraalkylammonium ions,  $\text{ClO}_4^-$ ,  $\text{AuCl}_4^-$ , and other halometallic complex ions, etc.<sup>8</sup>)

Thus the two most important effects are those of ion hydration and complex formation. There is a competition between the water molecules and the anions to solvate the cations. Because, in dilute solution, the cations and anions, on the average, are far apart, and because there is an overwhelming preponderance of water molecules, the latter usually predominate in solvating the cation (unless there is a strong chemically-bonded complex possible). A cation-anion interaction must also be present, namely, the electrostatic interaction which leads to the Debye-Hückel environment of anions,<sup>9</sup> but the most important effect in the dilute aqueous phase is the ion-water interaction.

The situation is somewhat different in the resin phase. Restricting the discussion for the moment to a sulfonic

(8) D. C. Whitney and R. M. Diamond, *J. Inorg. Nucl. Chem.*, **24**, 1405 (1962).

(9) P. Debye and E. Hückel, *Physik Z.*, **24**, 185 (1923).

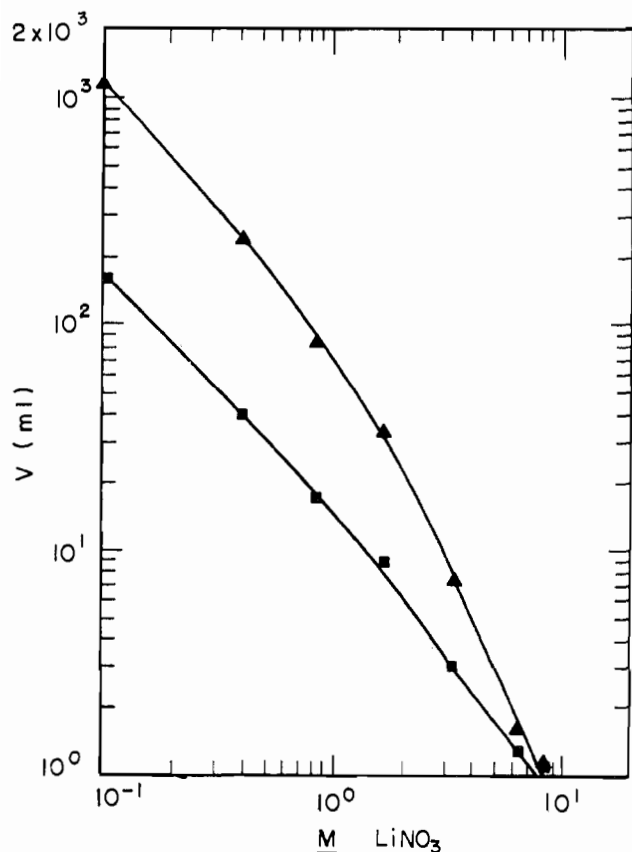


Fig. 5.—Corrected peak elution volume  $V$  (ml.) on Dowex-50W vs.  $\text{LiNO}_3$  molarity for alkali tracers:  $\blacksquare$ , Na;  $\blacktriangle$ , Cs; ———, slope  $-1.0$ .

acid resin of the usual range of cross linking, the internal solution corresponds to a concentrated electrolyte solution of 4–7  $M$ . Due to the spatial limitations imposed by the resin hydrocarbon matrix and to the smaller number of water molecules available per ion in the resin phase, a cation cannot organize as complete a hydration shell there as in the dilute external phase. This may be partially compensated for by the resin sulfonate anion taking part in the cation solvation; the concentration of resin anions is much larger than the anion concentration in a dilute external aqueous solution, so that cation-anion contacts will be more numerous and their interactions more important. Such interactions will be further enhanced by the lower effective dielectric constant of the resin phase,<sup>8</sup> but since sulfonate is a poorer solvating agent than water,<sup>10</sup> the net result is still that a (hydrated) cation can achieve more complete solvation in a dilute aqueous phase than in the concentrated resin sulfonate phase. Thus, in an ion-exchange reaction involving alkali cation (or more highly hydrated ions) in dilute solution, the crystallographically smaller ion, with the greater requirement for solvation, will favor the dilute external phase and will push the crystallographically larger ion, which has less need of solvation, into the more poorly solvating sulfonic resin phase. This maximizing of the ion-water interactions of the system as a whole yields the dilute solution elu-

(10) For example, the toluenesulfonate anion does not compete too well with water in solvating the proton, as shown by the acid strength of toluenesulfonic acid.

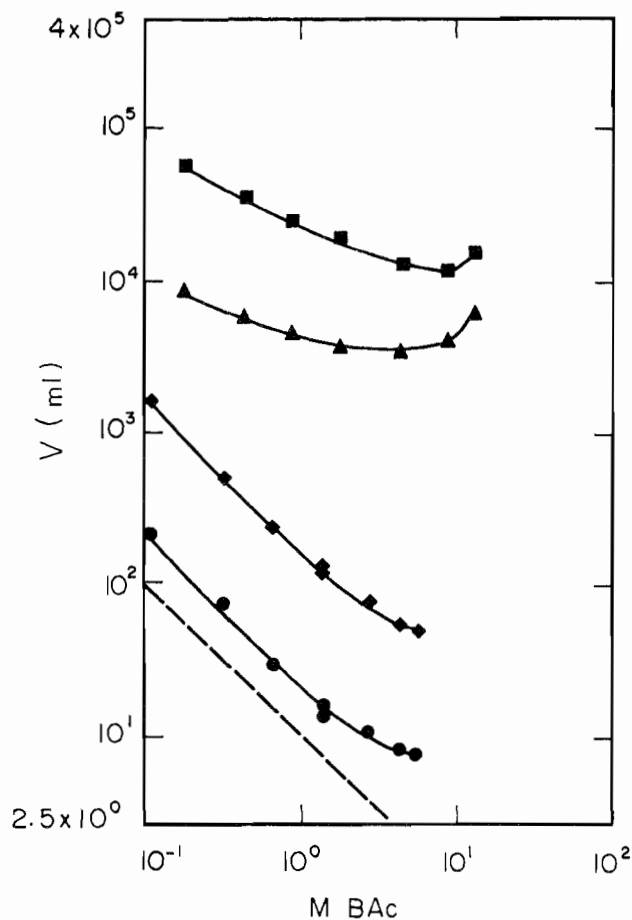


Fig. 6.—Corrected peak elution volume  $V$  (ml.) on Dowex-50W vs. acetate molarity for alkali tracers with LiOAc:  $\bullet$ , Na;  $\blacklozenge$ , Cs; and with HOAc:  $\blacktriangle$ , Na;  $\blacksquare$ , Cs; ———, slope  $-1.0$ .

tion order observed,  $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$ .

This is in contrast to the usual explanations for the order of selectivity,<sup>2,11–14</sup> which ascribe it primarily to a bonding or interaction of the cations with the sulfonate groups, that is, to a resin phase differentiation. Then the order is considered to depend upon the strength of the bond to the sulfonate, *i.e.*, upon ion pairing, and so to parallel the hydrated size of the cations, with the ion of smallest hydrated radius (*e.g.*,  $\text{Cs}^+$  among the alkalis) bound most tightly. It should be noted that on the present hypothesis the selectivity order is obtained primarily because of the more complete cation hydration in the dilute external solution than in the resin phase, that is, it is an aqueous phase differentiation.

As the external solution becomes more concentrated, however, three main changes occur. First, the water activity decreases; there is less "free" water available for the ions and so their hydration becomes less complete. Second, the number of anions in the vicinity of a cation increases rapidly in the external phase, so that anion-cation contacts become more frequent. Consequently, in the competition to solvate the cation, the anions increasingly play a more important

(11) J. L. Pauley, *J. Am. Chem. Soc.*, **76**, 1422 (1954).

(12) G. E. Boyd, J. Schubert, and A. W. Adamson, *ibid.*, **69**, 2818 (1947).

(13) T. R. E. Kressman and J. A. Kitchner, *J. Chem. Soc.*, 1190 (1949).

(14) F. E. Harris and S. A. Rice, *J. Chem. Phys.*, **24**, 1258 (1956).

role. The dilute solution complexing of the cation by water tends to go over in the concentrated solution into "anion complexing," using the expression in a very general sense. If the anion can form a chemical bond with the cation, a complex in the more usual sense will be formed, e.g.,  $\text{Fe}^{+3} + \text{Cl}^- \rightleftharpoons \text{FeCl}^{+2}$ , etc.; but with any anion, more subtle forms of cation-anion interaction are possible, and in this paper are included in the term "complexing" (see later discussion). Third, non-exchange electrolyte enters the resin phase. When the external solution is very dilute the high sulfonate ion concentration in the resin blocks the entrance of any other anion into that phase, that is, the resin behaves like a Donnan membrane.<sup>15</sup> As the external concentration increases, the resin becomes permeable to the external solution anion and so excess electrolyte enters. To a first approximation, we may treat the extra anions as new possible exchange sites, i.e., as an increase in the exchange site concentration of the resin,  $[\bar{B}]$ . As can be seen from eq. 3 or 4, this leads to an increase in  $D$ , thus in the elution volume, for all cations. Actually, of course, since the nonexchange anions are different from the resin sulfonate or carboxylate groups, they will interact with the cations to a different extent, but the main effect is still a general increase in the elution volumes for all cations.

It is mainly the first two effects, however, the dehydration of the ions and the increasingly important anion-cation interactions, which lead to the changes and differentiation in the ion-exchange behavior of the cations with concentrated solutions. Figure 1 shows a plot of the water activity vs. molarity for most of the solutions used in this study and gives an indication of the relative importance of ion dehydration in these solutions. The anion-cation interactions require further discussion, however. For cations as poorly bonding as the alkalis, nonspecific electrostatic interactions, rather than chemical bonds, are more likely involved. In concentrated solutions, electrostatic attractions between a cation and its neighboring anions are certainly intensified. One reason is that the dielectric constant of solutions of electrolytes decreases with increasing concentration,<sup>16,17</sup> and this alone enhances individual ion-ion interactions. Another is that the average distance between anion and cation decreases and the frequency of their collisions increases. Furthermore, as the water activity falls and the hydration shell around the ions diminishes, the collisions can be closer ones. Certainly for short times (perhaps of only the period of a few molecular collisions) an anion may bind to one of the highly polarized water molecules in the primary hydration shell of the cation,<sup>18</sup> or even replace a water mole-

(15) F. G. Donnan, *Chem. Rev.*, **1**, 73 (1924).

(16) G. H. Haggis, J. B. Hasted, and T. J. Buchanan, *J. Chem. Phys.*, **20**, 1452 (1952).

(17) F. E. Harris and C. T. O'Konski, *J. Phys. Chem.*, **61**, 310 (1957).

(18) This is the "localized hydrolysis" hypothesis put forth by R. A. Robinson and H. S. Harned, *Chem. Rev.*, **28**, 419 (1941), to explain the anomalous order of the activity and osmotic coefficients of the alkali acetates and hydroxides. One of the present authors has discussed the possibility that this mode of cation-anion association is more general and can occur even with anions derived from what are usually considered strong acids, namely, the hydrohalic acids [cf. R. M. Diamond, *J. Am. Chem. Soc.*, **80**, 4808 (1958)].

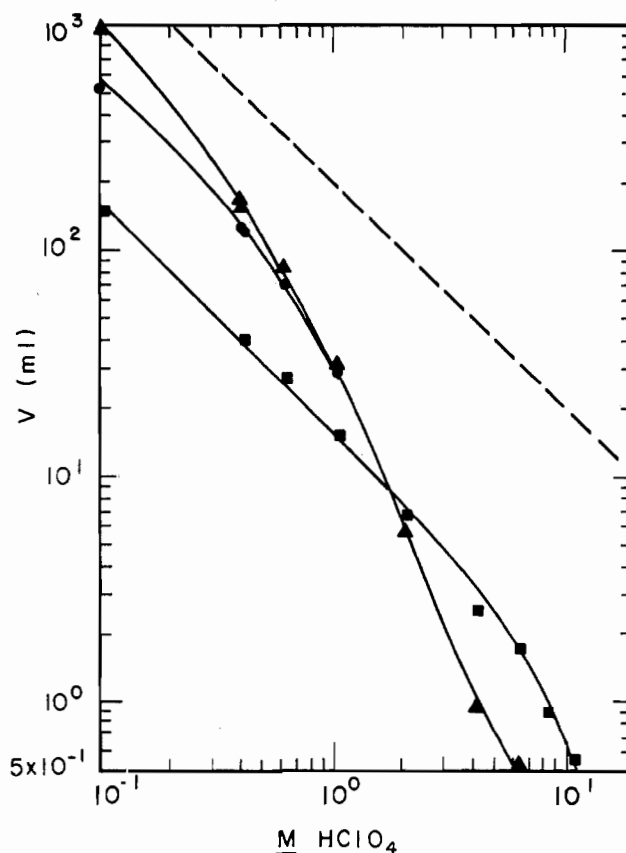


Fig. 7.—Corrected peak elution volume  $V$  (ml.) on Dowex-50W vs.  $\text{HClO}_4$  molarity for alkali tracers: ■, Na; ●, Rb; ▲, Cs; — — —, slope  $-1.0$ .

cule as the nearest neighbor of the cation, a type of electrostatic ion-pairing of the bare ions. In either case, a transitory type of anion-cation association occurs with a resultant lowering in the activity of the salt. Among a family of similar ions, such as the alkalis, the association with a particular anion and consequent decrease in the activity coefficient will be greater, the smaller the cation.

Obviously, if such cation-anion interactions or association can occur with many anions usually thought of as noncomplexing toward the alkalis, the ion-exchange behavior of tracer alkali ions will increasingly depend upon the nature of the macroanion present as the external solution concentration is increased. That is, as the water activity decreases and the ions begin to lose their hydration shells, anionic solvation of the cations begins to compete with hydration. The smaller ion will tend to seek out that phase in which it will receive the stronger anionic interactions. If this is with the macroanion in the aqueous phase, no change in the elution order will occur with increasing macroelectrolyte concentration; the smaller ions will continue to prefer the aqueous phase and to push the larger ions into the resin. If the interaction with the resin group anion is stronger than that with the aqueous phase anion, however, the smaller cation will decreasingly prefer the aqueous phase as the water activity falls, and at some point will begin to favor the resin phase. The result will be an inversion in the elution order; the

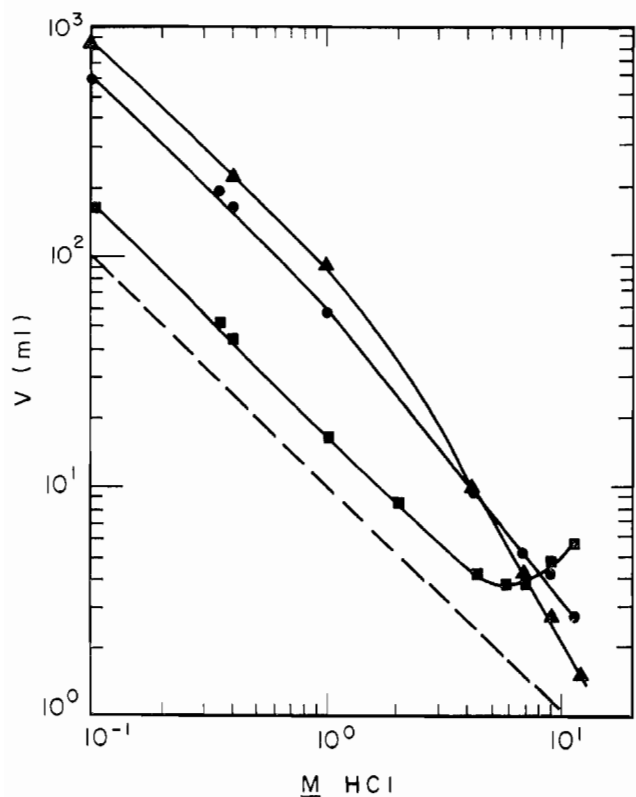


Fig. 8.—Corrected peak elution volume  $V$  (ml.) on Dowex-50W vs. HCl molarity for alkali tracers: ■, Na; ●, Rb; ▲, Cs; — — —, slope  $-1.0$ .

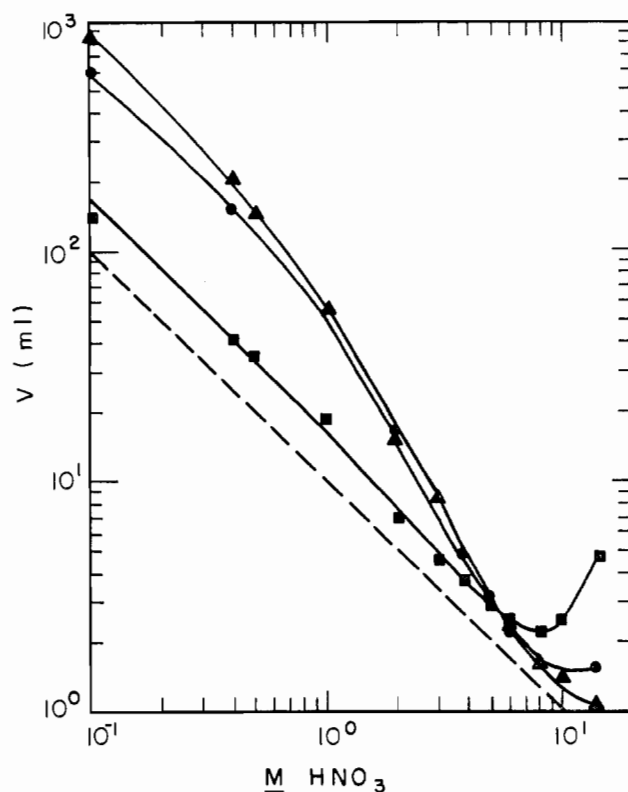


Fig. 9.—Corrected peak elution volume  $V$  (ml.) on Dowex-50W vs.  $\text{HNO}_3$  molarity for alkali tracers: ■, Na; ●, Rb; ▲, Cs; — — —, slope  $-1.0$ .

larger ion will now be pushed into the more poorly solvating aqueous phase and will have a smaller  $D$  and elution volume than the smaller ion. If a resin with a still more strongly complexing anionic group is used, *e.g.*, carboxylate, the solution concentration at which the elution order reverses should then be still lower.

A rough estimate of the order of such anion-alkali cation interactions can be made from a comparison of the strengths of the parent acids. As with chelate complexes,<sup>19</sup> it might be expected that the alkali cation association order of the anions would resemble that of increasing association with the proton, namely,  $\text{ClO}_4^- < \text{I}^- < \text{Br}^- < \text{Cl}^- < \text{NO}_3^- \leq \text{toluenesulfonate} < \text{OAc}^-$ .<sup>20</sup> A better estimate can be made by comparing the activity coefficients of the corresponding salts at a given concentration. If the cations are independent of the anions, there will be a marked decrease in the activity coefficients in going from the lithium to the cesium salt due to the great decrease in the hydration of the cation.<sup>18</sup> If the anion takes part in the type of cation association described above, the activity coefficients of the salts will be still lower, and the decrease will be greater the smaller the cation (the greater the interaction). So, for such an anion, the decrease in the coefficients in going from the lithium to the sodium to the cesium salt will be smaller, the larger the interaction with the anion. In fact, the order of the coefficients

may even reverse (*i.e.*,  $\text{Li}^+ < \text{Cs}^+$ ) if the strength of the anion association is great enough.

In Table I are listed the activity coefficients of 1.0 *m*

TABLE I  
ACTIVITY COEFFICIENTS OF 1.0 *m* SOLUTIONS AT 25°<sup>a</sup>

	$\text{ClO}_4^-$	$\text{I}^-$	$\text{Br}^-$	$\text{Cl}^-$	$\text{NO}_3^-$	Toluene-sulfonate	Acetate ( $\text{OAc}^-$ )
$\text{H}^+$	0.823	0.963	0.871	0.809	0.724	0.535	
$\text{Li}^+$	.887	.910	.803	.774	.743	.617	0.689
$\text{Na}^+$	.629	.736	.687	.657	.548	.554	.757
$\text{K}^+$		.645	.617	.604	.443	.506	.783
$\text{Rb}^+$		.575	.578	.583	.430		.792
$\text{Cs}^+$		.533	.538	.544	.422		.802

<sup>a</sup> R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth Scientific Publications, London, 1955.

solutions of several acids and salts of interest in the present work. It can be seen that the perchlorates show the largest fractional decrease between the lithium and sodium salts, as might be expected for such a large anion of a very strong acid. At the other extreme, the acetates show an inverted order with the coefficients increasing from  $\text{Li}^+$  to  $\text{Cs}^+$ ; of the anions considered, this one interacts the most strongly with the cations. With one exception, the fractional decreases in the coefficients from  $\text{Li}^+$  to  $\text{Cs}^+$  for the other anions fall in between these limiting cases in the same order as the strength of their parent acids. The exception is  $\text{NO}_3^-$ . As determined by the decrease in activity coefficients from the lithium to the cesium salts, nitrate comes between iodide and bromide in the

(19) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, pp. 151-159.

(20) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1960.



strength of its interaction with the alkali cations, but toward the proton it is a much stronger base; the possible explanation of this peculiarity is beyond the scope of this paper. The important result is that the order of cation-anion interactions in the concentrated solutions can be estimated from the activity coefficients of the anions; the acetate anion (considered as a model for the resin carboxylate groups) interacts the most strongly with the alkali cations, and the toluenesulfate anion (considered as a model for the resin sulfonate groups) interacts less strongly, but more so than the other anions considered. It should be remembered, however, that the cation-anion interactions being considered are weak with respect to the usual type of complex ion formation.

The results for the systems included in this study will now be treated on the basis of these considerations, that is, in terms of the three effects—ion dehydration, anion-cation interactions, and less importantly, resin invasion. First we will deal with Dowex-50W, after which the results on Bio-Rex 70 will be used to show the effects of enhancing the coordinating or solvating ability of the resin anion.

The first solution to be considered is  $\text{LiClO}_4$  (Fig. 2). As can be seen from Table I, the  $\text{ClO}_4^-$  ion is a very poor complexing ion or solvating species for cations, which means that, in the competition for solvating the cations, water and the resin sulfonate ( $\text{RSO}_3^-$ ) groups will play the major role in determining the distribution ratios (elution volumes) of the tracers. As the  $\text{LiClO}_4$  concentration increases, the water activity drops quite rapidly (Fig. 1), which enhances the ability of  $\text{RSO}_3^-$  to compete with water for the cations. The smaller the cation, the higher its charge density and the more avidly it seeks solvation. The effect of the drop in water activity in concentrated solutions is to force the small macrocation,  $\text{Li}^+$ , into the resin more strongly in order to replace the falling hydration with sulfonate coordination and, in the exchange, to push the larger tracer ions into the external aqueous phase. Since the hydration and coordination tendencies of  $\text{Na}^+$  are almost as great as those of  $\text{Li}^+$ , only a small decrease in the elution volume for  $\text{Na}^+$  below that for mass-action or "ideal" exchange, eq. 8, is expected, and is apparently compensated for by the increase due to resin invasion by nonexchange electrolyte. Thus, the  $\text{Na}^+$  curve in Fig. 2 approximates the mass-action line of eq. 8 to high concentrations due to a cancellation of effects and not due to the continuing validity of the assumptions made in deriving the equation. For an ion as large as  $\text{Cs}^+$ , the much weaker needs for solvation do not permit effective competition with the  $\text{Li}^+$  and so  $\text{Cs}^+$  is increasingly held in the aqueous phase as the latter becomes a poorer solvating medium with respect to the resin phase owing to the increasing  $\text{LiClO}_4$  concentration. As a result, the elution volume curve for  $\text{Cs}^+$  falls increasingly below the mass-action curve, yielding a slope steeper than  $-1$ , and actually crossing the  $\text{Na}^+$  curve. The increasing dehydration of the cations and their increasing interactions with the resin sulfonate groups

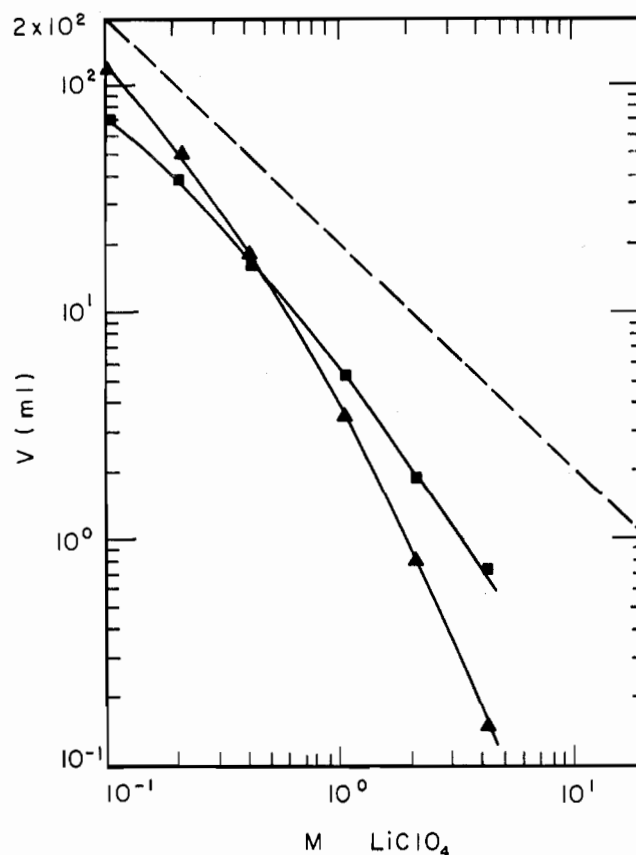


Fig. 10.—Corrected peak elution volume  $V$  (ml.) on Bio-Rex 70 vs.  $\text{LiClO}_4$  molarity for alkali tracers: ■, Na; ▲, Cs; ---, slope  $-1.0$ .

is sufficient to cause the dilute solution selectivity order to invert to  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$  at concentrations above  $3 M \text{LiClO}_4$ .

Although  $\text{LiI}$  was not studied in detail in this work, a few column elutions were done which showed that  $\text{Na}^+$  and  $\text{Cs}^+$  reversed their order between  $3.5$  and  $4 M \text{LiI}$ , that is, at a higher concentration than with  $\text{LiClO}_4$ . Since at a comparable concentration, the water activity is lower in a  $\text{LiI}$  solution than in one of  $\text{LiClO}_4$ , the resulting dehydration of the ion should cause the reversal in elution order to occur even earlier than in  $\text{LiClO}_4$ . The over-compensating effect is the greater ability of the (smaller)  $\text{I}^-$  ion to enter into the type of cation-anion interaction already described. (Indeed, Table I indicates that  $\text{I}^-$  interacts more strongly with the alkalis than  $\text{ClO}_4^-$ .) This holds the smaller ions in the aqueous phase and so tends to delay the reversal of the elution order until a still lower water activity, and hence a higher external solution concentration, than with  $\text{LiClO}_4$ .

A comparison of the water activity curves in Fig. 1 and of the activity coefficients in Table I for  $\text{LiBr}$  and  $\text{LiI}$  solutions shows that both the ion dehydration effect and that of anion interaction contribute to causing the elution order reversal with  $\text{LiBr}$  solutions to occur at a still higher concentration than with  $\text{LiI}$ . Again complete curves were not run, but the concentration of  $\text{LiBr}$  at which the  $\text{Na}^+ - \text{Cs}^+$  reversal takes place is about  $7 M$ —higher, as expected, than with  $\text{LiI}$ .



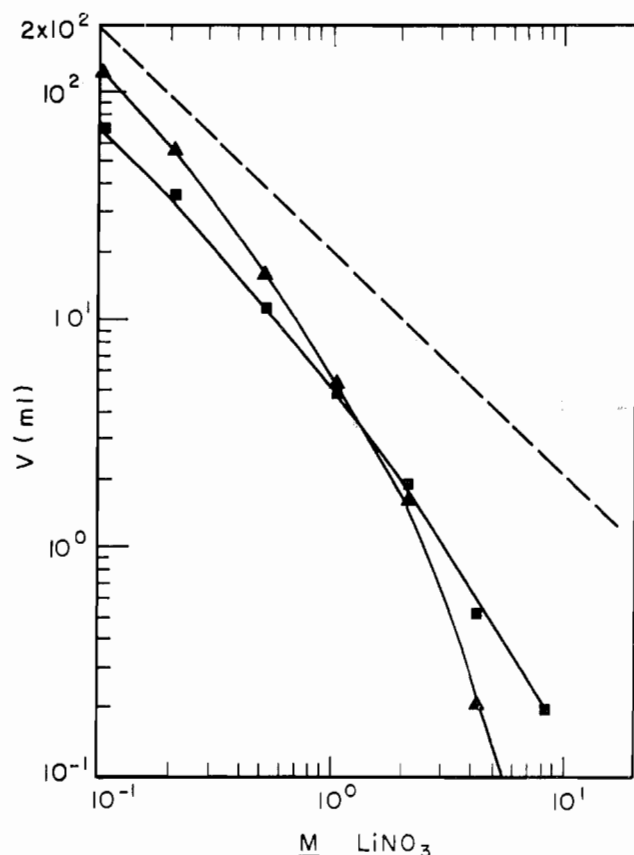


Fig. 11.—Corrected peak elution volume  $V$  (ml.) on Bio-Rex 70 vs.  $\text{LiNO}_3$  molarity for alkali tracers:  $\blacksquare$ , Na;  $\blacktriangle$ , Cs; — — —, slope  $-1.0$ .

This trend should continue with LiCl solutions. The water activity is greater than in LiBr solutions of comparable concentration, and  $\text{Cl}^-$  associates more strongly than  $\text{Br}^-$  with the cations. The result is to hold the smaller ions still more strongly in the external aqueous phase and thus yield higher values of  $D$  for the larger ions in concentrated LiCl solutions than in concentrated LiBr solutions as shown by the experimental curves (Fig. 3); the LiCl concentration at which the  $\text{Na}^+$  and  $\text{Cs}^+$  curves intersect is at a still higher value, about 10  $M$ .

However, to show that the elution order, though drastically changed by the nature of the macroanion, still depends fundamentally upon the dehydrating action of the concentrated solution, the elution behaviors of  $\text{Na}^+$  and  $\text{Rb}^+$  were studied in CsCl solutions. Such solutions have much higher water activities than the corresponding LiCl solutions (Fig. 1), and it can be seen in Fig. 4 that up to 7  $M$  CsCl there is no indication of a reversal in elution order at a higher concentration as is becoming evident with LiCl. The deviation upward from the ideal mass-action law for both the  $\text{Na}^+$  and  $\text{Rb}^+$  curves in CsCl indicates, most likely, the effect of resin invasion by nonexchange electrolyte, that is, the effect of additional anionic "sites." The parallel upturn of ions as different in size as  $\text{Na}^+$  and  $\text{Rb}^+$  supports this view over other possible explanations.

From Fig. 1 it can be seen that  $\text{LiNO}_3$  solutions have a higher water activity than LiCl, but from a compari-

son in Table I of the lithium and cesium salts it appears that  $\text{NO}_3^-$  is a poorer "complexing" agent than  $\text{Cl}^-$ , falling between  $\text{Br}^-$  and  $\text{I}^-$ . Thus, compared to LiCl solutions,  $\text{LiNO}_3$  solutions are both poorer at dehydrating and at "complexing" the alkalis; the two factors oppose each other in changing the ion-exchange behavior. Experimentally, as shown in Fig. 5, they must just about balance out. The  $\text{Na}^+$  and  $\text{Cs}^+$  curves in  $\text{LiNO}_3$  are very similar to those with LiCl solutions; no crossing has occurred at 8  $M$   $\text{LiNO}_3$ , but it is obviously imminent.

The last salt system studied, that of LiOAc (Fig. 6), best illustrates the effect of anion association with the alkali cations in the external phase. (In fact, it was to explain the properties of these solutions that led to the localized hydrolysis hypothesis.) As a result of this association the smaller cations, particularly  $\text{Li}^+$ , always find better solvation in the aqueous phase than in the resin (in dilute solution from hydration, in concentrated LiOAc from coordination with  $\text{OAc}^-$ ), and so prefer that phase, pushing the larger cations into the resin phase in the exchange. Thus, the  $D$  values and elution volumes for  $\text{Na}^+$  and especially  $\text{Cs}^+$  are far larger at a high LiOAc concentration than at a comparable concentration in any other salt solution studied and no reversal in elution order is found. However, it is of interest to note that the initial slope is the same (*i.e.*,  $-1.0$ ) as for the other salts. In the more concentrated region the  $\text{Na}^+$  and  $\text{Cs}^+$  curves deviate upward from the ideal mass-action slope of  $-1.0$  due to both the effective decrease in the macro lithium ion concentration caused by the acetate complexing and the effect of resin invasion by the aqueous solution.

The elution curves for the alkalis using the acids rather than the lithium salts as the macroelectrolyte are, in general, similar to those of the salts. There is an added complication, however, in the possible association of the acid. Such association is least important in acids as strong as  $\text{HClO}_4$ , and so the behavior of the tracers in  $\text{HClO}_4$  (Fig. 7) is very similar to that in  $\text{LiClO}_4$ , except that the crossing of the  $\text{Na}^+$  and  $\text{Cs}^+$  curves occurs at a slightly lower concentration. Recently published work<sup>4</sup> agrees with that reported here for the region of the  $\text{Na}^+$  and  $\text{Cs}^+$  crossing, but shows a leveling off of both curves at higher concentrations, as opposed to the sharp decrease shown in Fig. 7; the discrepancy may be due to a difference in the method of subtracting a free-column volume or to the different cross linking of the resins used.

A detailed study with HI was not performed, but, as with LiI, the concentration at which  $\text{Na}^+$  and  $\text{Cs}^+$  reversed their order was determined. The value,  $\sim 3.4 M$ , is larger than that for  $\text{HClO}_4$  for exactly the same reasons that the value with LiI exceeds that for  $\text{LiClO}_4$ . Similarly, although elutions with HBr were not studied in this series of experiments, they have been reported upon in the literature,<sup>4</sup> where it was found that the  $\text{Na}^+$ - $\text{Cs}^+$  reversal occurs at  $\sim 5$ -6  $M$  HBr, that is, at a still lower water activity and higher concentration than with HI. Again this is what is predicted from the

somewhat stronger cation-anion interactions for  $\text{Br}^-$  than for  $\text{I}^-$ , as indicated in Table I.

The results with HCl solutions (Fig. 8) continue the trend described for HI and HBr. Chloride ion is still better at interacting with the alkalis, and HCl solutions have still higher water activities than the other acids at the same concentration, and so the  $\text{Na}^+$ - $\text{Cs}^+$  reversal occurs still later, at about 8 M HCl. However, a new feature is added in concentrated HCl solutions to the otherwise similar case of the LiCl system, and that is association of the HCl itself. The resulting effective decrease in the  $\text{H}^+$  concentration means that the mass-action effect of the  $\text{H}^+$  to displace all cations from the resin is somewhat reduced. So all alkali elution volumes are a little larger than would otherwise be expected, as, for example, in comparison with LiCl elutions at the same high concentration. This increase should be greatest for those cations most badly in need of solvation and therefore most likely to enter the resin phase. Furthermore, the effective decrease in the  $\text{Cl}^-$  concentration means less  $\text{Cl}^-$  complexing and so again the smaller ions are helped into the resin phase with respect to the corresponding LiCl system. Thus, the reversal in elution order should come at a lower concentration than with LiCl, principally because of an increase in the elution volumes of the smaller ions. A comparison of the LiCl and HCl results, Fig. 3 and 8, indicates just such a contrast in behavior. The elution curves are similar up to about 4-5 M, beyond which point the HCl curves (particularly that for  $\text{Na}^+$ ) rise above the LiCl curves; the  $\text{Na}^+$ - $\text{Cs}^+$  crossing occurs at about 8 M for HCl and at about 10 M for LiCl.

With  $\text{HNO}_3$  elutions the effect of acid association becomes even more important, as  $\text{HNO}_3$  is about 50% associated at 10 M. This complexing of  $\text{H}^+$  by  $\text{NO}_3^-$  in the aqueous phase permits  $\text{Na}^+$ , and to a lesser extent  $\text{Cs}^+$ , to compete better for association with the sulfonate groups in the resin phase. A comparison of the  $\text{LiNO}_3$  and  $\text{HNO}_3$  results, Fig. 4 and 9, shows that the  $\text{Na}^+$  curve in the latter does indeed rise compared to that in  $\text{LiNO}_3$ , lowering the  $\text{Na}^+$ - $\text{Cs}^+$  crossing point in  $\text{HNO}_3$  to about 5 M. Furthermore, a comparison of the HCl and  $\text{HNO}_3$  results shows that the upturn for  $\text{Na}^+$  is greater with  $\text{HNO}_3$ , the weaker acid, and that even the  $\text{Rb}^+$  and  $\text{Cs}^+$  curves are beginning to turn up. It is puzzling, however, that the elution volumes for both  $\text{Na}^+$  and  $\text{Cs}^+$  with concentrated  $\text{HNO}_3$  solutions are not still larger in magnitude.

With HOAc as the macroelectrolyte, the association of  $\text{H}^+$  and the anion,  $\text{OAc}^-$ , is almost complete. The main result is very large elution volumes (Fig. 6). Other differences from the  $\text{LiOAc}$  results are the upturn in the curves, particularly the  $\text{Na}^+$  one, and the consequent greater tendency to cross at high HOAc concentrations. This is a continuation of the trend already noted and discussed for the HCl and  $\text{HNO}_3$  results. The fact that the  $\text{Na}^+$  and  $\text{Cs}^+$  curves do not cross is, of course, due to the complexing ability of the small amount of equilibrium  $\text{OAc}^-$  in the solution.

It is of interest to note that the elution volume for

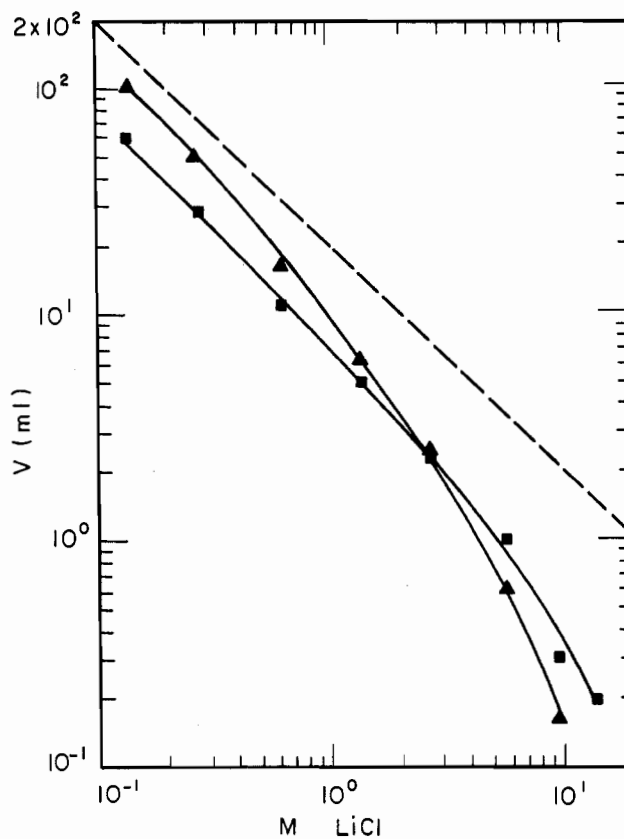


Fig. 12.—Corrected peak elution volume  $V$  (ml.) on Bio-Rex 70 vs. LiCl molarity for alkali tracers: ■, Na; ▲, Cs; ---, slope  $-1.0$ .

$\text{Cs}^+$  has a value of  $5.2 \times 10^4$  ml. for 0.174 M HOAc; this solution has a hydrogen ion concentration of  $1.8 \times 10^{-3}$  M. If the  $\text{Cs}^+$  curve for any of the other acids is extrapolated to  $1.8 \times 10^{-3}$  M acid concentration, assuming a slope of  $-1.0$ , the elution volume is  $4.8 \times 10^4$ , in close agreement with the HOAc data. Thus, it appears that at low concentrations the presence of the un-ionized HOAc has little effect on the ion-exchange process.

The results for Dowex-50W can now be compared with those for Bio-Rex 70. The same reasoning should apply, except that the greater complexing ability toward alkalis of carboxylate vs. sulfonate must be taken into account. That is, the resin carboxylate groups can compete more successfully with the water to solvate the smaller cations than can sulfonate groups, so that even in dilute solution those cations which solvate most strongly ( $\text{Li}^+$ ,  $\text{Na}^+$ ) will have larger distribution ratios relative to the more poorly solvating ions ( $\text{Rb}^+$ ,  $\text{Cs}^+$ ) than with sulfonate resin. The result is that even in the dilute solution case, where the usual elution order,  $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ , is retained, the elution volumes of all the alkalis are more nearly alike than with the sulfonate resin, and thus their separation is poorer. For example, the ratio of the  $V$  or  $D$  values (the separation factor) for tracer  $\text{Cs}^+$  and  $\text{Na}^+$  in 0.1 M  $\text{LiClO}_4$  with Dowex-50W is about 6, while that with Bio-Rex 70 is 1.7 (see Fig. 2 and 10).

Similarly, as the concentration of electrolyte rises and the water activity falls, the smaller, more highly

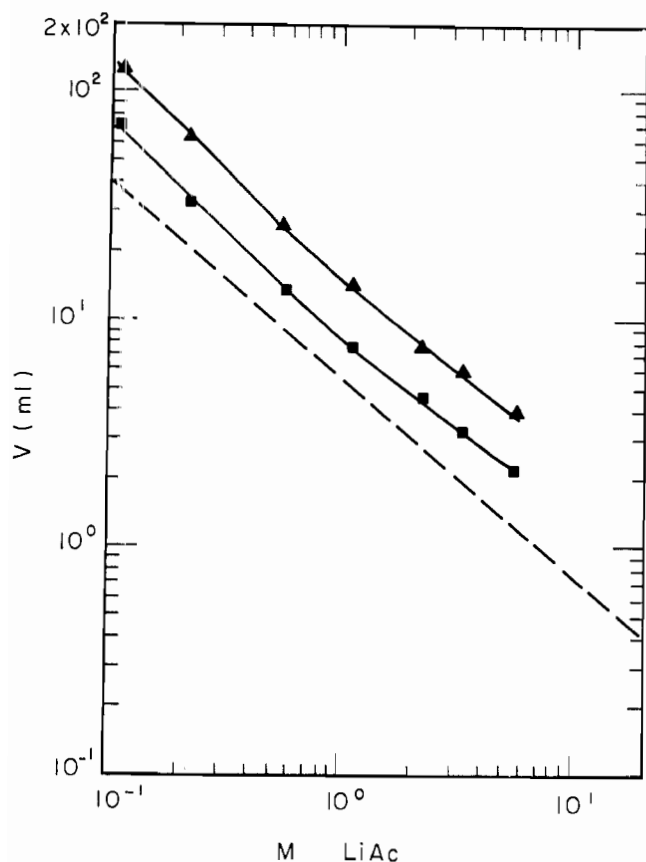


Fig. 13.—Corrected peak elution volume  $V$  (ml.) on Bio-Rex 70 vs.  $\text{LiOAc}$  molarity for alkali tracers:  $\blacksquare$ ,  $\text{Na}^+$ ;  $\blacktriangle$ ,  $\text{Cs}^+$ ; — — —, slope  $-1.0$ .

solvating ions, such as  $\text{Li}^+$ , are attracted into the resin phase, even more strongly with the carboxylate resin than with the sulfonate, producing a correspondingly larger decrease in the  $D$  values for the larger, less solvated ions. With  $\text{LiClO}_4$ ,  $\text{LiNO}_3$ , and  $\text{LiCl}$  solutions, Fig. 10–12, the  $\text{Cs}^+$  curve falls below the  $\text{Na}^+$  curve at concentrations  $1/4$  or  $1/5$  those of the sulfonate resin case. It may be noted, however, that the order of the lithium salts with respect to the concentration at which the  $\text{Na}^+$  and  $\text{Cs}^+$  tracer curves cross remains the same, namely,  $\text{LiClO}_4 < \text{LiNO}_3 < \text{LiCl}$ . This indicates that although the earlier crossing with the carboxylate resin is caused primarily by the greater attraction of the carboxylate group for  $\text{Li}^+$ , the order of the salts depends mainly upon the complexing ability of the aqueous phase anions and not upon the nature of the resin group. At the highest external solution concentrations studied, the preference of the resin carboxylate for  $\text{Li}^+$  becomes so great that the corrected peak elution volume for  $\text{Cs}^+$  tracer becomes negligibly small ( $\leq 0.1$  ml.) and that for  $\text{Na}^+$  is only slightly greater.

When  $\text{LiOAc}$  is used as the eluting agent, no reversal in the elution order is observed (Fig. 13). This is because acetate ion has a complexing ability comparable to that of the resin so that as the concentration increases and availability of water decreases, the  $\text{Li}^+$  is not forced to enter the resin phase to seek solvation but can coordinate with the  $\text{OAc}^-$  groups in the aqueous phase instead. The upward deviation of the curve from the

line predicted by eq. 8 can be ascribed to resin invasion by nonexchange electrolyte.

It is of interest to compare these results with those obtained by other workers on various weak-acid resins. Gregor, *et al.*,<sup>21</sup> using a methylacrylic acid–divinylbenzene polymer, found the ratio of the distribution coefficients for dilute aqueous solutions to fall in the order  $\text{K}^+ > \text{Na}^+ > \text{Li}^+$  when the resin was in the  $\text{Li}^+$  form, with a separation factor of less than two between  $\text{K}^+$  and  $\text{Li}^+$ ; these results on a slightly different resin are in agreement with those of the present work. Kennedy, Marriot, and Wheeler have investigated the exchange properties of polymeric diallyl phosphate (HDAP), which contains  $(\text{C}_3\text{H}_5\text{O})_2\text{POO}^-$  groups, in both acid and sodium salt forms.<sup>22</sup> HDAP is an acid, intermediate in strength between the carboxylate resin, Bio-Rex 70, and the sulfonate resin, Dowex-50W, used in the present studies and it gave the same dilute solution elution order, namely,  $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$ , but with smaller separation factors than for a sulfonate resin. Presumably, in concentrated electrolyte solutions such as those used in this work, the elution order would reverse, and this would occur at concentrations intermediate between those for the sulfonate and carboxylate resins.

Of greater interest for the present study are the results obtained by Bregman and Murata<sup>23</sup> and continued by Kennedy, *et al.*,<sup>22</sup> with a resin polymer containing  $-\text{PO}(\text{OH})_2$  groups. They found that under dilute acid conditions where the resin functions as a monobasic acid of moderate strength (exchange group in the form  $-\text{P}(\text{OH})\text{OO}^-$ ), the normal elution order of the alkalis prevails. In dilute basic solutions, however, the resin behaves as a dibasic acid, and the elution order reverses, with  $\text{Na}^+$  held more tightly than  $\text{Cs}^+$ . In this case the exchange group is  $-\text{PO}_3^{2-}$ , and the reversal can be interpreted as due to the increased ability of the divalent group to compete with  $\text{H}_2\text{O}$  to complex or solvate the cations. That is, the electrostatic interactions are much greater between a dinegative anionic group and two univalent cations than between two mononegative anionic groups and the same cations. Roughly, this can be seen to be a consequence of Coulomb's law, and the somewhat greater hydration of  $-\text{PO}_3^{2-}$  compared to two  $-\text{SO}_3^-$  groups does not change this ordering.

It thus can be seen that the order of resin selectivity is determined by the cation complexing ability of the resin exchange group (usually paralleled by the order of proton complexing or basic strength of the anionic group), by the hydration of the cations, and by the interaction with the macroanions present. For dilute solutions, the third effect is unimportant, and with the most weakly basic resin group,  $-\text{SO}_3^-$ , the dilute solution selectivity order is  $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$

(21) H. P. Gregor, M. J. Hamilton, R. J. Oza, and F. Bernstein, *J. Phys. Chem.*, **60**, 283 (1956).

(22) J. Kennedy, J. Marriot, and V. J. Wheeler, *J. Inorg. Nucl. Chem.*, **22**, 269 (1961).

(23) J. I. Bregman and Y. Murata, *J. Am. Chem. Soc.*, **74**, 1867 (1952); J. I. Bregman, *Ann. N. Y. Acad. Sci.*, **57**, 125 (1953).

