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ION EXCHANGE STUDIES
IN CONCENTRATED SOLUTIONS

I. THE ALKALI CATIONS WITH A
SULFONIC ACID RESIN

Berkeley, California

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I. The Alkali Cations With A Sulfonic Acid Resin

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Abstract

An investigation of the cation exchange behavior on Dowex-50W (sulfonic-acid type) resin of Na, Rb, and Cs tracers in 0.1 M to saturated solutions of HClO_4 , HCl , HNO_3 , $\text{H}_2\text{C}_2\text{O}_4$, the corresponding Li salts, and CsCl 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 sulfonate 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 non-exchange 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.

ION EXCHANGE STUDIES IN CONCENTRATED SOLUTIONS

I. The Alkali Cations With A Sulfonic Acid Resin¹D. C. Whitney² and R. M. DiamondLawrence Radiation Laboratory
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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.³ It has been noted, however, that in concentrated solutions of strong acids, HCl ,^{4,5} HBr ,⁵ and HClO_4 ,⁵ this order becomes reversed, and a reversal has been reported for 13 M LiCl ^{6,7} also. In the original discussion of the reversal of the elution order in concentrated HCl solutions⁴ 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 non-exchange electrolyte, the shrinkage of the resin, and possible interaction with the chloride anions playing secondary roles.

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1. This work was supported by the U. S. Atomic Energy Commission.
 2. Present address: Chemistry Department, University of California, Davis, California.
 3. F. Helfferich, Ion Exchange, McGraw-Hill Book Co., Inc., New York, 1962.
 4. R. M. Diamond, J. Am. Chem. Soc. 77, 2978 (1955).
 5. G. R. Choppin and R. H. Dinius, Inorg. Chem. 1, 140 (1962).
 6. W. A. Platek and J. A. Marinsky, J. Phys. Chem. 65, 2113 (1961).
 7. H. Kakihana, N. Maruichi and N. Namasaki, J. Phys. Chem. 60, 36 (1956).

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 HClO_4 , HNO_3 , HCl , and $\text{HC}_2\text{H}_3\text{O}_2$, as well as of their corresponding lithium salts, and of CsCl , has been performed and is reported upon herein. During the course of this work, studies of the HClO_4 ⁵ and of the LiCl ⁶ 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 and the ones to follow.

Experimental

Reagents. The cation exchange resin was Dowex AG 50W-X12, 50-100 mesh, a styrene-based sulfonic acid exchanger obtained from Bio-Rad Laboratories, Richmond, Calif. The capacity of the resin is 5.2 meq/g dry resin, and its water uptake is 0.75 g water/g dry resin. 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 H₂O. The Na²² tracer (as carrier-free NaCl) was purchased from Nuclear Science and Engineering Corp., Pittsburgh, Pa.; the Na²⁴ (as NaHCO₃) and Rb⁸⁶ (as RbNO₃) tracers were produced in the Livermore Pool-Type Reactor, Lawrence Radiation Laboratory, Livermore, California.; and the Cs¹³⁷ (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 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 four hours. 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

$$D = \frac{(\text{volume of equilibrated solution})}{(\text{weight of dry resin})} \times \frac{(\text{counts/min per ml of init. sol.} - \text{counts/min per ml of equil. sol.})}{(\text{counts/min per ml of equilibrated solution})} \quad (1)$$

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(ClO₄)₂. Variation of the shaking time

over the period 1-24 hours showed no appreciable difference in D, establishing that equilibrium had been attained.

For the 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(dry) resin. Each column was washed first with > 20 column volumes of 6 M HClO_4 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_4 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 volume of solution necessary to elute a tracer ion from the column was determined by placing 10 μ liters 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 corresponded to the peak elution volume.

Most of the column determinations were made using 2 or 3 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 elution volumes were generally reproducible to within 5%. No difference in exchange behavior was observed when Na^{24} produced by neutron irradiation of NaHCO_3 was used in place of carrier-free Na^{22} , or when a solution of tracer Na^{22} in 10 M HCl was saturated with NaCl and 10 μ liters of this saturated solution was used to load the column. This lack of change indicates that the elution volumes obtained were independent of the amount of tracer cation as long as this amount was negligible in comparison with the capacity of the resin.

All experimental work was done at room temperature, $23 \pm 2^\circ \text{C}$.

Results

Distribution ratios from the batch experiments 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 exactly with the factor obtained by directly comparing a batch distribution ratio and column elution at the same aqueous phase concentration.

The peak elution volumes, in milliliters of solution for the standard column, then had one interstitial, or external, column volume subtracted.⁸ In Figs. 2-9 are shown the results of the measurements as log-log plots of the corrected peak elution volumes of the Na^+ , Rb^+ and Cs^+ tracers vs. the aqueous molarity of the salt or acid solutions used.

8. This interstitial or external volume is that volume of the column external to the resin phase. For the standard column it ranged from 1.31 ml in 0.1 M solution (as determined by the elution of I^- tracer) to 1.6 ml in 10 M HClO_4 (asymptotic value for Cs^+ tracer elution).

Discussion

The equation for the exchange of an alkali ion A^+ , with a monovalent cation, 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

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

where parentheses denote activity, brackets indicate concentration in arbitrary units and the γ 's are the corresponding species activity coefficients.

For dilute aqueous solutions (below 0.1 molar) 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, γ_B/γ_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 $[B]$ remains constant. This implies that the activity coefficient ratio in the resin phase also remains constant, since for constant $[B]$, $\gamma_{\bar{B}}$ is constant, and $\gamma_{\bar{A}}$ has a characteristic constant value as long as $[A]$ is in tracer concentration (Harned's Rule).

We may now choose our concentration units for the resin phase as millimoles (or counts) per g (dry) resin, and for the aqueous phase as millimoles

(or counts) per ml of solution, or molarity. Then,

$$K[B] \frac{\gamma_A \gamma_B^-}{\gamma_A^- \gamma_B} = C^{\text{dilute}} = \frac{[\bar{A}][B]}{[A]} \quad (4)$$

where C^{dilute} is a constant under our dilute aqueous phase assumptions.

From the plate theory of Mayer and Tompkins⁹ the previously defined distribution ratio, D , can be related to column elution behavior, that is, to the corrected peak elution volume, by the relationship.

$$D \equiv \frac{[\bar{A}]}{[A]} = \frac{\text{ml solution in corrected peak elution volume}}{\text{g (dry) resin in column}} \quad (5)$$

which when substituted in Eq. (4) yields

$$C^{\text{dilute}} = D [B] = \frac{\text{ml solution in corrected peak elution volume}}{\text{g (dry) resin in column}} [B] \quad (6)$$

For a particular column (weight of resin), and abbreviating the corrected peak elution volume by $V(\text{ml})$, this reduces to

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

and taking logarithms and rearranging,

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

As shown in Figs. 2-9, the log-log plots of corrected peak elution volume, $V(\text{ml})$, vs. solution molarity, $[B]$, for each of the tracers with each of the solutions used (with the exception of HAc) either has or approaches a slope -1.0 at the lowest solution concentration employed (0.1 molar), as

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

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 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 molar and may even lead, for concentrated solutions, to non-exchange 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 molar 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. These can contribute to a deviation from the mass-action law which dominates in dilute solution exchange.

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 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. A further type of ion-ion interaction, that between a cation and another cation, would be much less important and will be ignored in this discussion. Finally, when dealing with ions for which ion hydration is significant, as is the case with the alkali ions of this paper and is certainly true for more highly charged ones, the effect of the water-water interactions, that is, of the hydrogen-bonded water structure, on the ion will be relatively unimportant and so will also be neglected. (But this last factor becomes important for large, poorly hydrated ions such as the tetraalkyl ammonium ions, ClO_4^- , AuCl_4^- and other halometallic complex ions, etc. See ref. 10)

So the two most important effects are those of ion hydration and complex formation. That is, 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).

The cations organize and orient the nearby water molecules around themselves to a greater or lesser degree depending upon their size and charge and specific electronic structure. A cation-anion interaction must also be present, namely the electrostatic interaction which leads to the Debye-Hückel environment

10. D. C. Whitney and R. M. Diamond, J. Inorg. Nucl. Chem., in press.

of anions,¹¹ but the most important effect in the dilute aqueous phase is the ion-water interaction.

The situation is somewhat different in the resin phase. For a sulfonic acid resin of the usual range of cross-linking, the internal solution corresponds to a concentrated electrolyte solution of 4-7M. 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. Cation-anion interactions will be further enhanced by the lower effective dielectric constant of the resin phase.¹⁰ But for as poor a complexing anionic group as sulfonate, the net result is still that a 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 cations (or more highly hydrated ions) in dilute solution, the smaller ion, with the greater requirement for solvation, will favor the dilute external phase and will push the 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 elution order observed, $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$.

But it should be noted that on this hypothesis the sequence is obtained primarily because of the more complete cation hydration in the dilute external solution than in the resin phase. This is in contrast to the usual explan-

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

ations for selectivity^{3,12-15} 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 sulfonate bonding and so to parallel the hydrated size of the cations, with the largest ion (smallest hydrated radius) bound most tightly.

As the external solution becomes more concentrated, however, three main changes occur. Firstly, the water activity decreases; there is less "free" water available for the ions and so their hydration becomes less complete. Secondly, 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 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, eg., $\text{Fe}^{+++} + \text{Cl}^- \rightarrow \text{FeCl}^{++}$, 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). Thirdly, 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.¹⁶ But as the external concentration increases, the resin becomes

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

13. G. E. Boyd J. Schubert, and A.W. Adamson, J. Am. Chem. Soc. 69, 2818 (1947).

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

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

16. F. G. Donnan, Chem. Revs. 1, 73 (1924).

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, [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 non-exchange anions are different from the resin sulfonate groups, they will interact with the cations to a different extent. But even with very concentrated external solutions which may yield resin invasion electrolyte concentrations approaching the resin sulfonate concentration itself, the main effect is still a general increase in the elution volumes for all cations.

Thus, it is the first two effects, 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 the ion dehydration effect for these solutions. But the anion-cation interactions require further discussion. For cations as poorly bonding as the alkalis, non-specific 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,^{19,20} and this alone enhances individual ion-ion

17. R. A. Robinson and R. H. Stokes, Electrolyte Solutions (Butterworths Scientific Publications, London, 1955).

18. Landolt-Börnstein Tables Springer-Verlag, Berlin, 1923, Supplement 3, Part 3, 2145.

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

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

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 shells around the ions diminish, the collisions can be closer ones. In fact, for short times (perhaps of only the period of a few molecular vibrations) an anion may bind to one of the highly polarized water molecules in the primary hydration shell of the cation, or even replace a water molecule as the nearest neighbor of the cation.

The former type of interaction is the "localized hydrolysis" hypothesis which Robinson and Harned²¹ put forth to explain the anomalous order of the activity and osmotic coefficients of the alkali acetates and hydroxides.²² One of the present authors discussed the possibility that this mode of cation-anion association was more general and could occur even with anions derived from what are usually considered strong acids, namely the hydrohalic acids.²³ In this way the anomalous order of the activity and osmotic coefficients of the lithium halides, $\text{LiCl} < \text{LiBr} < \text{LiI}$, (Table I) compared to the expected order as seen with the cesium halides, $\text{CsCl} > \text{CsBr} > \text{CsI}$, could be explained.

21. R. A. Robinson and H. S. Harned, Chem. Revs. 28, 419 (1941).

22. Robinson and Harned reasoned that a cation can polarize the nearest water molecules, making their hydrogens more acidic than those of ordinary water. If the anion present is a proton acceptor, i.e., the anion of a weak acid, its interaction (through hydrogen-bonding) with such a polarized water molecule would be enhanced over that with an ordinary water molecule. This type of cation-anion association through an intermediary water molecule (or more than one) lowers the osmotic and activity coefficients of the salt, and the more so, the smaller and more strongly polarizing (hydrolyzing) the cation. Thus, with the anion of a weak enough acid, the coefficients will fall in the order $\text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li}$ as is observed with the acetates, hydroxides, and possibly the fluorides.

23. R. M. Diamond, J. Am. Chem. Soc. 80, 4808 (1958).

Actually, an alternative explanation of these activity and osmotic coefficient anomalies is furnished by a type of electrostatic ion-pairing of the bare ions. That is, after a close collision, the cation and anion stay together for a short period, say for a few collisions with water molecules, before becoming separated again. In either this case, or in the previously mentioned case of interaction through a polarized water molecule (and both probably occur), the result is the same. A transitory type of anion-cation association occurs with a resulting 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 non-complexing toward the alkalis, the ion-exchange behavior of tracer alkali ions will increasingly depend upon the nature of the macro-anion present as the external solution concentration is increased. That is, as the water activity decreases and the ions begin to lose their hydration shells, the smaller ion will tend to seek out that phase in which it will receive the stronger anionic interactions. If this is with the macro-anion in the aqueous phase, no change in the elution order will occur with increasing macro-electrolyte concentration; the smaller ions will continue to prefer the aqueous phase and to push the larger ions into the resin. But if the interaction with the resin group anion is stronger than that with the aqueous phase anion, 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 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 strengths of such anion-alkali cation interactions can be made from a comparison of the strengths of the parent acids. As with chelate complexes,²⁴ it might be expected that the alkali cation association order of the anions would resemble that of increasing association with the proton, namely, $\text{ClO}_4^- < \text{I}^- < \text{Br}^- < \text{Cl}^- < \text{NO}_3^- \leq \text{toluene sulfonate} < \text{Ac}^-$.²⁵ 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 from the lithium to the cesium salt due to the great decrease in the hydration of the cation (see ref. 23). If the anion takes part in the type of interaction described above, the activity coefficients of the salts will be decreased, but 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 cesium salt will be smaller. In fact, the order of the coefficients may even reverse if the strength of the association is great enough.

In Table I are listed the activity coefficients of 1.0 molal 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

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

25. R. P. Bell, The Proton in Chemistry, (Cornell University Press, Ithaca, New York, 1960).

strong acid. At the other extreme, the acetates show an inverted order with the coefficients increasing from Li^+ to Cs^+ ; of the anions considered, this one interacts the most strongly with the cations. With one exception, the fractional decreases in the coefficients from Li^+ to 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 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 strength of its interaction with the alkali cations, but towards 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, and that the toluene sulfonate anion (considered as a model for the resin sulfonate groups) interacts relatively strongly with the alkali cations as compared to the other anions. 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.

The first solution to be considered is LiClO_4 (Fig 2). As can be seen from Table I, the 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 (RSO_3^-) groups will play the major role in determining the distribution ratios (elution volumes) of the tracers. As the LiClO_4 concentration increases, the water activity drops quite rapidly

(Fig. 1), which enhances the ability of 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, so that the effect of the drop in water activity in concentrated solutions is to force the small macro-cation, Li^+ into the resin more strongly, and, in the exchange, to push the larger tracer ions into the external aqueous phase. The result is a decrease in the elution volume for Cs^+ below that for mass-action or "ideal" exchange Eq.(4). Since the hydration of Na^+ is almost as great as that of Li^+ , only a small decrease is expected for Na^+ , and this is apparently compensated for by the increase due to resin invasion by non-exchange electrolyte. Thus, the Na^+ curve in Fig. 2 approximates the mass-action line of Eq. (4) to high concentrations due to a cancellation of effects and not due to the continuing validity of the assumptions made in deriving Eq. (4). Furthermore the Cs^+ curve falls more steeply and crosses the Na^+ one. The increasing dehydration of the cations and their increasing interaction with the resin sulfonate groups is sufficient to cause the dilute-solution selectivity order at concentrations above 3 M LiClO_4 to invert to $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$.

Although LiI was not studied in detail in this work, a few column elutions were done which showed that Na^+ and Cs^+ reversed their order between 3.5 and 4 M LiI , that is, at a higher concentration than with LiClO_4 . But since at a comparable concentration, the water activity is lower in a LiI solution than in one of LiClO_4 , the resulting dehydration of the ions should cause the reversal in elution order to occur even earlier than in LiClO_4 . The over-compensating effect is the greater ability of the (smaller) I^- ion to enter into the type of cation-anion interaction already described. (Indeed, Table I indicates that I^- interacts more strongly with the alkalis than 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 LiClO_4 .

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

This trend should continue with LiCl solutions. The water activity is greater than in LiBr solutions of comparable concentration, and Cl^- associates more strongly than 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. These expectations are borne out by the experimental curves (Fig. 3); the LiCl concentration at which the Na^+ and 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 macro-anion, still depends fundamentally upon the dehydrating action of the concentrated solution, the elution behavior of Na^+ and 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 Na^+ and Rb^+ curves in CsCl indicates, most likely, the effect of resin invasion by non-exchange electrolyte, that is, the effect of additional anionic "sites".

The parallel upturn of ions as different in size as Na^+ and Rb^+ support this view over other possible explanations.

From Fig. 1 it can be seen that LiNO_3 solutions have a higher water activity than LiCl , but from Table I it appears that NO_3^- is a poorer "complexing" agent than Cl^- , falling between Br^- and I^- . Thus, compared to LiCl solutions, 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 Na^+ and Cs^+ curves in LiNO_3 are very similar to those with LiCl solutions; no crossing has occurred at 8 M LiNO_3 , but it is obviously imminent.

The last salt system studied, that of LiAc (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.) The result of this association is to more effectively solvate the smaller cations, particularly Li^+ , in the aqueous phase, and so hold them there, while pushing the larger cations into the resin phase in the exchange. Thus, the D's and elution volumes for Na^+ and especially Cs^+ are far larger at a high LiAc concentration than at a comparable concentration in any other salt solution studied. 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 Na^+ and 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 macro-electrolyte 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 HClO_4 , and so the behavior of the tracers in HClO_4 (Fig. 7) is very similar to that in LiClO_4 , except that the crossing of the Na^+ and Cs^+ curves occurs at a slightly lower concentration. Recently published work⁵ agrees with that reported here for the region of the Na^+ and 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 Na^+ and Cs^+ reversed their order was determined. The value, $\sim 3.5 \text{ M}$, is larger than that for HClO_4 for exactly the same reasons that the value with LiI exceeds that for LiClO_4 .

Elutions with HBr were not studied in this series of experiments, but they have been reported upon in the literature.⁵ It was found that the Na^+ - Cs^+ reversal occurs at $\sim 5\text{-}6 \text{ M}$ 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 Br^- than for I^- 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 Na^+ - 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 H^+ concentration

means that the mass-action effect of the 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 Cl^- concentration means less 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, Figs. 3 and 8, indicate 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 Na^+) rise above the LiCl curves; the $Na^+ - Cs^+$ crossing occurs at about 8 M for HCl and at about 10 M for LiCl.

With HNO_3 elutions the effect of acid association becomes even more important, as HNO_3 is about 50% associated at 10 M. This complexing of H^+ by NO_3^- in the aqueous phase permits Na^+ , and to a lesser extent Cs^+ , to better compete for association with the sulfonate groups in the resin phase, and should increase their elution volumes over the corresponding values in $LiNO_3$. A comparison of the $LiNO_3$ and HNO_3 curves, Figs. 4 and 9, shows that the Na^+ curve does indeed rise compared to the $LiNO_3$ curve, lowering the $Na^+ - Cs^+$ crossing point in HNO_3 to about 5 M. Furthermore, a comparison of the HCl and HNO_3 results shows that the upturn for Na^+ is greater with HNO_3 , the weaker acid, and that even the Rb^+ and Cs^+ curves are beginning to turn up. It is puzzling, however, that the elution volumes for both Na^+ and Cs^+ with concentrated HNO_3 solutions are not still larger in magnitude.

With HAc as the macro-electrolyte, the association of H^+ and the anion, Ac^- , is almost complete. The main result is very large elution volumes (Fig. 6). Other differences from the LiAc results are the upturn in the curves, particularly of the Na^+ one, and consequent greater tendency to cross at high HAc concentrations. This is a continuation of the trend already noted and discussed for the HCl and HNO_3 results. The fact that the Na^+ and Cs^+ curves do not cross is, of course, due to the complexing ability of the small amount of equilibrium Ac^- in the solution.

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

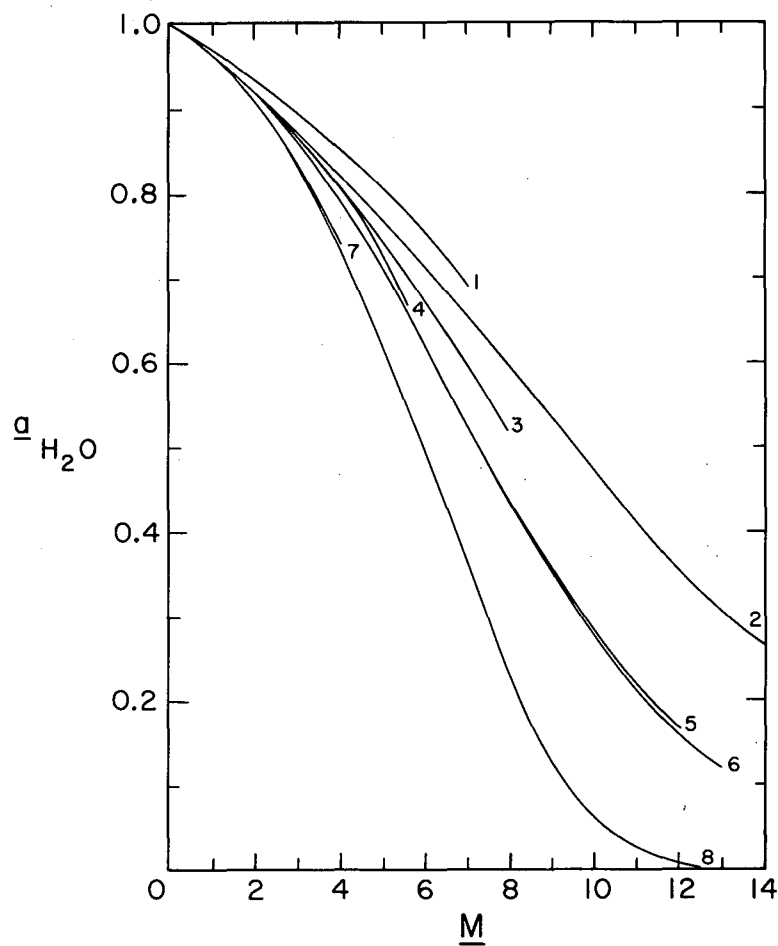
Summarizing, it can be seen that in dilute solution exchange there are two principal factors determining the order of cation selectivity with hydrated ions. (But the water structure must also be considered with relatively unhydrated ions (see ref. 10).) They are ion hydration and interaction with the resin anion in the resin phase; these are competing means of solvating the cations. Among a family of similar ions, the smaller the ion, the stronger are both these interactions. For a resin with as weakly interacting an anionic group as $-SO_3^-$, the hydration in the dilute external solution provides the most complete solvation for the cations, and so the smaller ion goes preferentially into that phase. In the exchange process, the larger ion is then forced into the resin phase, and the elution order $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ results. If a resin with a more strongly complexing anionic group is

used, the preference of the smaller ion for the aqueous phase will be reduced, and so the selectivity differences will be correspondingly reduced.

The relative importance of the interactions of the cations with the resin groups and with water molecules can also be influenced by raising the external solution concentration. As this is done, the growing difficulty of solvating the increasing number of ions with the smaller number of water molecules makes ion hydration less important and anion interactions (complexing) with the cations more important. If the resin anion interacts more strongly with the cations than does the external macro-anion, the smaller cations will preferentially go into the resin phase to obtain as complete solvation as possible. Conversely, if the cations interact more strongly with the macro-anion than with the resin group, the smaller cations will prefer the aqueous phase and will push the larger cations into the resin. As shown in the present paper, with increasing concentration of a macro-electrolyte containing a relatively strongly interacting anion, e.g., LiAc, solvation of the cations by water is, at least partially, replaced by anion solvation, and the elution order remains unchanged. But if a salt with a weakly interacting anion, e.g., LiClO_4 is used, at high concentrations (low water activities) the solvation of the smaller cations is best furnished by the resin sulfonate groups, and so the elution order reverses. For a given resin, the more poorly complexing the macro-anion and the lower the water activity, the lower the solution concentration at which the elution order reversal occurs.

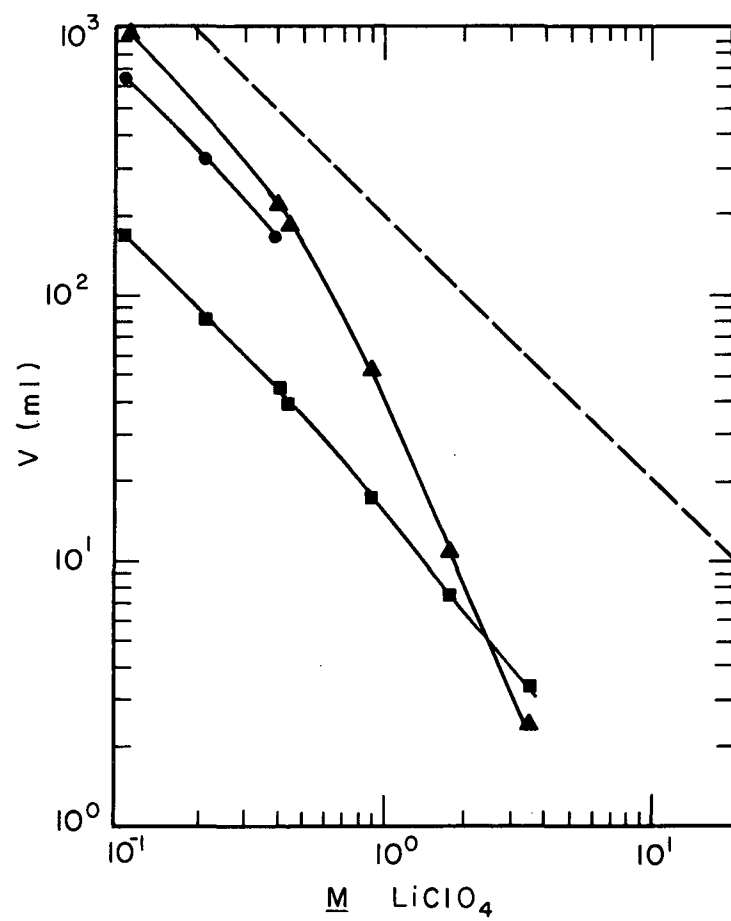
Table I. Activity coefficients of 1.0 Molal Solutions at 25°C.¹⁷

	ClO_4^-	I^-	Br^-	Cl^-	NO_3^-	toluene sulfonate	acetate (Ac^-)
H^+	0.823	0.963	0.871	0.809	0.724	0.535	
Li^+	0.887	0.910	0.803	0.774	0.743	0.617	0.689
Na^+	0.629	0.736	0.687	0.657	0.548	0.554	0.757
K^+		0.645	0.617	0.604	0.443	0.506	0.783
Rb^+		0.575	0.578	0.583	0.430		0.792
Cs^+		0.533	0.538	0.544	0.422		0.802



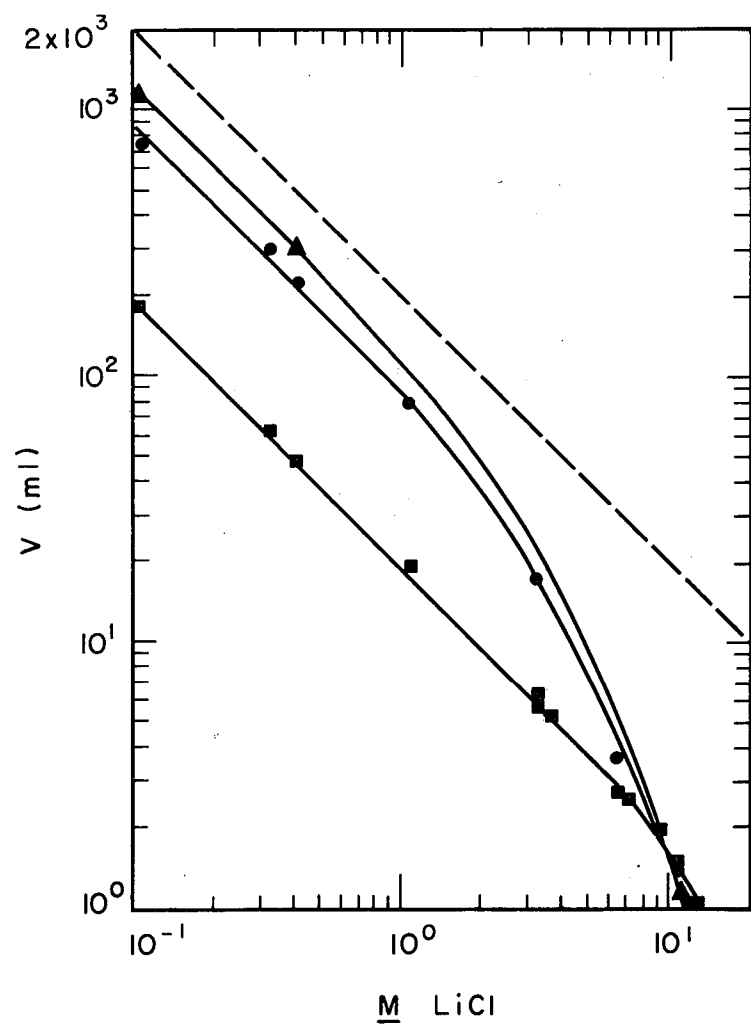
MU-28725

Fig. 1. Variation of water activity with aqueous molarity¹⁷ of:
 1, CsCl; 2, HNO_3 ¹⁸; 3, $LiNO_3$; 4, $LiAc$; 5, HCl ; 6, $LiCl$; 7,
 $LiClO_4$; 8, $HClO_4$.



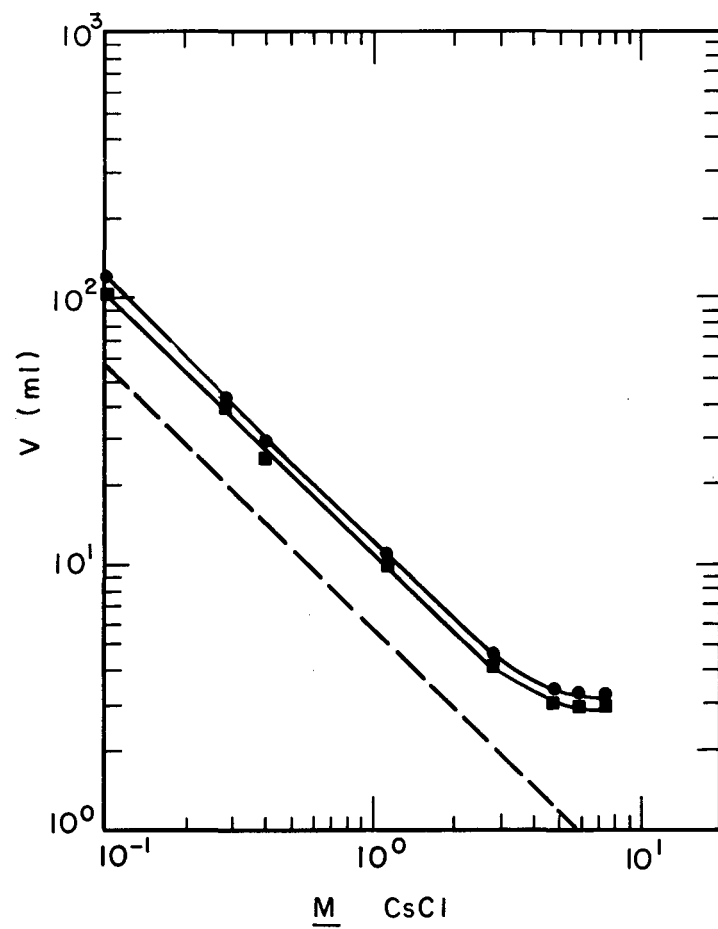
MU-29138

Fig. 2. Corrected peak elution volume, V (ml) on Dowex-50W vs LiClO_4 molarity for alkali tracers: ●, Na; ▲, Rb; ■, Cs. — —, slope -1.0.



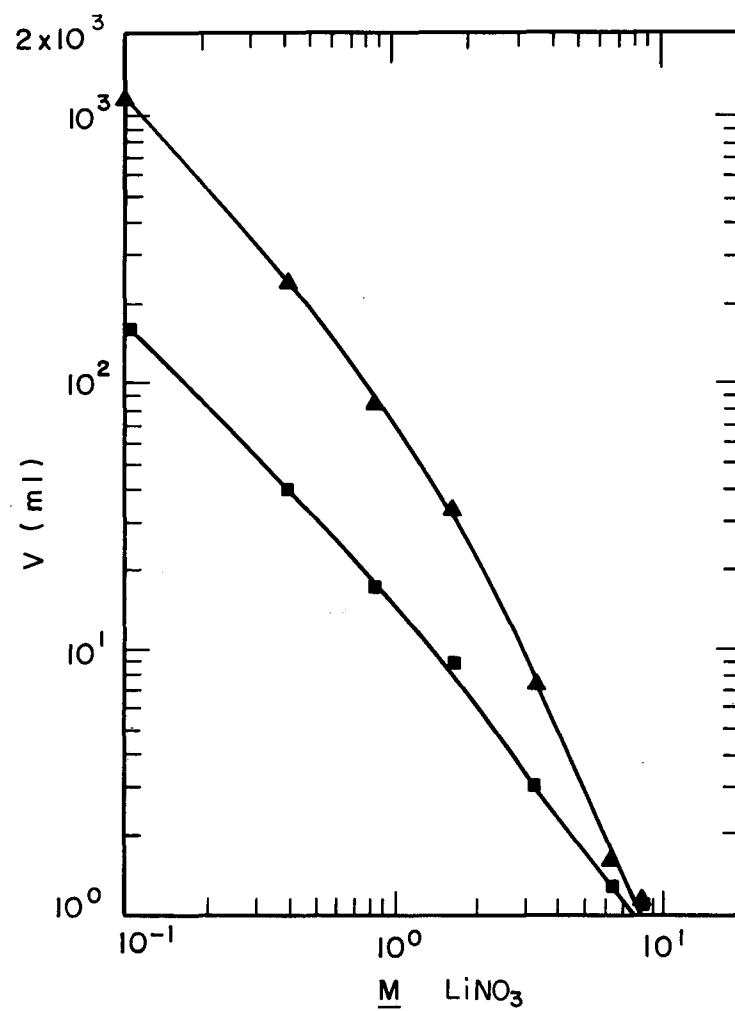
MU-29135

Fig. 3. Corrected peak elution volume V (ml), on Dowex-50W vs LiCl molarity for alkali tracers; $\bullet$, Na; $\blacktriangle$, Rb; $\blacksquare$, Cs. --, slope -1.0.



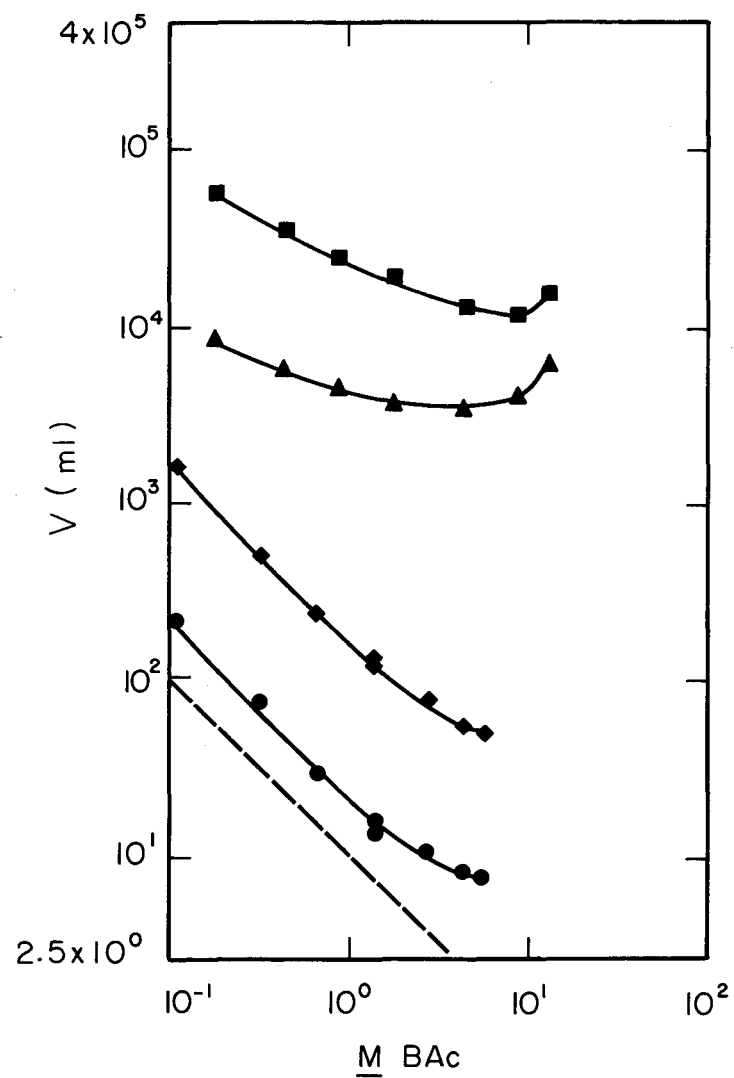
MU-29133

Fig. 4. Corrected peak elution volume V (ml), on Dowex-50W vs CsCl molarity for alkali tracers: $\circ$, Na; $\triangle$, Rb; $\blacksquare$, Cs. --, slope -1.0.



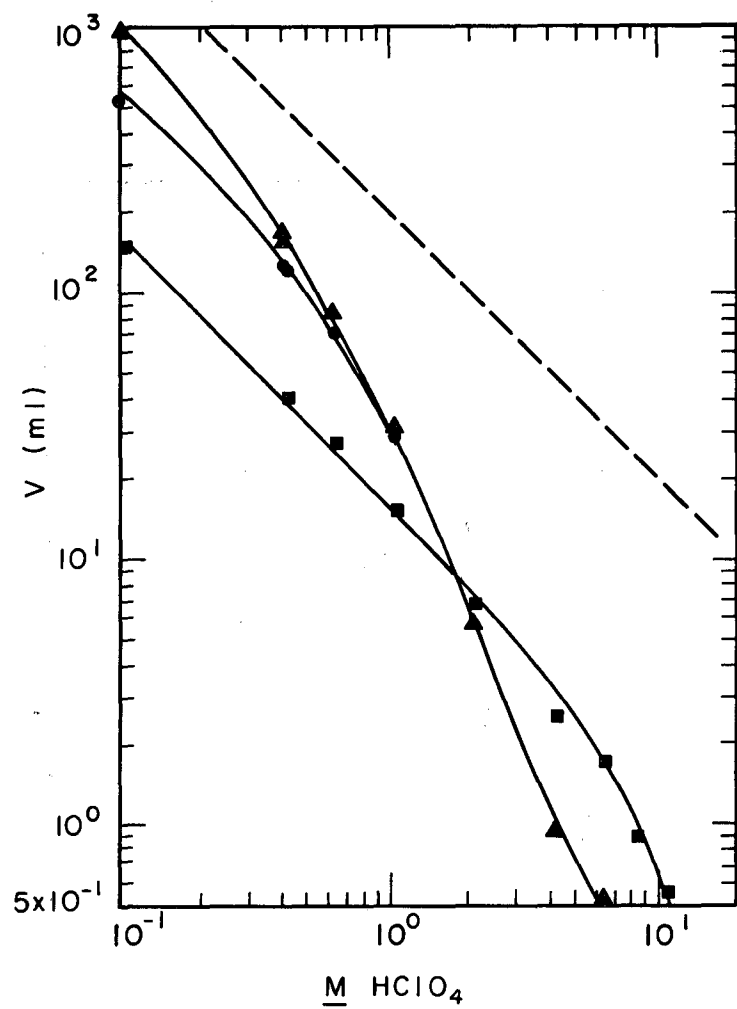
MU-29139

Fig. 5. Corrected peak elution volume $V(\text{ml})$ on Dowex-50W vs LiNO_3 molarity for alkali tracers: ●, Na; ▲, Rb; ■, Cs. — — , slope -1.0.



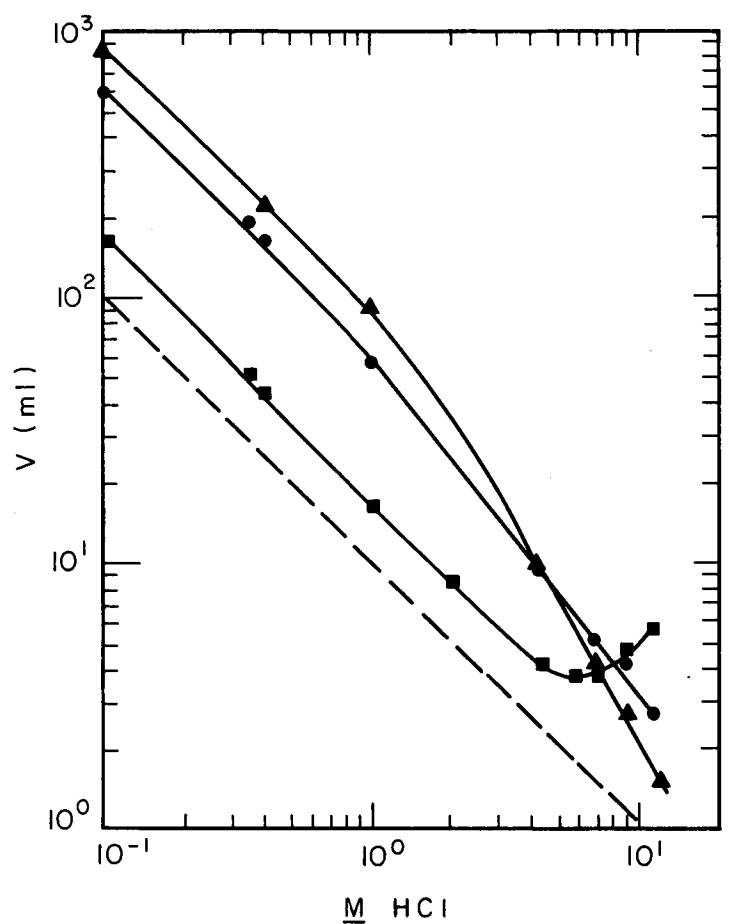
MU-29132

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



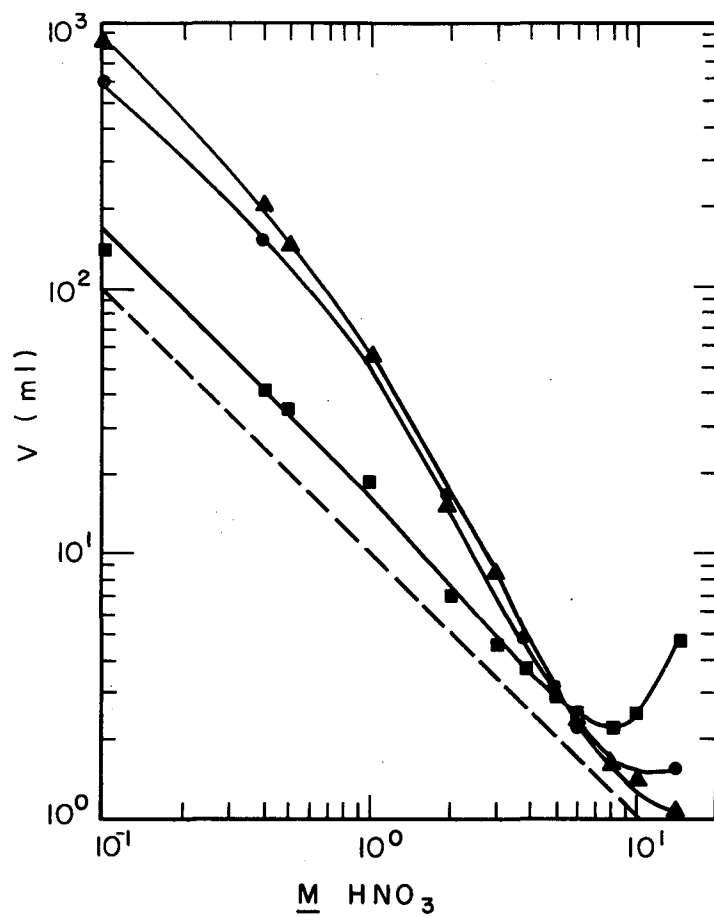
MU-29136

Fig. 7. Corrected peak elution volume, $V(\text{ml})$, on Dowex-50W vs HClO_4 molarity for alkali tracers: $\bullet$, Na; $\blacktriangle$, Rb; $\blacksquare$, Cs. --, slope .1.0.



MU-29137

Fig. 8. Corrected peak elution volume, V (ml), on Dowex-50W vs HCl molarity for alkali tracers: $\circ$, Na; $\triangle$, Rb; $\blacksquare$, Cs. --, slope -1.0.



MU-29134

Fig. 9. Corrected peak elution volume, $V(\text{ml})$, on Dowex-50W vs HNO_3 molarity for alkali tracers: ○, Na; ▲, Rb; ■, Cs. --, slope -1.0.

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