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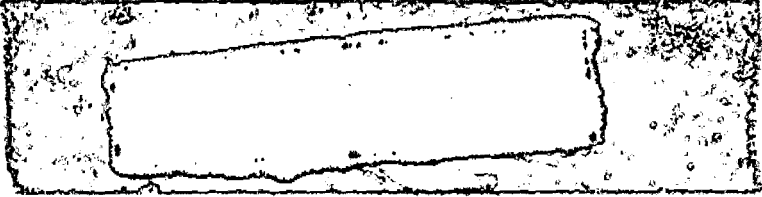
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May 1959

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ABSTRACT

An explanation is offered for the interesting feature that distribution ratios of anions with strong-base exchange resins are generally lower from concentrated HCl solutions than from comparable LiCl solutions. It is suggested that this behavior is due to the invasion of the resin by nonexchange electrolyte at the high external-solution concentrations and to the partial association of the acid species in the resin phase. That is, because of the nature of the latter phase, normally strong acids are differentiated, the weaker ones partially associating. This does not occur as readily with the lithium salts, and so the preferential association of nonexchange H^+ with the weaker-acid anion (Cl^- in most of the cases studied) represses the absorption of the other anion as a nonexchange electrolyte. If the anion of interest were the anion of a weaker acid than that of the macroelectrolyte, the reverse of the usual behavior should occur, namely, exchange from acid solution should yield larger distribution ratios than exchange from lithium salt solutions. This is shown to be the case for Cl^- tracer exchanging with concentrated HBr and LiBr solutions.

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INTRODUCTION

Hydrochloric acid is one of the commonest and most important eluants used in anion-exchange-resin separations and studies.¹ Since the aqueous activity coefficients of HCl and LiCl are moderately similar up to very concentrated solutions, it certainly might be expected that the exchange behavior of anions from LiCl and HCl solutions would also be similar. However, this has been found not to be true.^{2,3} Most anions, and particularly the metal-chloride complex ions, show values of the distribution ratio, D, which are one to three orders of magnitude greater for concentrated LiCl solutions than those for HCl solutions of the same concentration. The distribution ratio is defined as

$$D = \frac{\text{amount of ion of interest per gram of resin}}{\text{amount of ion of interest per milliliter of solution}}$$

Examples are shown in Figs. 1 and 2, and other cases are in the literature.^{2,3} Such behavior can be useful in metal-ion separations, and, for example, the larger D values obtained in LiCl solution have been used in the separation of the transplutonium ions from the rare earth ions.² But this difference in behavior is also an interesting feature to be explained in understanding the ion-exchange-resin process. An explanation that has been tentatively advanced^{1,2} is that the complex metal anions are the anions of somewhat weak acids, and that at high HCl concentrations the undissociated complex acid forms in the external aqueous solution. Such association would lower the concentration of the distributing metal anion, and so would lead to the observed lower

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value of D in HCl solutions.

But there are difficulties with this explanation. Firstly, the extraction behavior of the complex metal acids into oxygenated organic solvents indicates that they are not weak, but very strong acids, stronger than HCl.^{4,5} Their strength is of the order of that of HClO_4 , which is indeed a good model acid for the metal-complex acids. Secondly, the distribution ratio of bromide ion is also larger from LiCl than from HCl solutions (reference 1 and Fig. 1). But HBr is certainly a strong acid, stronger than HCl, and so by the above explanation should have a higher value of D from the HCl solution than from the LiCl solution. Curiously, the difference in the values of D for Br^- with HCl and LiCl is not as great as those for the chlorometallic complex ions such as GaCl_4^- , FeCl_4^- , and InCl_4^- . In fact, it appears that the magnitude of the difference in D between HCl and LiCl solutions increases with increasing acid strength of the anion under consideration. This is just the reverse behavior of that to be expected from the above explanation, but a clue to an alternative explanation to be presented in this paper.

EXPERIMENTAL

Resins: The resins used in this work were of the strongly basic quaternary-amine type, namely Dowex-1 resins of 10 and 16% divinylbenzene content.⁶ They were conditioned before use by alternate repeated washings with 3 M HCl and water and were then dried at $98 \pm 1^\circ\text{C}$ overnight. After cooling, they were dry-sieved (10% DVB to 60 to 100 US mesh; 16% DVB to 200 to 400 US mesh), and stored in a desiccator over anhydrous $\text{Mg}(\text{ClO}_4)_2$.

Tracers: The $(\text{Re}^{186}\text{O}_4)^-$ ($T_{1/2} = 89$ hr) and $(\text{Br}^{82})^-$ ($T_{1/2} = 36$ hr) were obtained from Union Carbide Nuclear Company, Oak Ridge, Tennessee. The $(\text{Cl}^{34})^-$ ($T_{1/2} = 32$ min) was produced by irradiating sodium hydrogen phosphate in the Berkeley 60-inch cyclotron. No detectable change in the gamma-ray spectra of the tracers occurred during the period of their use, and the tracers decayed with the correct half lives, indicating that no appreciable radioactive impurities were present. The radioactive samples were counted with a well-type NaI scintillation counter employing a single-channel analyzer.

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Method: The values of D for ReO_4^- were obtained by the batch equilibration method, those for Cl^- by the column technique, and those for Br^- by both methods. In the batch method, 50 μl of the tracer in 10 ml of the macroelectrolyte solution were shaken for 4 to 12 hr with small amounts (0.03-0.2 g) of resin. Duplicate 3-ml aliquots of the solution were withdrawn through glass-wool filters and gamma-counted. After correction for background, comparison of the counting rates with those of aliquots of the initial solution before the introduction of the resin allowed the calculation of D . The method becomes quite inaccurate for small values of D , and for such cases the column technique is more suitable. This consists of adsorbing a few microliters of the tracer on the top of a column of resin (pre-equilibrated with the macroelectrolyte solution at the concentration to be studied), and then eluting the tracer with the solution of macroelectrolyte. The volume of solution necessary to elute the tracer (neglecting one free-column volume) is proportional to the distribution ratio of the tracer.⁷

RESULTS AND DISCUSSION

The variation in the distribution ratios for several tracer anions, Br^- , I^- , ReO_4^- , InCl_4^- , CoCl_4^{2-} , and ZnCl_4^{2-} , with Dowex-1 resins of 2, 10, and 16% DVB content from various chloride solutions, HCl , LiCl , NaCl , KCl , CsCl , $\text{N}(\text{CH}_3)_4\text{Cl}$, and $\text{N}(\text{C}_2\text{H}_5)_4\text{Cl}$, have been studied.⁸ It has been found that the plot of $\log D$ vs. chloride concentration for HCl is anomalous. This curve always shows a more negative slope at high chloride concentrations than those for the alkali chlorides. Figure 3 is an example, showing some of the data for tracer ReO_4^- . Note that the curve for HCl falls steeply across the others.

For such exchange of univalent ions, X^- and Cl^- , the equilibrium expression may be written as

$$1 = \frac{(\overline{\text{Cl}}) (\bar{\text{X}}) \bar{r}_{\text{MCl}} \bar{r}_{\text{MX}}}{(\text{Cl}) (\text{X}) \bar{r}_{\text{MCl}} r_{\text{MX}}} \quad (1)$$

where the bar indicates the resin phase and MCl is the macroelectrolyte. A distribution ratio, D' , can be defined as

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$$D' = \frac{\text{molality of ion in the resin phase}}{\text{molality of ion in the external solution}} = \frac{(\bar{X})}{(X)} = \frac{(\bar{Cl}) \bar{\gamma}_{MCl} \gamma_{MX}}{(Cl) \gamma_{MCl} \bar{\gamma}_{MX}} \quad (2)$$

It should be noted that D' is not the same as the more easily measured ratio, D , which has already been defined, but D is equal to rD' where r is the ratio of the milliliters of solution that contain one gram of water to the grams of resin that contain one gram of water. Then for dilute external solutions, where $\gamma_{MCl}/\gamma_{MX} \rightarrow 1$, we have

$$D' \approx \frac{(\bar{Cl}) \bar{\gamma}_{MCl}}{(Cl) \bar{\gamma}_{MX}} \quad (3)$$

Furthermore, if the ion of interest X^- is present in only tracer quantities and there is no resin invasion by nonexchange electrolyte, we have $(\bar{R}') = (\bar{Cl}) = \text{constant}$, where (\bar{R}') is the concentration of resin sites in milliequivalents per gram of resin water, and $\bar{\gamma}_{MCl}/\bar{\gamma}_{MX} = \text{constant} = K$. From these we obtain

$$D \approx D' = K \frac{(\bar{R}')}{(Cl)} = K'/(Cl) \quad (4)$$

At very low external solution concentrations, no dependence of the distribution ratio on the nature of the chloride solution is to be expected. The ratio depends only upon the chloride concentration. Experimentally, the difference between the HCl and LiCl (as well as the other alkali chloride) curves is negligible at low external solution concentrations, but increases with increasing chloride concentration. This suggests that the effect may be connected with the presence of nonexchange electrolyte in the resin phase, that is, with the increasing amount of electrolyte that invades the resin phase at increasing external solution concentrations.

The increasing amount of nonexchange electrolyte present in the resin phase makes the expression for D' , Eq. (3) or (4), more complicated. Equation (2) is still correct, but instead of $(\bar{Cl}) = (\bar{R}')$, we have $(\bar{Cl}) = (\bar{R}') + (\bar{M})$. Thus we obtain

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$$D' = \left[\frac{(\bar{R}')}{(Cl)} + \frac{(\bar{M})}{(Cl)} \right] \frac{\bar{\gamma}_{MCl} \gamma_{MX}}{\bar{\gamma}_{MX} \gamma_{MCl}} =$$

$$\left[\frac{(\bar{R}')}{(Cl)} + \frac{-(\bar{R}') + \sqrt{(\bar{R}')^2 + 4(\gamma_{MCl} / \bar{\gamma}_{MCl}) (M) (Cl)}}{2(Cl)} \right] \frac{\bar{\gamma}_{MCl} \gamma_{MX}}{\bar{\gamma}_{MX} \gamma_{MCl}} \quad (5)$$

The first term on the right side gives the exchange contribution, but this decreases as $(Cl)^{-1}$, so that the second term, due to the resin-invasion electrolyte, may become dominant at high external-solution concentrations. Thus D' does not decrease as steeply with increasing (Cl^-) as the first term alone and becomes dependent on the nature of the cation of the macroelectrolyte solution. This dependence is reflected in variations in (R') and in the ratios of activity coefficients, $\gamma_{MCl} / \bar{\gamma}_{MCl}$ and $\gamma_{MX} / \bar{\gamma}_{MX}$.

For simple univalent tracer anions, the order of decreasing distribution ratios with the various concentrated alkali chloride solutions is the same as that of the resin invasion by the chloride salts themselves, namely, $Li > Na > K > Cs > NMe_4 \supset NEt_4$.⁸ This is not surprising, as from Eq. (5) it can be seen that the order of the distribution ratios depends upon the relative amount of resin-invasion cation, (\bar{M}) . The reasons for the differing amounts of resin invasion and what effect this has on the distribution ratios will be discussed in greater detail in a later paper,⁸ but for the present it is sufficient to point out the parallel between the amount of resin invasion by the macroelectrolyte, and the order of distribution ratios of a given tracer. In contrast to this general behavior, the distribution ratios for most tracer anions are lower from HCl than from LiCl solutions, even though the solubility of HCl in the resin phase is greater than that of LiCl from solutions of the same concentration.^{8,9} This behavior becomes more marked as the external solution concentration increases. We believe that the origin of this anomaly lies in the formation of undissociated HCl in the resin-phase solution. This undissociated HCl may be either molecular HCl or an ion pair; it has not been possible to differentiate these cases. But there are several reasons for believing that association occurs. Firstly, there is some association in any

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concentrated HCl solution, and the amount increases with increasing total concentration. The resin phase solution is a very concentrated electrolyte. For example, when the external aqueous HCl concentration is ~ 12 m, the total ionic strength of the internal resin-phase solution is about double that, ~ 16 m in HCl and ~ 8 m in resin chloride. There is thus relatively less water in the resin phase than in the external solution to solvate the ions and keep the H^+ and Cl^- apart. Furthermore, the lower effective dielectric constant of the resin phase increases the electrostatic interaction between ions. The suggested association of HCl in the resin phase explains its greater solubility there than that of LiCl. In fact, this association explains both the greater amount of HCl over LiCl absorbed per unit weight of resin from solutions of the same molality, and the curious feature that the concentration of total HCl inside the resin is greater than that of the equilibrating solution, at high HCl concentrations. The resin solution contains more HCl in the form of a new (associated) species than the external solution. Experimentally, such acid association has also been observed with $SO_4^{=}$, since HSO_4^- appears to be a weaker acid in the resin phase than in an ordinary aqueous solution,⁹ and should be a perfectly general phenomenon in the resin phase.

More importantly for this discussion, it provides an explanation for the anomalously low values of the distribution ratios of tracer anions from concentrated HCl solutions. The association of the HCl in the resin phase results in a smaller number of "free" nonexchange cations there than with LiCl solutions. If the tracer anion of interest is from a stronger acid than HCl, few of these anions can enter the resin phase as nonexchange electrolyte from HCl solutions, because the chloride ion preferentially unites with the nonexchange hydrogen ion. A much smaller amount of association, occurs with the nonexchange lithium ion in the resin phase, and so the distribution ratio from HCl solutions falls increasingly below that from LiCl solutions as the amount of nonexchange electrolyte in the resin increases with increasing external solution concentration.

Such behavior follows directly from the present hypothesis that $\bar{\gamma}_{HCl}$ is less than $\bar{\gamma}_{LiCl}$ as long as the tracer anion is derived from an acid stronger than HCl. This can be seen from Eq. (5) because γ_{LiX} and γ_{LiCl} are

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approximately equal to γ_{HX} and γ_{HCl} , respectively, so that $D'_{LiCl}/D'_{HCl} \propto \frac{\bar{\gamma}_{LiCl} \bar{\gamma}_{HX}}{\bar{\gamma}_{LiX} \bar{\gamma}_{HCl}}$. The difference in D between HCl and LiCl solutions should, in fact, increase with the strength of the acid, HX, and it appears that the magnitude of the "HCl effect" does increase from Br^- to I^- to ReO_4^- to $InCl_4^-$. This is the order of increasing acid strength for HCl, HBr, and HI, and that expected for $HReO_4$ and $HInCl_4$. However, it is difficult to test this point with other anions from such strong acids as, because of their great strengths, they would not be expected to show great differences from each other in their resin behavior, and their exact acid strengths are not usually known.

However, if the hypothesis of relatively greater acid association in the resin phase than in the external solution is correct, the relative distribution ratios for a tracer anion from lithium and acid macroelectrolyte solutions should also be a function of the relative strength of the macroelectrolyte acid, as can be seen from Eq. (5). If a weaker acid than HCl and its lithium salt were used, a greater variation in the distribution ratios of the tracer anion might be expected than from HCl and LiCl. If a stronger acid were used, less difference in the distribution ratios might be expected, (as long as the macroacid were weaker than the tracer acid; see last paragraph below).¹⁰

Figure 4 presents the results of such a study with ReO_4^- tracer using the acid-salt pairs, HBr-LiBr and HNO_3-LiNO_3 . Hydrobromic acid is stronger than HCl and HNO_3 is weaker, and it can be seen that the difference in D' values for the HNO_3-LiNO_3 case is indeed larger than that for the HBr-LiBr pair.

This larger difference between HNO_3-LiNO_3 solutions than between HCl-LiCl solutions has also been noted recently with the rare earth ions.¹¹ The idea that the resin phase solution is more conducive to ion association than the external solution because of its lower water content and effectively lower dielectric constant leads to an explanation for the absorption of the rare earth ions from $LiNO_3$ solutions and for their order of absorption. Since it is most unlikely that the rare earth ions form anionic complexes with nitrate, the absorption of the former by the resin is as nonexchange cations. Nitrate ion will preferentially associate with H^+ , and so from HNO_3 solutions there will be little chance for the rare earth ions to enter the resin phase; the

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nonexchange electrolyte will be predominantly HNO_3 . From LiNO_3 solutions, however, the nonexchange electrolyte cations are lithium and the rare earth ions. Observation of activity-coefficient tables¹² shows that nitrate salts have low values relative to chloride salts, and that this difference becomes more pronounced as one goes from the alkalis to the alkaline earths and, presumably, on to the rare earths. Such lower values are indicative of ion association, and that the higher the charge on the cation, the larger the effect. Thus, although the rare earth ions cannot compete with H^+ for the nonexchange NO_3^- , they can do so very favorably with Li^+ , and so go into the resin phase with nitrate ion as (partially ion associated) nonexchange electrolyte. The values of D should increase with increasing nonexchange electrolyte concentration, and hence, increasing external solution concentration, as is observed. Furthermore, the strength or degree of the rare earth-nitrate ion association should be a function of the ionic size of the rare earth ion, increasing with decreasing size of the hydrated ion. Since the hydrated size of the rare earth ions increases from La to Yb, as indicated by their limiting equivalent conductances,¹³ greater association with nitrate ion should be expected in the reverse order. At a given nitrate concentration, the distribution ratios should decrease in the order La to Yb, which is the order observed experimentally. The striking effect of even very small amounts of HNO_3 (10^{-12} M) in reducing the values of D is also accounted for.

Still one more test of the hypothesis of acid association predominantly in the resin phase has been made. The distribution ratios for a tracer anion derived from an acid whose strength is weaker than that of the macroelectrolyte anion should show the opposite behavior from H^+ and Li^+ solutions than that shown in Figs. 1, 2, 3, and 4. Now the tracer anion associates in the resin phase with the nonexchange H^+ more than does the macroelectrolyte anion, yielding values of D which are larger from concentrated acid solutions than from lithium solutions of the same molality. This can be seen again from Eq. (5). For example, the roles of Br^- and Cl^- as tracer anion and macroelectrolyte, respectively, (illustrated in Fig. 1) can be reversed, and the distribution behavior of tracer Cl^- can be studied from concentrated solutions of HBr and LiBr. The experimental results are shown in Fig. 5, and it can be seen that the expectation of larger D values for the HBr solutions than for those of LiBr are fulfilled.

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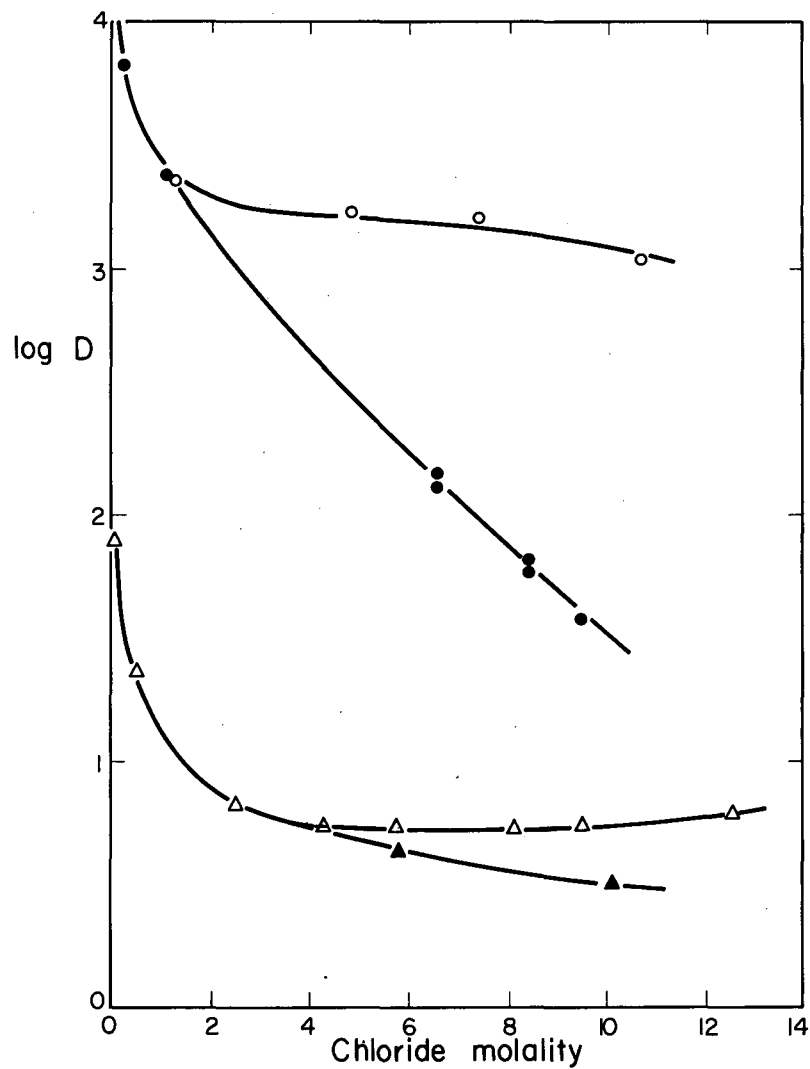
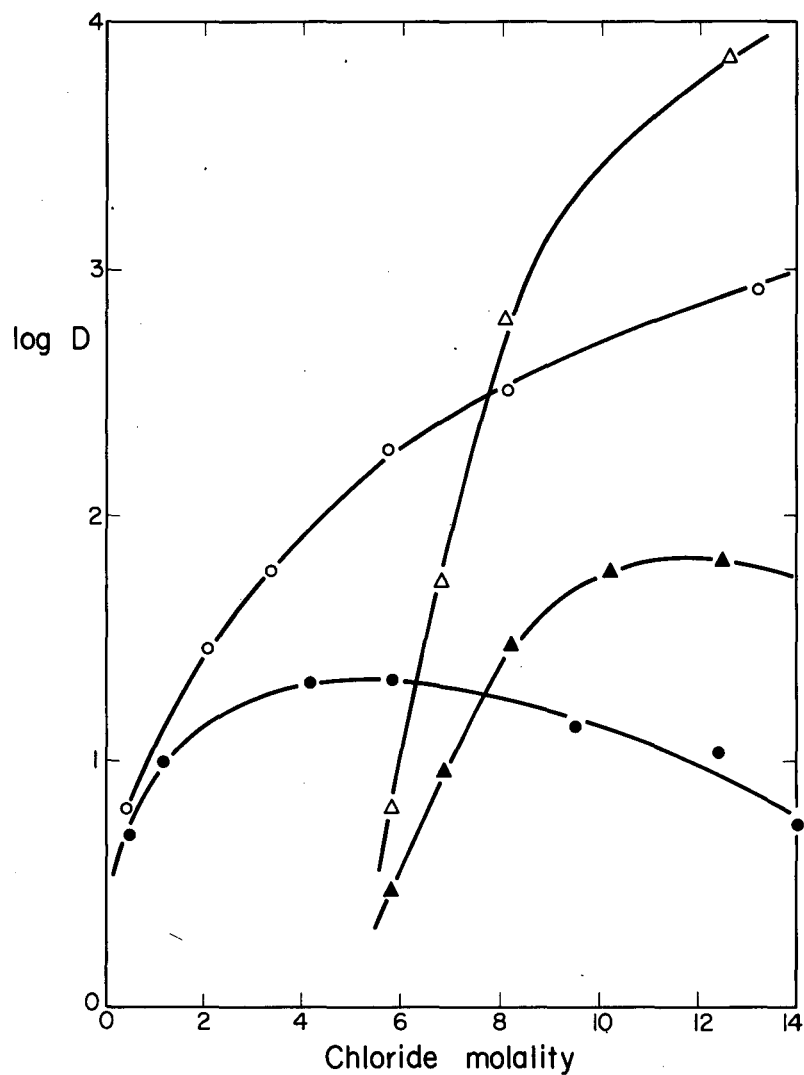


Fig. 1. Distribution ratio vs. chloride molality for tracer perrhenate, Δ — Δ , and for tracer bromide, O — O . Open symbols are LiCl solutions; closed symbols are HCl solutions.



MU-17261

Fig. 2. Distribution ratio vs. chloride molality for tracer indium(III), $\circ-\circ$, and for tracer cobalt(III), $\triangle-\triangle$. Open symbols are LiCl solutions; closed symbols are HCl solutions.

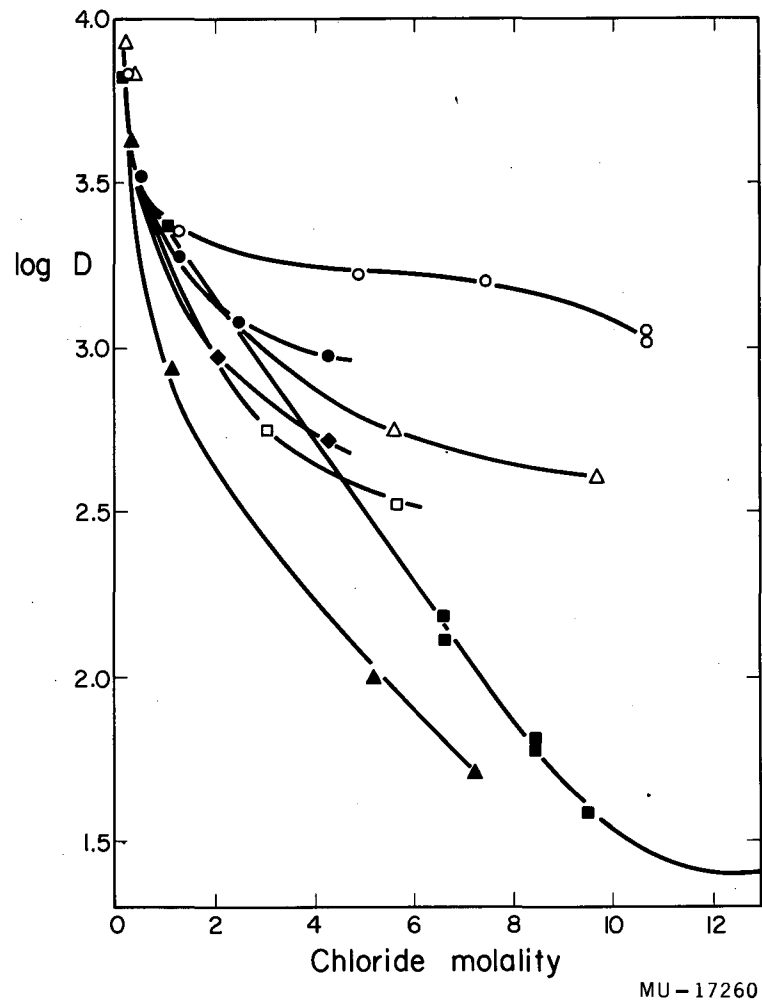
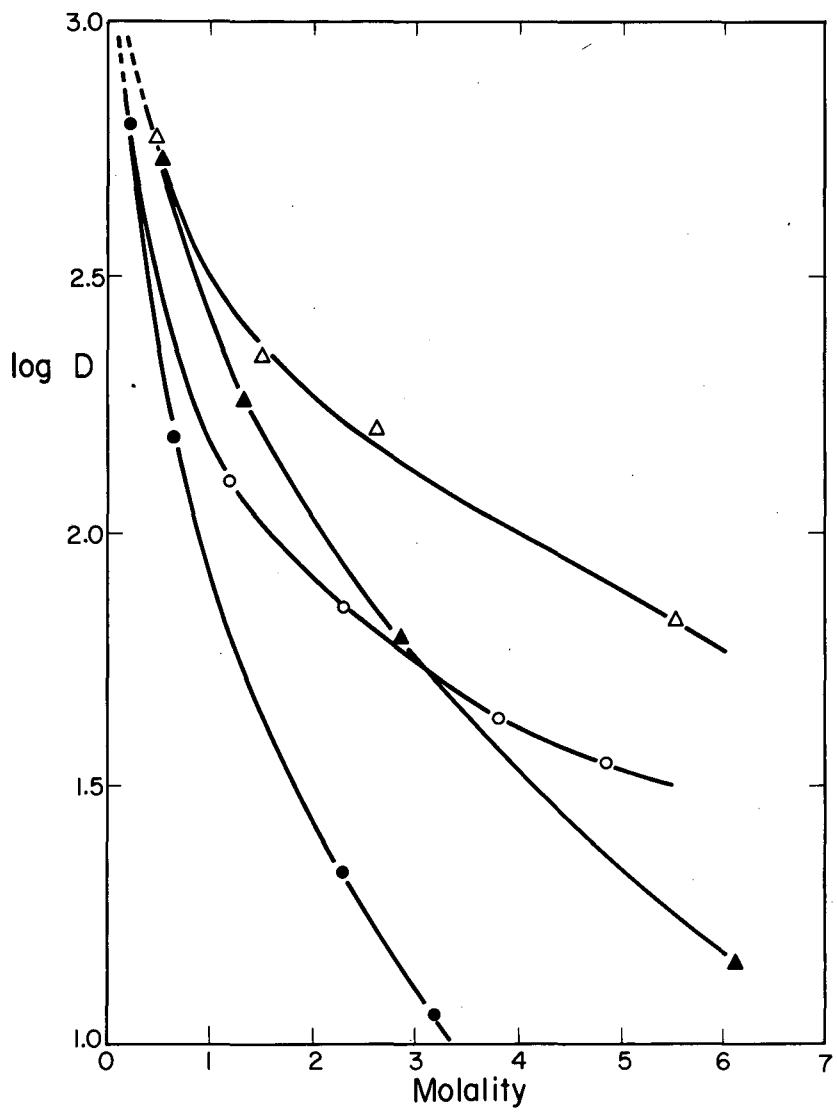
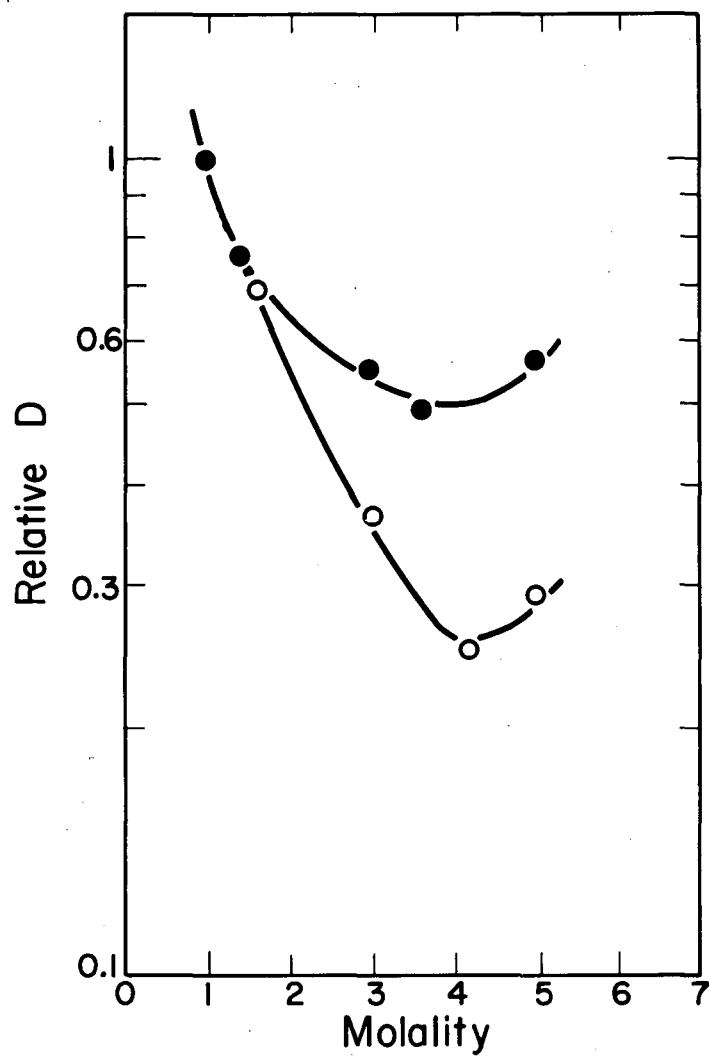


Fig. 3. Distribution ratio vs. chloride molality for perrhenate ion from LiCl, ○—○, HCl, +—+, NaCl, ●—●, KCl, ■—■, CsCl, □—□, NMe₄ △—△, NEt₄Cl, ▲—▲, solutions.



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Fig. 4. Distribution ratio for perrhenate tracer vs. bromide, $\Delta-\Delta$, and nitrate, $O-O$, molality. Open symbols are for lithium salts; closed symbols are for acids.



MU - 17259

Fig. 5. Distribution ratio vs. bromide molality for tracer chloride ion. Open symbols are for lithium salts; closed symbols are for acid.

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