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ANION EXCHANGE IN AQUEOUS-ORGANIC SOLVENT MIXTURES, II*

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Abstract

The uptake by Bio-Rad AG1-X4 anion resin of LiCl and of solvent from isopropyl alcohol-water solutions has been measured. As with dioxane-water solutions, the resin selectively absorbs water. The values of the distribution ratios, D, for tracer ReO_4^-, I^-, Br^-, and F^- with macro Cl^- concentrations was determined as a function of alcohol mole fraction, as was also D vs. acetone mole fraction for tracer ReO_4^-, Br^-, and F^-. The distribution ratios for the larger anions decreased with increasing solvent mole fraction, while those for F^- increased. For reasons discussed in the text this is expected to be a general phenomenon. The behavior of complex anions is also indicated.

Introduction

A previous paper has discussed the anion-exchange selectivity shown by (organic) ion-exchange resins with water-dioxane solutions.[1] Experimentally, the selectivity dropped markedly with an increase in dioxane content, so that by 50% mole-fraction dioxane, the ratio of the distribution coefficients of I^- to F^- was only ~ 4, instead of the ~ 100 in water alone. That paper pointed out, as is generally recognized, that water is a much better solvating agent for anions than is dioxane, for a number of reasons.[2-5] Thus, anions would compete to follow the distribution of water between the resin and external phases, and the smaller, more basic anion, which stands to gain the most in solvation energy, would win and push the other larger, less-basic anion into the dioxane-rich phase. Since it was also found that the resin phase took up water in preference to dioxane, this means that the smaller anions, which strongly favor the external phase with dilute aqueous solutions, should prefer that phase less and less as the proportion of dioxane increases. This is just what was observed.

But if this idea has validity, it would be interesting to compare the behavior of the same anions and resin when using mixtures of water and a hydroxylic solvent, such as an alcohol. Certainly a less marked decrease in selectivity with increasing organic-solvent mole fraction should be expected than was the case with dioxane, for the alcohol molecule can hydrogen-bond to an anion and so offer it better solvation, though still not as complete as with water. Isopropyl alcohol was chosen for this study.

Experimental

Reagents.— The anion-exchange resin used was the same Bio-Rad AG1-X4, 100-200 mesh, employed in the previous study.[1] Its capacity and water uptake were 4.04 meq and 1.73 g, respectively, per g of dry Cl^--form resin. The isopropyl alcohol used was Matheson, Coleman, and Bell, spectral grade, and the acetone was Baker and Adamson, reagent grade. The LiCl was Baker and Adamson, reagent grade; a saturated solution was made, filtered, diluted and analyzed with standard $AgNO_3$ using dichlorofluorescein as indicator. The $^{82}Br^-$ and $^{186}ReO_4^-$ tracers were prepared by neutron irradiation of LiBr and $KReO_4$ at the Vallecitos Reactor. The $^{18}F^-$ tracer was prepared by the $^{16}O(\alpha,d)^{18}F$ reaction on conductivity water at the Lawrence Berkeley Laboratory 88" cyclotron. The ^{59}Fe tracer was purchased from New England Nuclear Corp. as Fe(III) in dilute HCl.

Procedure.— The uptake by the resin of isopropyl alcohol and water from solutions of varying composition was determined in the same manner as previously,[1] using the index of refraction of the solutions to determine their composition.

The ion-invasion of the resin by 0.010 M LiCl in the solutions of different alcohol mole fraction was studied in the same manner as previously,[1] including making a correction for liquid adhering to the outside of the resin beads by using an equal volume of glass beads of 170-230 mesh.

The distribution measurements were made by batch experiments as before,[1] except that 60 ml glass-stoppered bottles were used. The value of the distribution ratio, D, is given by

$$D = \frac{\overline{[X^-]}}{[X^-]} = \frac{[(\text{counts/min})_{\text{initial}} - (\text{counts/min})_{\text{equil.}}][\text{volume of solution}]}{(\text{counts/min})_{\text{equil.}}[\text{g of dry } Cl^-\text{-form resin}]} \quad . \quad (1)$$

Results and Discussion

Solvent Uptake.— It can be seen in Fig. 1 that above an external-phase mole fraction of ~ 0.07 isopropyl alcohol, this strong-base resin in the Cl^- form preferentially takes up water into the resin. In the very dilute alcohol region, isopropyl alcohol is somewhat preferentially absorbed. Both of these results are in agreement with earlier studies on alcohol uptake by other investigators.[6,7] At this time it is hard to give a detailed explanation for this behavior, but we believe the following description is essentially correct.

The dominating feature of the solvent uptake from aqueous solutions of dioxane, and of isopropyl, n-propyl, ethyl, and to a smaller extent, methyl alcohols is the preferential absorption of water by the strong-base resin. Since it requires more work to place charges in the aqueous-organic mixture (of lowered bulk dielectric constant) that in the original aqueous system, there is an increase in the electrostatic free energy of the system when water molecules are replaced by the organic molecules. Upon addition of solvent, the resin phase will suffer a much larger electrostatic free energy increase than the external phase, because it has a high concentration of charge while the external solution is usually dilute, or may not have any electrolyte present at all. Water and the organic diluent distribute in such a way as to minimize this increase in free energy for the whole system, and clearly, this can best be done if the solvent that can provide the best electrostatic solvation moves preferentially into the resin phase. Molecules with the largest bond dipole moments and with the smallest size, so as to furnish the largest number of moments per unit volume, will provide the maximum of such solvation to the resin-phase ions. In comparison to most of the usual polar organic solvents,

water, with a dipole moment of 1.85D (Ref. 8) and a small molar volume (18 ml), is by far the best solvating agent. So with increasing organic-diluent mole fraction, the resin phase preferentially takes up water rather than diluent, thus minimizing the electrostatic free energy of the concentrated resin phase and of the system as a whole.

It should also be noted that the free energy of short-range chemical solvation ordinarily leads to the same conclusions. Water molecules usually provide anions with the best hydrogen-bonded first-shell coordination; small highly charged anions obtain additional solvation by means of additional shells of oriented water molecules. Since the concentration of counter anions is greater in the resin phase than in the dilute external solution, we would expect (from chemical solvation) a preferential uptake of water in the resin phase, the degree of uptake depending on the type of counter ion. Therefore we might anticipate 1) the smaller Cl^- to require more water in the Cl^--form resin than ClO_4^- in the ClO_4^--form resin, 2) F^-- or OH^-- or polyvalent anion-form resins (those greatly in need of hydration) to be very selective in water uptake, and 3) resins containing large singly-charged anions such as $AuBr_4^-$ to be much less selective, or even to prefer polar organic solvents with large dipole moments. The first expectation has been observed,[6,7] the second has been substantiated by work with OH^--form[9] and $SO_4^=$-form[7] resins, the third has yet to be tested.

It remains to explain the behavior at very low alcohol mole fraction, where the resin shows a small preference for the alcohol over water. We believe this is due to the difference of the water structure in the two phases. In the external solution of nearly pure water the hydrocarbon tail of the

alcohol interacts with the hydrogen-bonded water structure about as any hydrocarbon would, namely it tends to be pushed out of the way of the water structure into the less highly hydrogen-bonded structure in the resin phase.[10] That is, the presence of the hydrocarbon tightens up the water structure around it lowering both the enthalpy and the entropy of the water.[11,12] In the resin phase, the water structure is much less complete, due to the high concentration of ions there and to the fact that the resin matrix itself occupies about half of the volume, forcing the water into small layers and pores having at least one dimension of the order of only a few Angstroms. Because there is less water structure for the organic molecules to counter in the resin phase, positive values of ΔH and $T\Delta S$ should accompany their transfer from the aqueous into the resin phase, and the larger value of $T\Delta S$ should be the driving force,[13] just as with their transfer from an aqueous to an organic diluent phase.[11,12] The value of $T\Delta S$ should be larger, the larger the hydrocarbon tail. We believe this is the origin of the initial preferential uptake of alcohol by the resin, and the uptake does seem to be larger, the larger the alcohol. As the proportion of organic diluent is increased, however, the three-dimensional hydrogen-bonded water structure of the external phase is destroyed, both because the organic molecules occupy space (just like the resin matrix), and because the alcohol or dioxane molecules themselves can hydrogen-bond to water but form a much less extensive three-dimensional network. The main effect quickly becomes that of solvating the much higher concentration of ions in the resin phase, as described earlier, and a marked resin preference for water then shows.

Supporting evidence for the point of view expressed in the previous paragraph can be extracted from a study of ion-exchange resin separations of

carboxylic acids by Davies and Owen[14] and from a study by Reichenberg and Wall[15] on the absorption of such acids and of alcohols by ion-exchange resins. They found that methyl, ethyl, and propyl alcohols and formic, acetic, propionic, butyric, and phenylacetic acids were absorbed by resins from aqueous solution, sometimes to well beyond the resin capacity, and in order of increasing size. This behavior was attributed mainly to van der Waals' interactions in the resin phase. But we believe the fact that the absorption decreases when dioxane is added to the system rules out the importance of such interactions in the resin phase (except for effects of the π-electrons in aromatics); we wouldn't expect the presence of organic molecules mainly in the external phase to decrease the effect of van der Waal's interactions in the resin phase. But if the absorption of alcohol or carboxylic acid is caused by rejection by the water structure in the external phase, it follows that the absorption would decrease with addition of organic diluent, as the diluent does destroy the water structure. This is precisely the unidentified factor mentioned by Reichenberg and Wall as necessary to explain why the order of the acid absorption reverses with increasing organic acid concentration.

Finally it should be mentioned that it is not necessarily true that water molecules provide better solvation for anions than all polar organic molecules. Formamide, N-methylformamide, and dimethylformamide, for example, have dipole moments of 3.37D at 30°C in benzene (Ref. 16), 3.86D at 25°C in benzene (Ref. 17), and 3.86D at 25°C in benzene (Ref. 18), respectively, compared to 1.85D for water. Although the effectiveness for electrostatically solvating an anion may be more closely related to a bond dipole moment and its steric availability than to the overall molecular moment (and other important factors

in the total solvation of the anion include hydrogen bonding when the organic solvent is capable of donating a proton, and dispersion force interactions when it has delocalized orbitals) any one of the above molecules may be more effective than water, on a one-to-one basis, in shielding an ion's charge. Water, however, has the advantage of the smaller molar volume, so that more water dipoles can pack around the ion. Inside Dowex 1 Cl^--form resin, these two factors must just about balance out for formamide and water, as little selectivity is shown in this case for distributing between the external solution and the resin phase over the entire range of diluent mixtures.[6] Dimethylformamide, DMF, cannot provide chemical (hydrogen-bonded) solvation for small anions, as can water and formamide, and is larger; it is discriminated against with respect to water by the resin when small counter ions are involved. But when the resin form involves large, weakly basic anions, such as ClO_4^-, which do not require much hydrogen-bonded solvation, then the large bond moment and dispersion force interactions from the resonance $O{=}\overset{H}{C}{-}N\!< \rightleftharpoons O^-{-}\overset{H}{C}{=}N^+\!<$ can dominate the solvation, and DMF becomes even slightly preferred by the resin phase.[6]

Although we did not determine the resin uptake for acetone-water mixtures, we would predict, on the basis of the reasoning given above, that our Cl^--form resin would preferentially take up water, and possibly even more strongly than with isopropyl alcohol, as the acetone cannot chemically solvate (hydrogen bond to) the Cl^- counter ions in the resin phase. For nearly pure water solutions, however, acetone might well be taken up preferentially, as are the alcohols, and for the same reason. Fragmentary data (two points) in the literature[19] seem to indicate this behavior, and this is certainly true for uptake by a cation exchange resin.[20]

Non-Exchange Electrolyte Uptake.— A plot of the LiCl resin invasion in meq of Cl^- per g of dry Cl^--form resin vs. the equilibrium external-phase isopropyl alcohol mole fraction with a constant concentration of 0.010 M LiCl in the external solution is shown in Fig. 2. The curve is somewhat similar to that with dioxane,[1] but with increasing organic-solvent mole fraction, the alcohol curve increasingly shows less resin invasion by non-exchange electrolyte. This is likely due to the higher dielectric constant of the alcohol-water mixtures[21] (also shown in Fig. 2), for as a result, there will be less ion pairing in that system. Since ion pairs are not subject to the Donnan potential[22] and so to exclusion from the resin phase, to whatever extent there is less ion pairing of LiCl in the resin phase with alcohol-water mixtures over that with dioxane-water solutions, the amount of resin invasion by LiCl will be lower.

Anion Selectivity.— Our basic premise, as with purely aqueous systems, is that the ion which most needs solvation (the smaller, more highly charged one) goes into that phase which provides the better solvation, and in the exchange pushes the other ion into the poorer solvating phase.[1,10,23,24] The primary exchange reaction is

$$X^- + \overline{Cl^-} \rightleftharpoons \overline{X^-} + Cl^- \qquad (2)$$

with

$$\mathcal{K}_{X^-/Cl^-} = \frac{(\overline{X^-})(Cl^-)}{(X^-)(\overline{Cl^-})} = \frac{[\overline{X^-}][Cl^-]\ \overline{\gamma}_{RX}\gamma_{LiCl}}{[X^-][\overline{Cl^-}]\ \gamma_{LiX}\overline{\gamma}_{RCl}} \qquad (3)$$

$$K_{X^-/Cl^-} = \frac{[\overline{X^-}][Cl^-]}{[X^-][\overline{Cl^-}]} \tag{4}$$

$$D = \frac{[\overline{X^-}]}{[X^-]} = K_{X^-/Cl^-} \frac{[\overline{Cl^-}]}{[Cl^-]} \tag{5}$$

where parentheses indicate activities and brackets indicate concentrations.

For purely aqueous systems, solvation by water is best in the dilute external phase, and so the smaller, more highly charged, and more basic anions are held there. This leads to the predicted resin selectivity order, $AuCl_4^- > ReO_4^- = ClO_4^- > I^- > Br^- > Cl^- > F^-$, which is that observed experimentally. Now what happens when the water in the system is gradually replaced by alcohol? To answer this, we may perhaps start with a simpler example than anion exchange, namely the distribution of neutral hydrophilic organic molecules. Samuelson and his co-workers[25,26] have found that polyhydroxy substances such as sugars and polyalcohols distribute between the resin and the external solution, favoring the latter. These strongly hydrating substances find the best hydration there (just as do anions). But as alcohol replaces water in the system, the external-phase water mole fraction decreases more rapidly than that of the resin phase. So the polyhydroxy molecules decreasingly prefer that phase, and their uptake by the relatively water-rich resin phase increases. Similarly, a small, basic anion finds increasingly poorer solvation in the external phase as the organic mole fraction increases, and so its binding to the external solution decreases and its distribution into the resin increases. In an exchange, the distribution of the other larger, less basic

ion (less in need of solvation) must correspondingly decrease, leading to a decrease in selectivity. It might be expected, however, that the decrease in distribution ratios, D, for the larger anions (and increase in D for F^- when Cl^- is the macro-anion) would be less severe with isopropyl alcohol than with dioxane because the hydroxyl group of the former can hydrogen bond to the (smaller) anions and partially replace the chemical solvation lost with the gradual dehydration of the system. This would help to hold the smaller anions in the external solution and so would diminish the changes in D with increasing alcohol mole fraction, when compared with dioxane solutions.

Inspection of Figs. 3-5 giving plots (for 0.010, 0.030, 0.10 M LiCl) of D vs. external-phase alcohol mole fraction show that the values of D for tracer ReO_4^-, I^-, Br^- fall with increasing alcohol content, while that for F^- increases. Thus, the major result of adding isopropyl alcohol is the same as adding dioxane, and we think this is due, as already described, to the tendency of the smaller, more basic anions to follow the distribution of water into the resin phase. However, it must be noted that the values of the distribution ratios start to fall with the first addition of isopropyl alcohol, even though below an alcohol mole fraction of ~ 0.07 the resin phase prefers the alcohol somewhat to water. Possibly the water and organic molecules are not homogeneously distributed in the resin phase at low organic mole fraction. The individual waters may tend to cluster about the counter ions and the resin-bound charge sites, while the organic molecules fit around the hydrocarbon matrix. Even though the stoichiometric proportion of water in the resin phase is slightly less than in the external solution, the small amount of organic solvent there may essentially act like a part of the hydrocarbon framework and leave the

immediate vicinity of the resin-phase ions unchanged. Thus, the addition of a few mole percent solvent to the resin phase would not greatly affect the solvation of resin-phase ions there. But in the external phase, the addition of the same proportion of organic molecules to a purely aqueous solution does decrease the secondary solvation of the ions there, thus decreasing the selectivity of the external phase for the smaller, more highly hydrated anions.

A comparison of Figs. 3-5 with the corresponding figures in Ref. 1 for dioxane-water mixtures shows that the differences in results with dioxane-water and isopropyl alcohol-water mixtures are in the expected direction, but to us, surprisingly small. The D's with alcohol solutions change almost as rapidly as with dioxane mixtures, while we expected a significantly slower rate. It is true that the dioxane curves are a little high (artificially) due to the larger non-exchange resin invasion with that solvent. For in the batch experiments, the invasion electrolyte comes from, and so diminishes, the external solution LiCl concentration, and this increases D (eq. 5). However, this is an effect of at most tens of percent for the dioxane solutions of $\sim$ 0.5 mole fraction. More importantly, the dielectric constant is lower for dioxane-water mixtures than alcohol-water mixtures, and so there is an increased possibility of ion pairing with Li^+. This will tend to hold Cl^- more firmly in the external phase, leaving the larger ions in the resin.

This is certainly part of the explanation. Another possibility involves an idea already in the literature.[27] The dioxane molecule normally exists in the chair form, and consequently the two bond moments oppose each other resulting in a small overall dipole moment, 0.45D (Ref. 28). But there is a small amount of the boat form in the equilibrium mixture, and in this case the

two bond moments tend to add. In the Coulomb field of the ions, the dioxane equilibrium is shifted toward the boat form, and so the dioxane molecules around the ions can provide much better (dipole moment) solvation for anions than would be expected from the properties (dipole moment and dielectric constant) of bulk dioxane. Such an idea has been used by Hyne[27] to explain the lower-than-expected ion-pair formation of n-Bu_4NBr in dioxane-water mixtures, and was derived from similar reasoning employed earlier by Ramsey and co-workers[29] to explain the lower-than-expected ion pairing of n-$Bu_4N^+ClO_4^-$ in 1,2-dichloroethane. Yet another possibility is that we have greatly overestimated the ability of alcohol to hydrogen bond to small anions or the importance of such bonding.

To try to distinguish among these possibilities, particularly the last, we did some experiments with acetone-water mixtures. Acetone has a size, structure, and dielectric constant similar to isopropyl alcohol, but is missing the latter's hydroxyl hydrogen. As already mentioned, we did not determine the solvent uptake by the resin for acetone-water mixtures, but almost certainly the anion-resin phase will take up water preferentially for the same reasons that it does so for dioxane-water and alcohol-water solutions (in fact, it appears to do so[19]). If the ability to hydrogen-bond to the anions is an important feature of solvating them, as we think, then the replacement of water by acetone in dilute solutions of LiCl should drive the smaller anions into the resin phase more strongly than when using isopropyl alcohol. Consequently, we would expect the values of D for the larger anions to decrease more sharply with increasing acetone mole fraction than with isopropyl alcohol mole fraction, and to increase more rapidly for the small F^-. The results for tracer ReO_4^-,

Br^-, and F^- with macro Cl^- (the external solution is 0.010 M LiCl) are shown in Fig. 6, and it can be seen that these expectations are fulfilled. Apparently, acetone cannot solvate the F^- and Cl^- as well as isopropyl alcohol; the ability of the latter solvent to hydrogen-bond to anions makes a significant difference in the distribution ratios.

The problem that remains is why do the dioxane-water mixtures yield intermediate results rather than resembling the acetone solutions? But in fact, if one observes carefully the low-mole-fraction region of Fig. 6, it can be seen that for both ReO_4^- and Br^- tracers the dioxane curves fall even more steeply than the acetone curves out to a solvent mole fraction of ~ 0.2. Then at higher mole fraction the curves for dioxane tend to level off, coming between those for acetone and isopropyl alcohol. This behavior indicates that dioxane solvates the small anions poorly, even more poorly than acetone (due to its smaller dipole moment), as originally expected, but that some other phenomenon comes into prominence at higher proportions of dioxane in the mixtures. We believe this latter effect is the result of ion pairing of the smaller anions with the lithium cation in the external phase, since the dioxane-water mixtures have considerably lower dielectric constants than the corresponding alcohol- or acetone-water mixtures. Because the lithium cations are mainly in the external phase, ion pairing with them tends to hold the Cl^- there; consequently the values of D for ReO_4^-, I^-, and Br^- in dioxane-water mixtures tend to remain higher than they would otherwise, as observed.

But as can be seen in Fig. 6, the main effect of adding any of the three organic solvents used (and for the reasons given above we believe this to be a general phenomenon) is to decrease the value of D for the larger, less basic

(than Cl^-) anions and to increase it for the smaller, more basic ones. As a result, the selectivity coefficients become closer to unity (ReO_4^- and Br^- actually reverse their order in acetone-water and dioxane-water mixtures), and separations become poorer. This effect should be even more pronounced with anions differing still more widely in size and basicity. Thus, a larger, still less hydrated species than ReO_4^-, such as $AuCl_4^-$, should show even a more marked decrease than ReO_4^- from the enormous distribution ratio it has in aqueous solution. Qualitatively, this behavior is shown in the work of Burstall et al.[30] who have reported on the very marked uptake and concentration of the cyano complexes of gold and silver on anion-exchange resins, and then the subsequent elution of these complexes from the resin by acetone-aqueous HCl solutions. Another example is furnished in a paper by Dobud et al.,[31] where they show that the D for $AuCl_4^-$ on Amberlite IRA-400 from 4M HCl falls by a factor of over 100 in going from aqueous solution to ~ 0.25 mole fraction n-propyl alcohol. This is certainly a larger drop than we observe for ReO_4^-. But the situation here is not so clear because of the use of concentrated HCl rather than dilute LiCl. Two additional effects must be considered, both related to association of the H^+ and Cl^- ions. One is that in the resin phase (with a large Cl^- concentration) some HCl and HCl_2^- will form;[32,33] the latter species especially will cause a decrease in the value of D for $AuCl_4^-$. This effect is now well-known in aqueous anion resin systems where the use of moderately concentrated HCl leads to much smaller D's than are obtained with similar concentrations of LiCl.[32] The other effect is that as the effective dielectric constant in the external solution falls, the H^+ and Cl^- associate.[36] That is, the activity of HCl does not rise as rapidly as that of the same

stoichiometric concentration of LiCl with increase in organic-solvent mole fraction.[37] This makes the value of D for the other anion (if less basic than Cl^-) larger than in LiCl. Thus, the two effects just described tend to cancel in anion-resin systems (but not in cation-resin systems). For example, plots of D vs. isopropyl alcohol mole fraction for tracer Br^- from 0.20 M HCl and 0.20 M LiCl (now shown) are not greatly different; that for HCl drops a little below the one for LiCl above 0.3 mole-fraction alcohol.

In the paper on the exchange of $AuCl_4^-$ from 4M HCl, already mentioned above,[31] the bulk dielectric constant was cited as a main parameter in explaining the decrease in D with increasing organic solvent content, both because of increased ion association and because of decreased (positive) electrostatic free energy of transfer of the smallest anion from the external solution to the resin phase. These certainly do have an influence; the second result does lead to a decrease in D, and is encompassed in the change in free energy of solvation of the ions with organic-solvent mole fraction that we have discussed earlier. The first effect, however, leads to an increase in D for $AuCl_4^-$ (because HCl is surely more highly associated in the external solution than is $HAuCl_4$) and so is in opposition to experiment. In any case, a simple dependence on a bulk property like the dielectric constant is not likely to be useful beyond a homologous family of solvents, since is is the microscopic solvation properties that are important. These are more complicated, being related to the effective bond moments and their spatial arrangement, the dispersion-force interactions of mobile electrons such as the π-electrons in aromatics, etc. Examples in point are the marked differences observed in this work with acetone and isopropyl alcohol solutions, though they have nearly the same bulk dielectric constants.

Finally, we can treat the situation in which a (labile) complex anion must be produced as well as exchanged. Plots of D vs. aqueous HCl and aqueous LiCl are shown in Fig. 7 for Fe(III). At low Cl^- concentrations the iron is mainly in cationic complexes, and so there is little $FeCl_4^-$ present to exchange with the Cl^--form resin. As the Cl^- concentration increases, however, the proportion of $FeCl_4^-$ increases until this species is dominant. If it were not for resin invasion by the concentrated aqueous electrolyte and other "non ideal" behavior, the maximum in the distribution curve would represent the point where the average Fe(III) species is electrically neutral.[38-40] Beyond that Cl^- concentration, the average iron species is anionic, and the decrease in D is due to the normal mass-action effect on an anion of increasing the Cl^- concentration. In reality, resin invasion by the electrolyte may affect the peak position, as will other effects. In Fig. 7, the plot of D for aqueous HCl falls increasingly below that for LiCl at higher Cl^- concentration, due, as mentioned earlier, to the formation of HCl_2^- in the resin phase. If now at a particular HCl or LiCl concentration (below that of the maximum in the curve), the water is gradually replaced by an organic solvent, the activities of the ionic species will (at least initially) increase and the complexing equilibrium

$$Fe(H_2O)_x^{+3} + 4Cl^- \rightleftharpoons FeCl_4^- + xH_2O$$

will be shifted to the right. This will occur because the addition of the organic substance lowers the dielectric constant and water activity of the solution, and the product has a lower charge and less hydration than the reactants (Le Chatelier's Principle). Thus, above some minimum Cl^- value,

we would expect a maximum in D for Fe(III) to occur with an increase in organic mole fraction at constant Cl^- concentration. The value of D at this maximum would not necessarily be the same as when varying the Cl^- concentration in an aqueous system. If no additional effects are considered, the value of D would be lower, because the Cl^-, in the mixed external solution, would have a greater tendency to go into the resin phase and push out the larger anion than in a purely aqueous system (this is just our main argument for the decrease in D of large anions with increasing organic mole fraction). Figure 8 shows that this situation does hold for Fe(III). A maximum in D not much below the value at ~ 11 M aqueous LiCl is observed for a high fixed LiCl concentration and a low isopropyl alcohol mole fraction; the peak value of D decreases for lower fixed values of LiCl and occurs at higher alcohol mole fractions. The same story appears to hold for acetone-water mixtures, except that the decrease of D on the high organic mole-fraction side is even steeper than with isopropyl alcohol (corresponding to the steeper curves for ReO_4^- and Br^- with acetone), and so cuts off the maximum value of D at a lower value and at a lower organic mole fraction.

Summary

We have found that the strong-base resin in the Cl^--form preferentially takes up water from isopropyl alcohol-water solutions, just as from dioxane mixtures. The origin of this selectivity derives from the need to minimize the electrostatic free energy of the high concentration of charge in the resin phase and from the (hydrogen-bonding) solvation requirements of the resin counter ion, Cl^-. The initial preference of the resin for the organic molecules as noted with the first few percent mole fraction organic solvent is caused, we believe, by the hydrogen-bonded water structure in the dilute external solution pushing these molecules into the less-structured resin phase. As the water structure breaks down with increasing solvent mole fraction, this feature disappears.

Anion selectivity is considered to arise from the competition of the ions for that phase providing the most complete solvation; the smallest, highest charged, and most basic anion wins, leaving the other ion to go into the poorer solvating phase in the exchange. In a purely aqueous system, it is the dilute external phase that provides the most complete hydration, and so favors that ion most in need of solvation. But as alcohol (or dioxane or acetone) is added, the ability of the external phase to solvate anions decreases markedly while that of the (water-rich) resin phase decreases more slowly. As a result, the smaller anions are bound less strongly into the external phase, and so the distribution ratios for the larger anions fall. The ability of alcohols to hydrogen-bond to anions slows down the rate of decrease of D with organic mole fraction in comparison to the behavior with acetone, dioxane, and other aprotic solvents. Solvent mixtures with low dielectric constants, such as those with dioxane, introduce still another feature, namely ion pairing of the salts in the external

phase. This, too, tends to hold the smaller, more basic anions in the external phase (lowers their activity) and so leads to a smaller decrease in D for the larger anions than would otherwise be expected.

Several rather general conclusions and predictions can be made. Most organic solvents will be discriminated against with respect to water by the anion-resin phase. This comes about because water molecules usually provide more complete ion solvation than the organic molecules (water has a moderately large dipole moment, a very small molar volume, and is capable of hydrogen-bonding to the anion) and so are better able to lower the free energy of the concentrated resin phase. Such behavior is particularly true when the resin counter ion is small and basic, e.g. Cl^- or F^- or OH^-. It is most likely to be violated when the counter anion is large, e.g. ClO_4^-, as such an ion needs little (hydrogen-bonded) solvation.

With the usual organic solvents, the values of the distribution ratios of anions larger and less basic than the resin-phase counter ion will decrease with an increase in organic-solvent mole fraction and the values of D for anions that are smaller and more basic will increase. Thus, selectivity coefficients will approach unity. This should also be true for complex ions if the operating conditions are such that the average species is anionic (operating beyond the maximum in D for the complex ion). On the other hand, for the region below the maximum in D, where the average species is cationic, the value of D should increase with an increase in organic-solvent mole fraction.[41]

Footnotes and References

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Figure Captions

Fig. 1. The isopropyl alcohol mole fraction in the resin (left-hand ordinate scale) and total uptake of solution, g/g dry resin, (right-hand scale) vs. the isopropyl alcohol mole fraction in the equilibrium solution. The resin is Bio-Rad AG1-X4 in Cl^- form.

Fig. 2. Uptake by the resin of non-exchange electrolyte from 0.010 M LiCl vs. isopropyl alcohol mole fraction. The left-hand ordinate scale is in meq of Cl^-/g of dry Cl^--form resin, and the resin capacity is 4.04 meq/g of dry Cl^--form resin. Also shown is a plot of the dielectric constant (right-hand scale) vs. the isopropyl alcohol mole fraction.

Fig. 3. Plots of D vs. isopropyl alcohol mole fraction in the solution for 0.010 M LiCl and the tracer anions: F^-, ▼; Br^-, ■; I^-, ●; and ReO_4^-, ▲.

Fig. 4. Plots of D vs. isopropyl alcohol mole fraction in the solution for 0.030 M LiCl and the same tracer anions and symbols as in Fig. 3.

Fig. 5. Plots of D vs. isopropyl alcohol mole fraction in the solution for 0.10 M LiCl and the same tracer anions and symbols as in Fig. 3.

Fig. 6. Plots of D vs. solvent mole fraction in the solution for 0.010 M LiCl and tracer F^- (half-filled symbols), Br^- (filled symbols), and ReO_4^- (open symbols). Data from isopropyl alcohol solutions are represented by triangles, from acetone by squares, and from dioxane solutions by circles.

Fig. 7. Plots of D for tracer Fe(III) vs. chloride molarity in purely aqueous systems: LiCl, □; HCl, O.

Fig. 8. Plots of D for tracer Fe(III) vs. solvent mole fraction for various concentrations of LiCl. The filled symbols represent acetone solutions, and values of D are to be read from the left-hand scale. Unfilled symbols

indicate isopropyl alcohol solutions, and values of D are to be read from the right-hand scale. LiCl molarities for each curve are given near it.

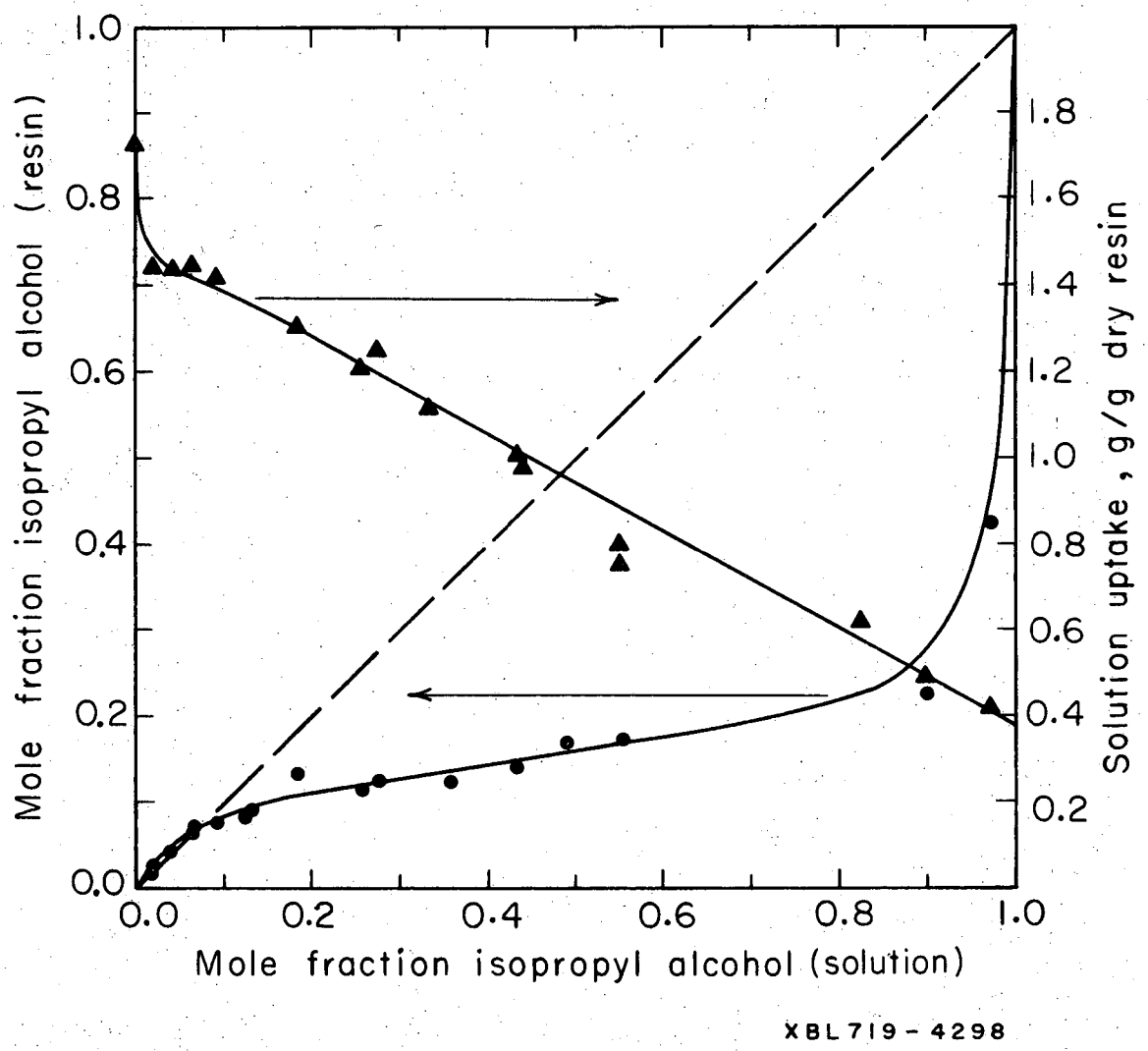
1.0
0.8
0.6
0.4
0.2
0.0
Mole fraction isopropyl alcohol (resin)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
Solution uptake, g/g dry resin
0.0
0.2
0.4
0.6
0.8
1.0
Mole fraction isopropyl alcohol (solution)
XBL719-4298

Fig. 1

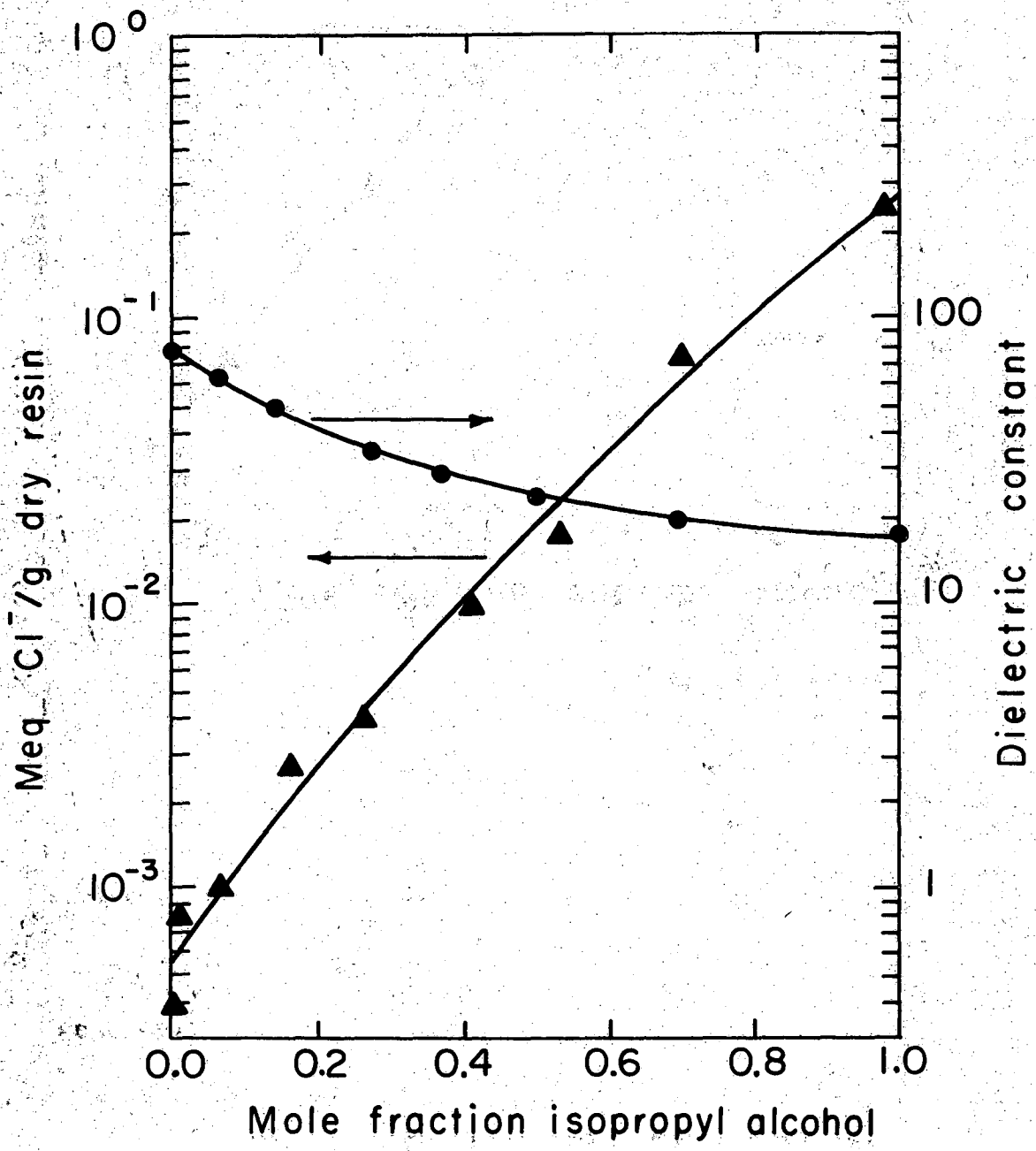

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Fig. 2

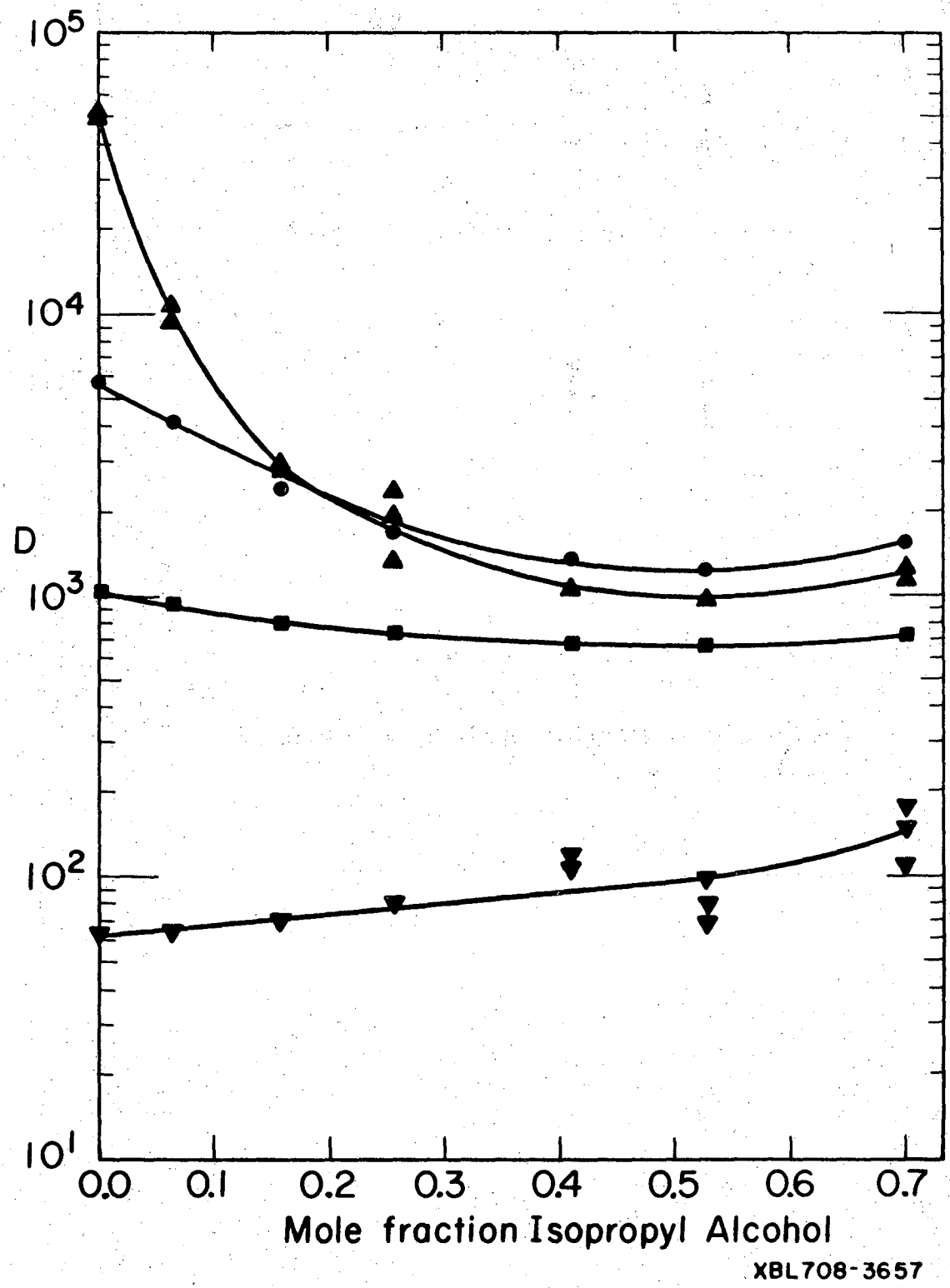
10^5
10^4
D
10^3
10^2
10^1
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Mole fraction Isopropyl Alcohol
XBL708-3657

Fig. 3

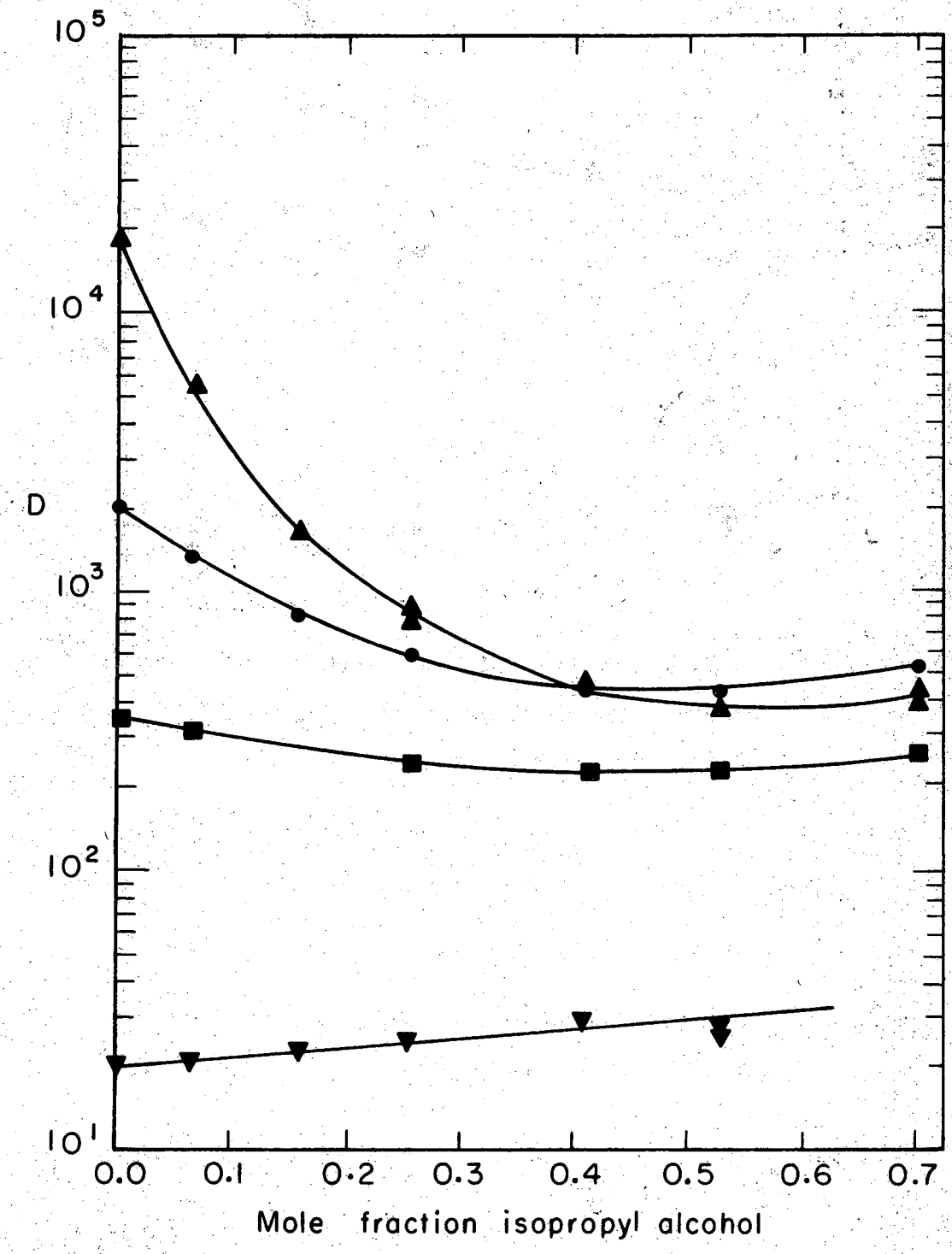

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Fig. 4

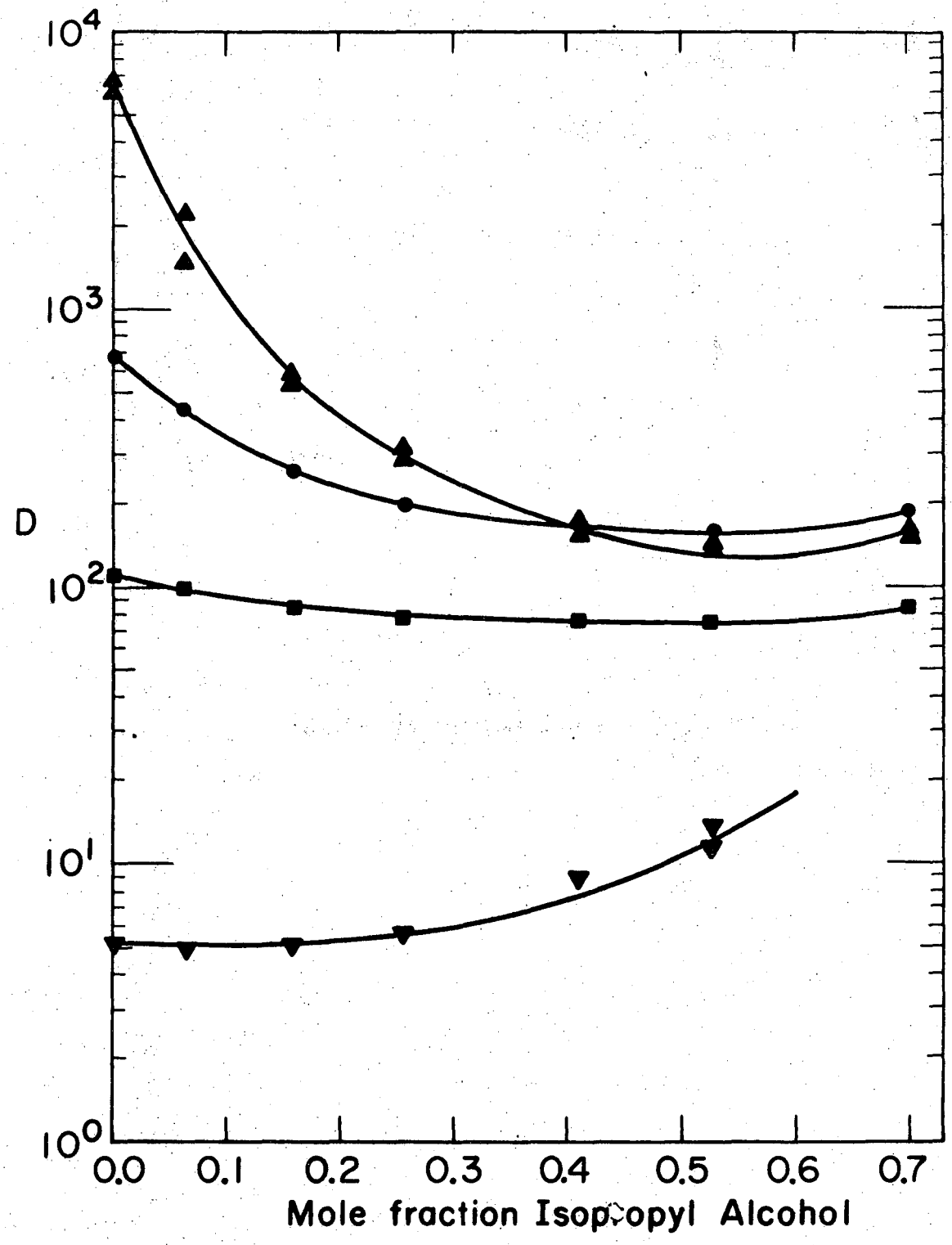

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Fig. 5

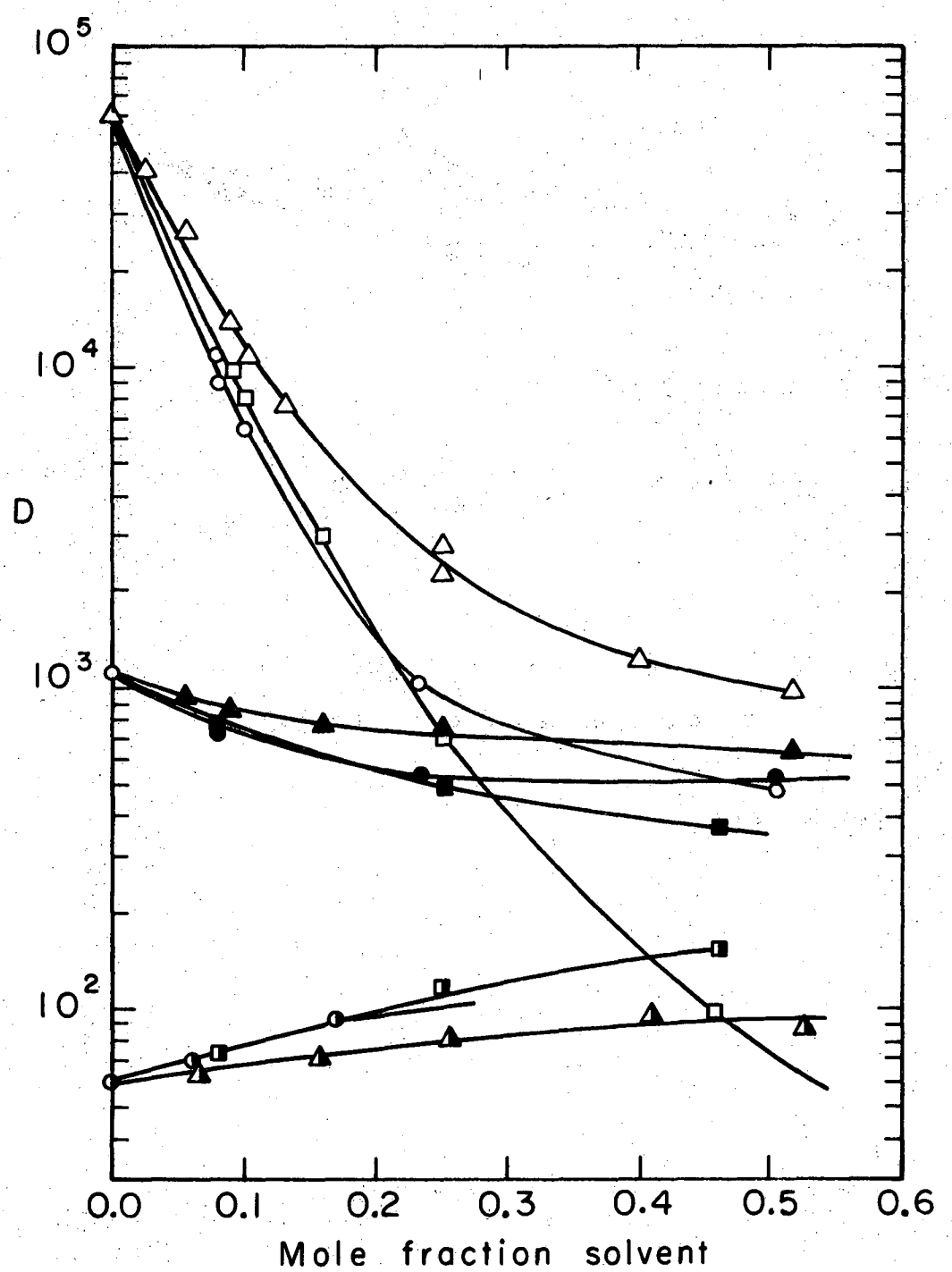

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Fig. 6

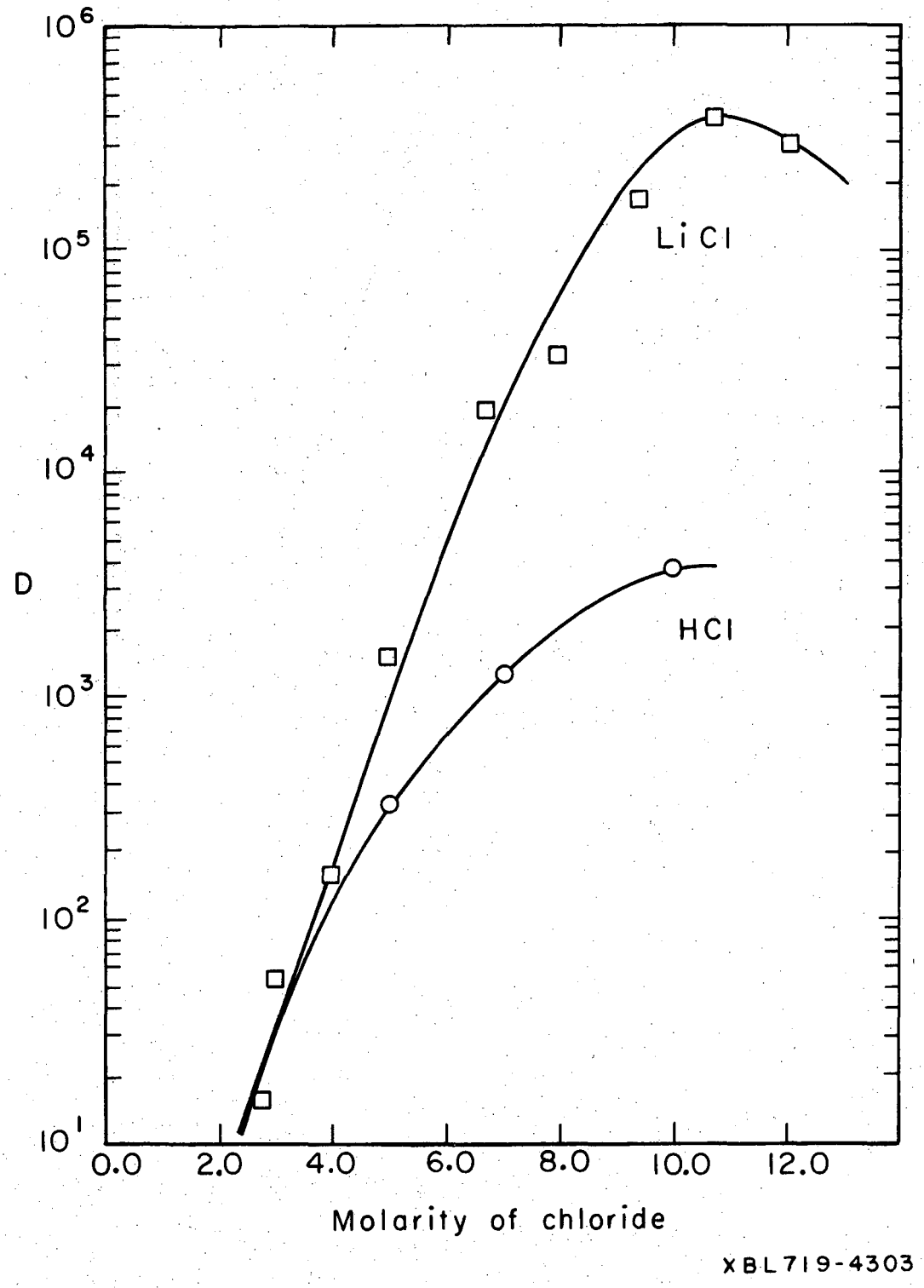
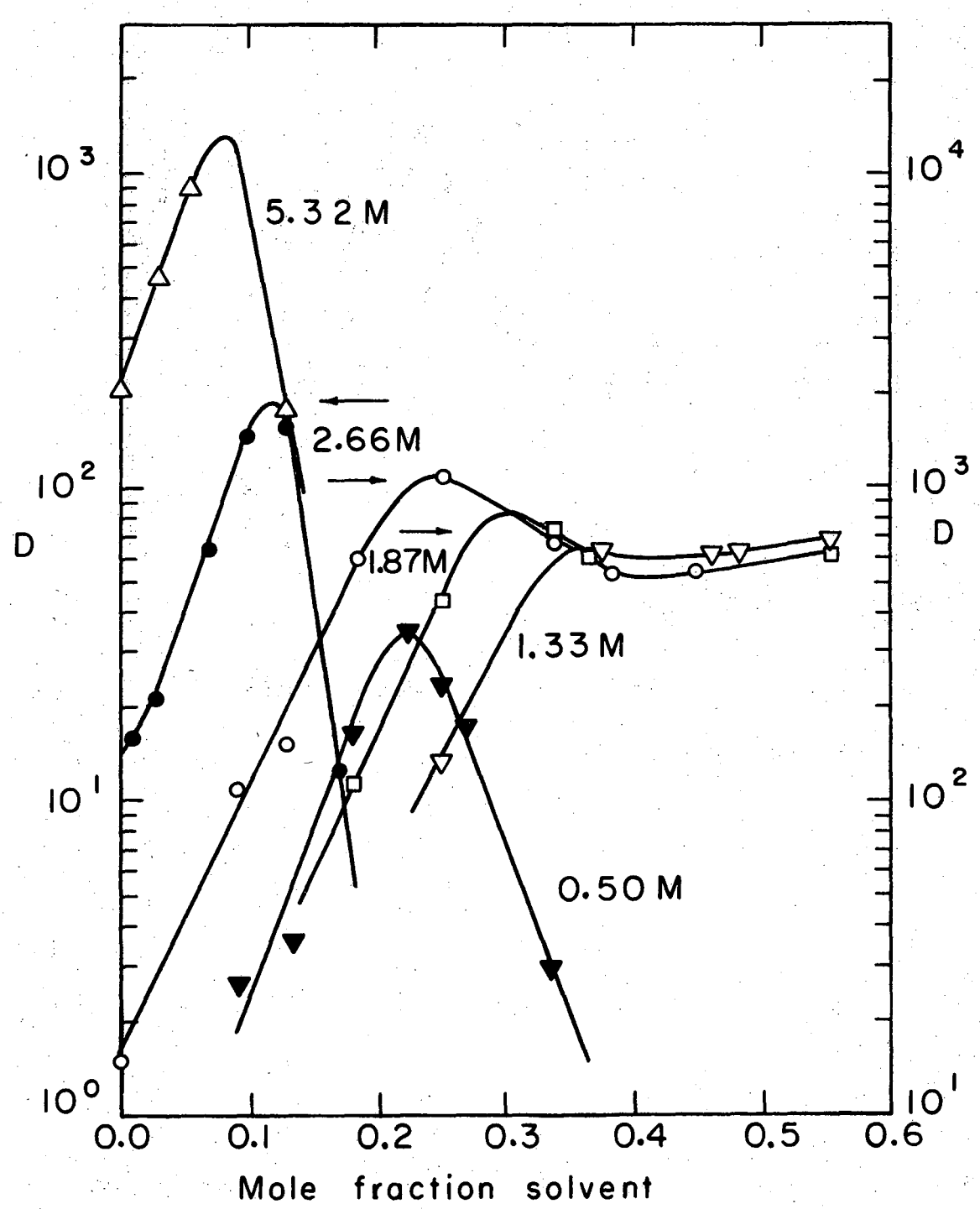

10^6
10^5
10^4
10^3
10^2
10^1
D
LiCl
HCl
0.0
2.0
4.0
6.0
8.0
10.0
12.0
Molarity of chloride
XBL719-4303

Fig. 7



XBL 719-4300

Fig. 8

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