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ANION EXCHANGE IN MIXED ORGANIC-AQUEOUS SOLUTIONS I. DIOXANE-WATER

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C. H. Jensen and R. M. Diamond

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ANION EXCHANGE IN MIXED ORGANIC-AQUEOUS SOLUTIONS. I.  
DIOXANE-WATER<sup>1</sup>

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January 1970

Abstract

The idea, developed earlier, that ion-exchange resin selectivity occurs as the result of a competition of the exchanging ions for that phase providing the best solvation, a competition won by the ion most in need of solvation, has been applied to the water-dioxane system. Usually, the dilute external aqueous phase provides the better solvating medium, so the smaller ion, or for ions of different structure the more basic anion, goes there, relegating the losing ion to the resin phase. But as dioxane replaces water, the mixed external solution becomes a poorer solvating agent, and since the resin phase preferentially takes up water, the latter becomes relatively a better solvating phase. Thus the ion most in need of solvation decreasingly prefers the external solution; separation factors should get smaller, and this is what is observed experimentally. In fact, by properly choosing the nature of the macro-electrolyte and of the resin group, the normal aqueous-phase selectivity order of the halides can be reversed in dioxane-water mixtures.

### Introduction

Earlier papers<sup>3-5</sup> have discussed the selectivity shown by (organic) ion-exchange resins with dilute aqueous solutions as a competition between the exchanging ions for solvation. That ion whose need is the more urgent goes into that phase which provides the better solvation, and so forces the remaining ion into the other phase, even through the latter ion also prefers the better-solvating phase. Water molecules usually provide the main means of ionic solvation, and so for the usual conditions of a dilute external solution and a (concentrated) resin phase with strongly acidic or basic exchange groups, the external solution furnishes the most favorable medium. For a family of similar ions such as the halides, the smallest ion goes into the aqueous phase and the largest ion is pushed into the resin phase, thus achieving a maximum hydration energy and a minimum free energy for the system. For still larger monovalent anions such as  $\text{ReO}_4^-$  and  $\text{AuCl}_4^-$ , it has also been suggested<sup>3-5</sup> that their free energy of hydration is reduced still further relative to the smaller ions by an entropy effect; they actually tighten up the water structure surrounding them. That is, the neighboring water molecules tend to hydrogen-bond out to each other rather than in to the large ion, and the zone of the "thawed" water existing around smaller ions, a disordered region in which water molecules can bond either in to the ion (or to the ions' hydration shell) or out to "ordinary" bulk water molecules,<sup>6,7</sup> disappears. Since this effect would be reduced in the less-structured water of the (concentrated) resin phase, large ions would tend to be still further squeezed out of the aqueous solution into the resin phase by such an entropy change, in addition to the effect of optimizing the heat of hydration.

Evidence for such behavior is shown by the corresponding case of the large tetraalkylammonium cations in cation exchange where, in fact, it has been shown<sup>8</sup> that the replacement of  $\text{Na}^+$  by  $\text{NPr}_4^+$  or  $\text{NBu}_4^+$  occurs because of a large positive  $\Delta S$  and in spite of a positive  $\Delta H$ .

Thus the dilute solution anion exchange selectivity order expected for the halides and  $\text{ReO}_4^-$  would be  $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^- < \text{ReO}_4^-$ , and this is indeed observed. Furthermore, it has been possible to affect this order in a predictable way by changing the nature of the exchange group and by substituting various concentrated solutions for the dilute external phase.<sup>4</sup> In this paper we want to consider the situation where the water in the system is partially replaced with an organic solvent which does not solvate anions very well but is miscible with water. Dioxane was chosen for this first study.

## Experimental

Reagents.— The anion-exchange resins used were Dowex 1-X4, 100-200 mesh, a strong-base resin with a polystyrene matrix, and Dowex 3-X4, 100-200 mesh, a weak-base resin having as functional groups a mixture of primary, secondary, and tertiary amino groups. The capacity and water uptake of the Dowex 1 were 4.04 meq and 1.73 g, respectively, per g of dry  $\text{Cl}^-$ -form resin, and the corresponding figures for the Dowex 3 were 5.5 meq and 0.58 g per g of dry  $\text{Cl}^-$ -form resin. The solutions of  $\text{LiCl}$ , and  $\text{N}(\text{CH}_3)_4\text{Cl}$  were prepared by volumetric dilution with conductivity water of analyzed stock solutions of reagent grade materials. The  $^{18}\text{F}^-$  tracer was prepared at the Lawrence Radiation Laboratory 88" cyclotron from conductivity water by the nuclear reaction  $^{16}\text{O}(\alpha, d)^{18}\text{F}$ . The  $^{82}\text{Br}^-$  was prepared by neutron irradiation of reagent grade  $\text{LiBr}$  at the Vallecitos Reactor. The  $^{131}\text{I}^-$  tracer (carrier-free in  $\text{Na}_2\text{SO}_3$ ) was purchased from New England Nuclear Corporation. The carrier-free  $^{183-184}\text{ReO}_4^-$  was chemically extracted from a tungsten deflector plate which had been subject to  $\alpha$  and  $d$  bombardment over an extended period of time at the 88" cyclotron.

Procedure.— Batch measurements were made with all tracer anions by placing weighed samples (0.1000-0.3500 g) of resin and 10.0 or 20.0 ml of solution of known tracer content into 30 ml polyethylene screw-cap bottles and shaking for at least 6 hours. Two 2.00 ml aliquots of solution were removed through filter paper and gamma-counted using a well-type  $\text{NaI}(\text{Tl})$  scintillation counter with single-channel analysis. Samples of the stock solution were also counted to give the initial tracer activity. After correction for background count, and for the moisture contained in the resins at 47 per cent humidity

(all resin used in the batch measurements was weighed at 47 per cent humidity), the distribution coefficient was calculated in the usual way,

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

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

The ion-invasion into the Dowex 1-X4 by the LiCl was determined at various concentrations of dioxane. Three small columns were each filled with one gram of resin at 47% humidity (17.3 per cent  $\text{H}_2\text{O}$ ). The columns were washed with the dioxane-water-LiCl solution until equilibrium was established, and were then placed in a centrifuge for 5 min to remove excess liquid. The columns were then washed with distilled water to remove all trace of LiCl and the  $\text{Cl}^{-}$  was titrated by the Fajans method. The quantity of LiCl adhering to the outside surface of the resin was estimated by repeating the above procedure using a volume of glass beads of 170-230 mesh equal to that of the resin.

The uptake of dioxane-water by the resin at various concentrations was determined in the following manner. A weighed amount of dry resin and a weighed amount of solution of known composition were placed in a two ml volumetric flask and shaken for about 8 hours to reach equilibrium. The solution was then filtered through a small polyethylene filter by centrifugation, and weighed. (A correction was made for solution caught in the filter and adhering to the walls.) The concentration (mole fraction dioxane) of the solution before and after equilibrium was determined by measuring its index of refraction with a Bausch and Lomb Abbé refractometer. From these data, the weight and composition of the solution taken up by the resin were calculated.

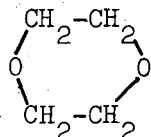


## Results

A plot of the resin-phase composition (dioxane mole fraction) for the Dowex 1-X4 resin vs. the equilibrium external-phase dioxane mole fraction is shown in Fig. 1. A plot of the LiCl resin invasion in meq of  $\text{Cl}^-$ /g of dry  $\text{Cl}^-$ -form resin vs. the equilibrium external-phase dioxane mole fraction for the Dowex 1-X4 resin with a constant concentration of 0.0104 M LiCl in the external solution is shown in Fig. 2. Figures 3-5 show the distribution ratio,  $D = \frac{\text{meq/g dry Cl}^- \text{-form resin}}{\text{meq/ml solution}}$ , for tracer  $\text{F}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{ReO}_4^-$  as a function of the dioxane mole fraction with LiCl of 0.0104 M (Fig. 3), 0.0311 M (Fig. 4), and 0.104 M (Fig. 5) as the macro-electrolyte in the external phase. Similarly, Figs. 6-8 show  $D$  for the same tracers as a function of the dioxane mole fraction with  $\text{N}(\text{CH}_3)_4\text{Cl}$  of 0.0101 M (Fig. 6), 0.0303 M (Fig. 7), and 0.101 M (Fig. 8) as the macro-electrolyte in the external phase. Finally, Figs. 9 and 10 give examples of the results obtained with the weak-base resin Dowex 3-X4. A plot of  $D$  for tracer  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{ReO}_4^-$  vs. dioxane mole fraction in the external phase is shown in Fig. 9 for 0.0104 M LiCl and in Fig. 10 for 0.0101 M  $\text{N}(\text{CH}_3)_4\text{Cl}$ .

Discussion

The partial replacement of water in an aqueous solution by dioxane will certainly have at least three effects. First of all, since the cyclic ether dioxane,



, does not possess any (acidic) hydrogen capable of hydrogen-bonding to (basic) anions, as does the water molecule, the mixed solvent will become a poorer and poorer solvating agent for anions. That is, if we can think of single-ion activity coefficients, these will rise steeply for anions with an increase in dioxane content,<sup>9</sup> and the more so, the greater the need of the anion for solvation. Secondly, the dioxane molecule will act as a base towards the water molecule, competing with the anions for hydrogen-bonding to the water, and breaking up the hydrogen-bonded water structure. Finally, the addition of dioxane, because of its low dielectric constant and because of the destruction of the water structure, will cause an increasingly marked drop in the dielectric constant of the mixed solvent.<sup>10</sup> (This is shown in Fig. 2.) For all of these reasons, the dioxane solution provides a much poorer solvating medium for anions than the original water solution (both chemically and electrostatically) and the effect is more marked the more the anion needs solvation. The results of this poorer solvating ability have been remarked on by a number of workers.<sup>9,11</sup>

But obviously then, to be able to predict the effect of dioxane on the selectivity order of a family of anions, one must first determine the distribution of dioxane between the resin phase and the external solution. Figure 1 shows

that with Dowex 1-X<sup>4</sup>, Cl<sup>-</sup>-form, the resin phase preferentially rejects dioxane and takes up water. Up to an external solution dioxane mole fraction of 0.8, the resin-phase dioxane mole fraction is only 1/2 to 1/3 that of the equilibrium solution. This behavior seems to be usual for most anion resins and for most of the mixed solutions studied, but not all.<sup>12-16</sup> Why should this be so? We do not know the answer in detail, but surely this is a combination of the hydration needs of the ions in the concentrated resin phase, and an electrostatic effect of the high charge density there. The first part of the previous sentence is obvious; the second part perhaps needs further explanation. The addition of dioxane results in a lowering of the dielectric constant of the mixture. But the resin phase, with its high density of charge, both fixed resin sites and mobile counter ions, will have a much larger increase in electrostatic free energy with lowering of the dielectric constant than will the much more dilute external phase. To keep the total system free energy at a minimum value, water must preferentially go into that phase with the highest concentration of charge to provide electrostatic (but not necessarily chemical) solvation. However all of this water is not likely chemically bound directly to the quaternary alkyl ammonium ions of the resin, but still has some freedom to solvate chemically the counter ions. Thus, as the concentration of dioxane in the total system increases, the resin phase absorbs a higher proportion of water than exists in the external solution, and the superiority of the external phase over the resin phase for solvating anions decreases.

With water alone as the solvent medium, anions will obtain the best solvation in the dilute external phase and so will choose that phase in the order of their need for solvation, resulting in the resin selectivity order

$F^- < Cl^- < Br^- < I^- < ReO_4^-$ . But as dioxane is added to the system, the external solution becomes increasingly richer in dioxane compared to the resin phase, and so less desirable to the (smaller) anions with the greater need for solvation. They are held less tightly in the external phase, and so the degree of separation or selectivity among the anions should decrease.

This is precisely the behavior observed with Dowex 1 with 0.0104, 0.0311, and 0.104 M LiCl as the macro-electrolyte and with  $F^-$ ,  $Br^-$ ,  $I^-$ , and  $ReO_4^-$  tracers, Figs. 3-5. The values of  $D$  for  $ReO_4^-$  and  $F^-$  from water solution differ by more than 1000, but with 20% mole fraction dioxane this ratio has decreased to about 15 and by 50% mole fraction to about 3.

Thus, it seems that the expectations based on the suggested model have been fulfilled. Actually, of course, other factors must also be taken into account with the addition of dioxane to the system. Two of the most important of these are a) the increase of non-exchange or "resin-invasion" electrolyte, and b) the occurrence of ion pairing in the system with the decrease in dielectric constant.

a) Because of the high concentration of charge sites on the resin matrix, most co-ions are excluded from the resin phase (the Donnan potential).<sup>17,18</sup> But as dioxane is added, the activity of the ions increases greatly. (The solubility of LiCl in dioxane is of the order of 100 times lower than in water.) Therefore, non-exchange electrolyte increasingly distributes into the resin phase of proportionately greater water content than the external solution. In addition, the occurrence of ion pairing (see b), below) also promotes resin invasion, as an ion pair, being electrically neutral, can distribute into the resin phase without much hindrance from the Donnan potential. The result is illustrated in Fig. 2 where the non-exchange electrolyte in meq  $Cl^-/g$  dry  $Cl^-$

form resin is plotted vs. the dioxane mole fraction in the external phase of 0.0104 M LiCl. It can be seen that with increasing dioxane content the amount of LiCl in the resin phase increases enormously, going from about  $10^{-3}$  meq/g for aqueous 0.0104 M LiCl to  $\sim 5$  meq/g for 0.0104 M LiCl in 0.9 mole fraction dioxane. Below 0.5 mole fraction dioxane, the region covered in this paper, this effect is not too important, but it does contribute to a slight turning up of the plots in Figs. 3-10 for the higher dioxane mole fractions. This is for two reasons. The more obvious, but less important, reason is that this  $\text{Li}^+$  concentration acts roughly to a first approximation as additional "resin capacity", as additional cationic sites. The other reason is due to the experimental technique employed in determining  $D$  by the batch method. Since the amount of resin used, 0.100-0.350 g, is equilibrated with a finite volume of solution, 10.0-20.0 ml, the LiCl absorbed by the resin must correspondingly decrease the actual concentration of LiCl in the external phase at equilibrium. For example, if 0.100 g of resin is mixed with 10.0 ml of 0.0100 M LiCl of 0.5 dioxane mole fraction, up to  $0.100 \times 0.100 = 0.0100$  meq of  $\text{Cl}^-$  would be absorbed, but the external solution only contains  $10.0 \times 0.0100 = 0.100$  meq of LiCl to start with. Thus, the equilibrium LiCl concentration in the external phase will be less than the initial value, and all  $D$ 's will be correspondingly higher. Both of these reasons can be summarized in the easily derived relation,  $D \propto \frac{[\overline{\text{Cl}}]}{[\text{Cl}^-]}$ .

b) The other factor to consider is the effect of the decrease in dielectric constant with increase in dioxane content (also plotted in Fig. 2). This will increasingly favor electrostatic, or Bjerrum-type ion pairing in both phases.<sup>19,20</sup> Since such Coulombic ion pairing can be expected to occur more readily between

the anions and the  $\text{Li}^+$  than between the anions and the large alkyl ammonium cations of the resin sites, the result of the occurrence of such ion pairing is to offer the smaller ions, or those which most urgently need solvation, an additional type of electrostatic solvation in the external phase. This tends to help hold these ions in that phase, and so partially compensates for the main effect already described upon adding dioxane to the system, namely a lowering of the anion solvation capabilities in the external solution. If this suggestion is correct, then the use of  $\text{N}(\text{CH}_3)_4\text{Cl}$  (providing a large cation similar to the resin group) rather than  $\text{LiCl}$  as the macro-electrolyte should reduce the amount of ion pairing, that is, should decrease this partial compensation. Under these conditions the halide tracer ions should show even less selectivity in dioxane solutions than with  $\text{LiCl}$ , and this should be most important for the smallest ions.

This is exactly what is observed if one compares the results with  $\text{N}(\text{CH}_3)_4\text{Cl}$  solutions, Figs. 6-8, and those with  $\text{LiCl}$  solutions, Figs. 3-5. With  $\text{N}(\text{CH}_3)_4\text{Cl}$ , the halides may even invert their order above 0.5 dioxane mole fraction; certainly the selectivity coefficients between these ions are near unity at that composition, even those involving the fluoride ion.

As has been described,<sup>4</sup> still another way to make the resin phase more inviting to the (smaller) anions needing solvation the most urgently is to change the nature of the resin group from a strongly basic quaternary ammonium cation to a weakly basic primary, secondary, or tertiary ammonium ion. Then the protons on the resin group can hydrogen-bond, even though weakly, to the anion. The effect of this additional measure of (chemical) solvation in the

resin phase for the smaller anions is shown in Fig. 9 where the values of  $D$  for tracer  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{ReO}_4^-$  are plotted vs. the dioxane mole fraction for a 0.0104 M LiCl solution with Dowex 3-X4, a weak-base resin. It can be seen that  $\text{Br}^-$  and  $\text{I}^-$  appear to reverse their selectivity around 0.4 mole fraction dioxane, but do not do so until about 0.6 mole fraction dioxane with Dowex 1-X4. Presumably the effect would be more obvious with the fluoride ion, but it cannot be easily studied (though possible) as it requires a slightly basic solution to prevent hydrolysis, while the weak-base resin, to be effective, requires a slightly acidic system. Combining the use of this resin with  $\text{N}(\text{CH}_3)_4\text{Cl}$  as the macro-electrolyte moves the point of  $\text{Br}^- - \text{I}^-$  reversal below 0.4 dioxane mole fraction, as can be seen in Fig. 10 for 0.0101 M  $\text{N}(\text{CH}_3)_4\text{Cl}$ , and again fluoride might be expected to show a bigger effect.

Although the only anions treated in this paper are the monoatomic halide ions and one stable complex ion,  $\text{ReO}_4^-$ , the arguments presented are quite general and should hold for all other simple and stable anions. Since the agreement between expectation and experiment has been good in the systems studied, we believe, in fact, that this will prove to be true for other anions, with one important caution. Consideration of complex metal anions such as  $\text{GaCl}_4^-$ ,  $\text{FeCl}_4^-$ ,  $\text{InBr}_4^-$ ,  $\text{ZnCl}_4^{2-}$ , etc., which must be produced in the solution by replacement of the first hydration shell of the metal cation with the ligand of the supporting electrolyte, has this additional feature of complex-formation to take into account, as the organic solvent replaces water in the system. This can be done, leading to somewhat different predictions, but that is another story. Finally, it should be pointed out that there is a practical result. Clearly, if the ideas presented are valid, one obtains the best possible

separation of stable anions in water solution, not in mixed low-dielectric-constant organic solvent aqueous media. But conversely, the rapid elution of a stable anion which has an enormously large  $D$  in water should be possible by the use of water-dioxane (or other miscible organic solvent) to lower the value of  $D$ . Such a scheme has already been presented for the cyano complexes of silver and gold on anion resin using acetone-aqueous HCl mixtures.<sup>21</sup>

#### Acknowledgments

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Footnotes and References

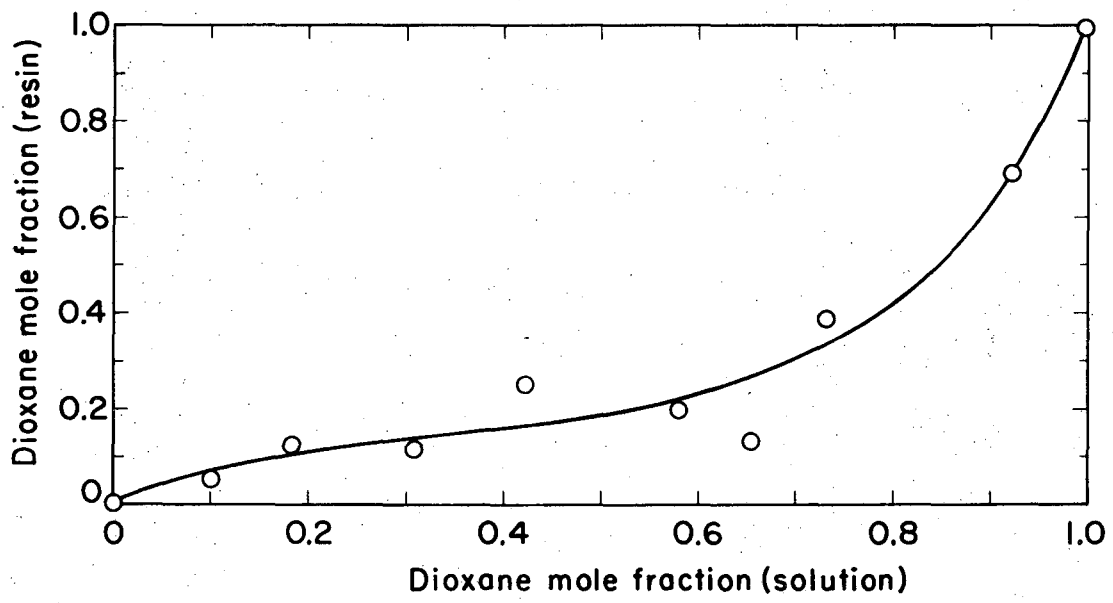
- (1) Work supported under the auspices of the U. S. Atomic Energy Commission.
- (2) Summer visitor, 1965, 1967, NSF College Teachers Research Participation Program. Permanent Address: Cabrillo College, Aptos, California.
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## Figure Captions

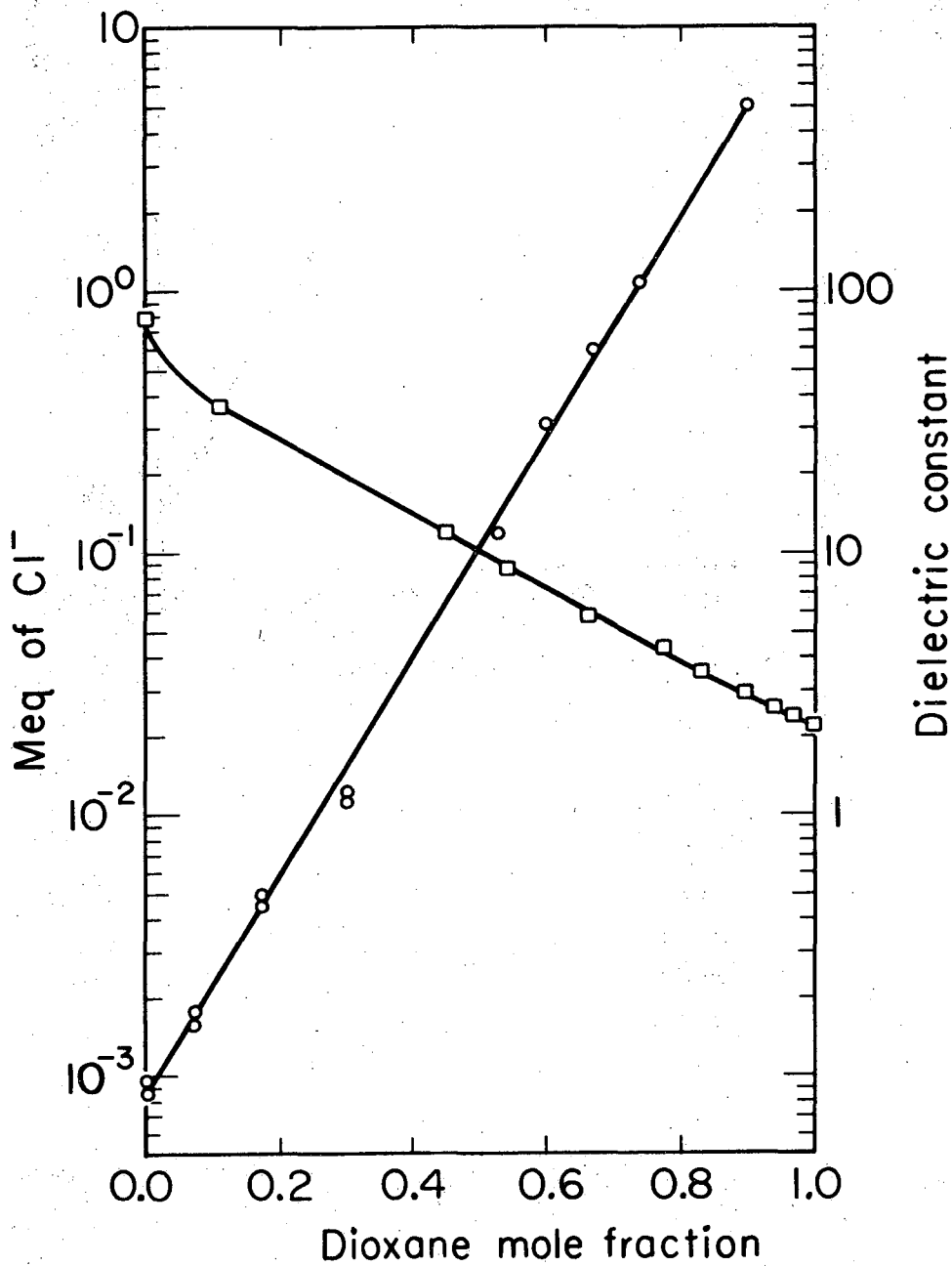
- Fig. 1. The mole fraction of dioxane in the resin phase for Dowex 1-X<sup>4</sup> vs. the mole fraction of dioxane in the equilibrium solution.
- Fig. 2. Non-exchange or resin-invasion electrolyte in Dowex 1-X<sup>4</sup> resin from 0.010<sup>4</sup> M LiCl solutions of dioxane-water vs. the mole fraction of dioxane (disregarding the LiCl) in the equilibrium solution. The left-hand ordinate scale is in meq of Cl<sup>-</sup>/g of dry Cl<sup>-</sup>-form resin; the resin capacity is 4.04 meq/g of dry Cl<sup>-</sup>-form resin. Also shown is a plot of the dielectric constant of a dioxane-water solution vs. the dioxane mole fraction; the ordinate is to be read off the right-hand scale.
- Fig. 3. Plot of  $D$  vs. dioxane mole fraction in the solution for 0.010<sup>4</sup> M LiCl and Dowex 1-X<sup>4</sup> resin and the tracer anion: F<sup>-</sup>, ▽ ; Br<sup>-</sup>, □ ; I<sup>-</sup>, ○ ; and ReO<sub>4</sub><sup>-</sup>, Δ .
- Fig. 4. Plot of  $D$  vs. dioxane mole fraction in the solution for 0.0311 M LiCl and Dowex 1-X<sup>4</sup> resin and the same tracer anions as in Fig. 3.
- Fig. 5. Plot of  $D$  vs. dioxane mole fraction in the solution for 0.10<sup>4</sup> M LiCl and Dowex 1-X<sup>4</sup> resin and the same tracer anions as in Fig. 3.
- Fig. 6. Plot of  $D$  vs. dioxane mole fraction in the solution for 0.0101 M (CH<sub>3</sub>)<sub>4</sub>NCl and Dowex 1-X<sup>4</sup> resin and the same tracer anions as in Fig. 3.
- Fig. 7. Plot of  $D$  vs. dioxane mole fraction in the solution for 0.0303 M (CH<sub>3</sub>)<sub>4</sub>NCl and Dowex 1-X<sup>4</sup> resin and the same tracer anions as in Fig. 3.
- Fig. 8. Plot of  $D$  vs. dioxane mole fraction in the solution for 0.101 M (CH<sub>3</sub>)<sub>4</sub>NCl and Dowex 1-X<sup>4</sup> resin and the same tracer anions as in Fig. 3.
- Fig. 9. Plot of  $D$  vs. dioxane mole fraction in the solution for 0.010<sup>4</sup> M LiCl and Dowex 3-X<sup>4</sup> resin and the tracer anions: Br<sup>-</sup>, □ ; I<sup>-</sup>, ○ ; and ReO<sub>4</sub><sup>-</sup>, Δ .

Fig. 10. Plot of  $D$  vs. dioxane mole fraction in the solution for 0.0101 M  $(\text{CH}_3)_4\text{NCl}$  and Dowex 3-X<sup>4</sup> resin and the same tracer anions as in Fig. 9.



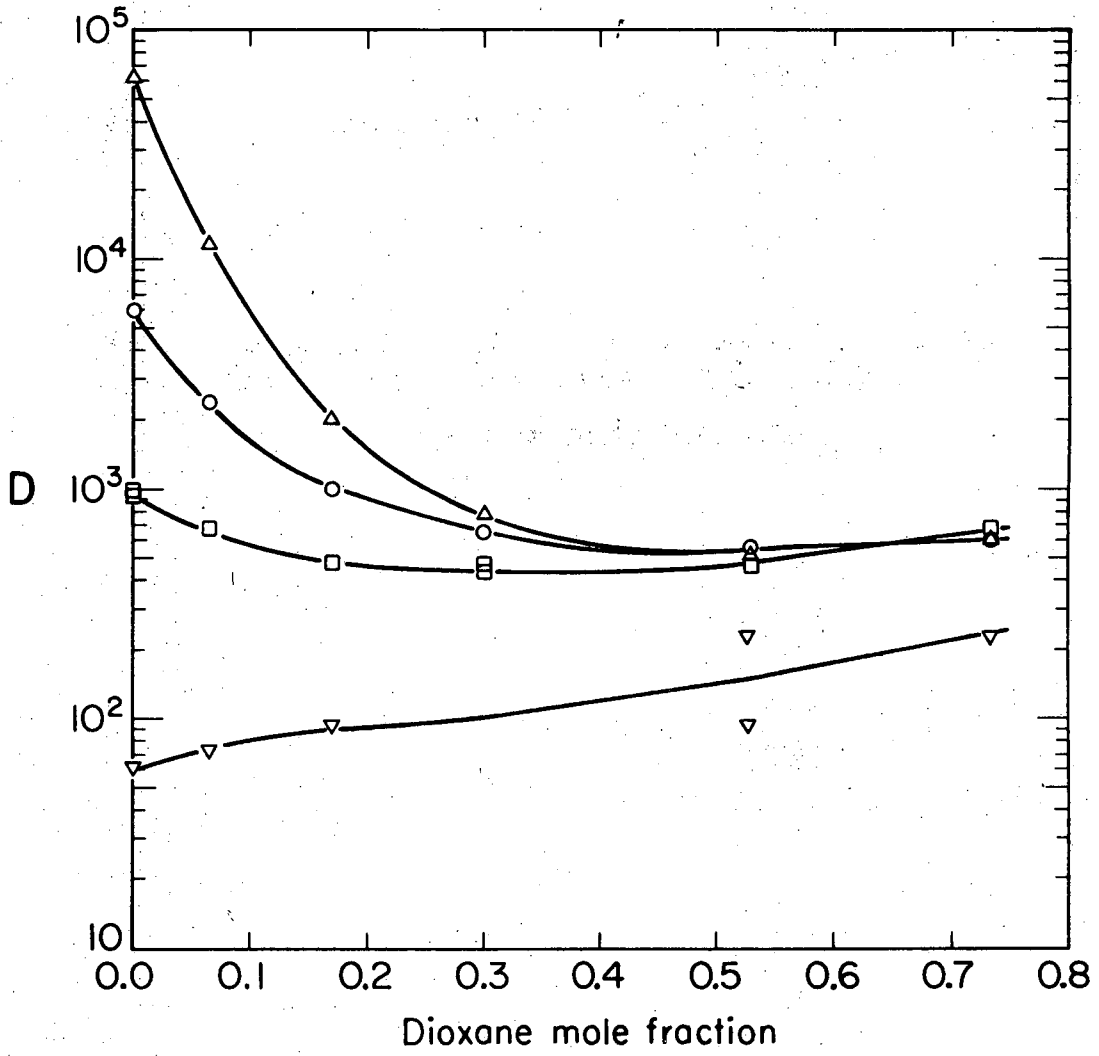
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Fig. 1.



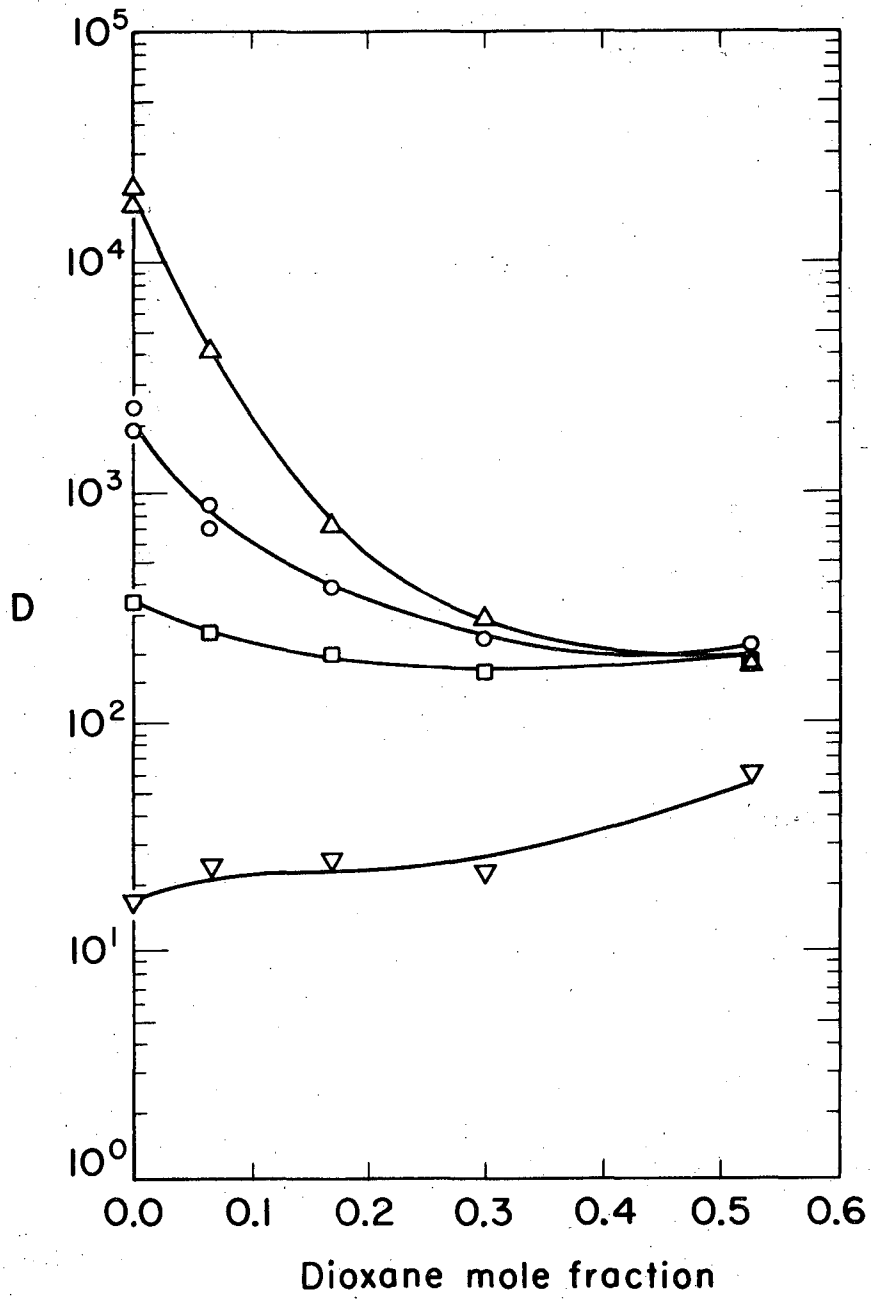
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Fig. 2.



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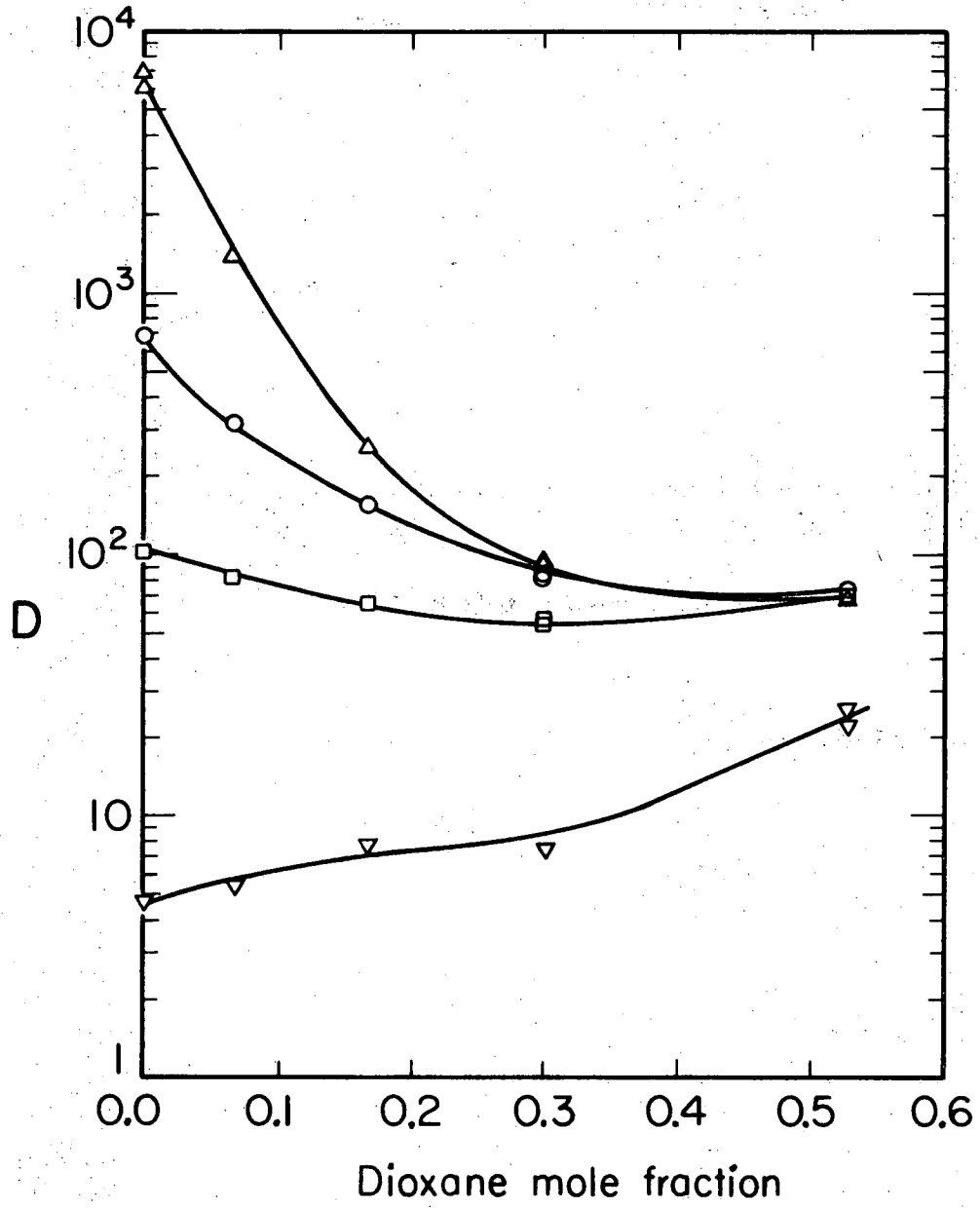
Fig. 3.



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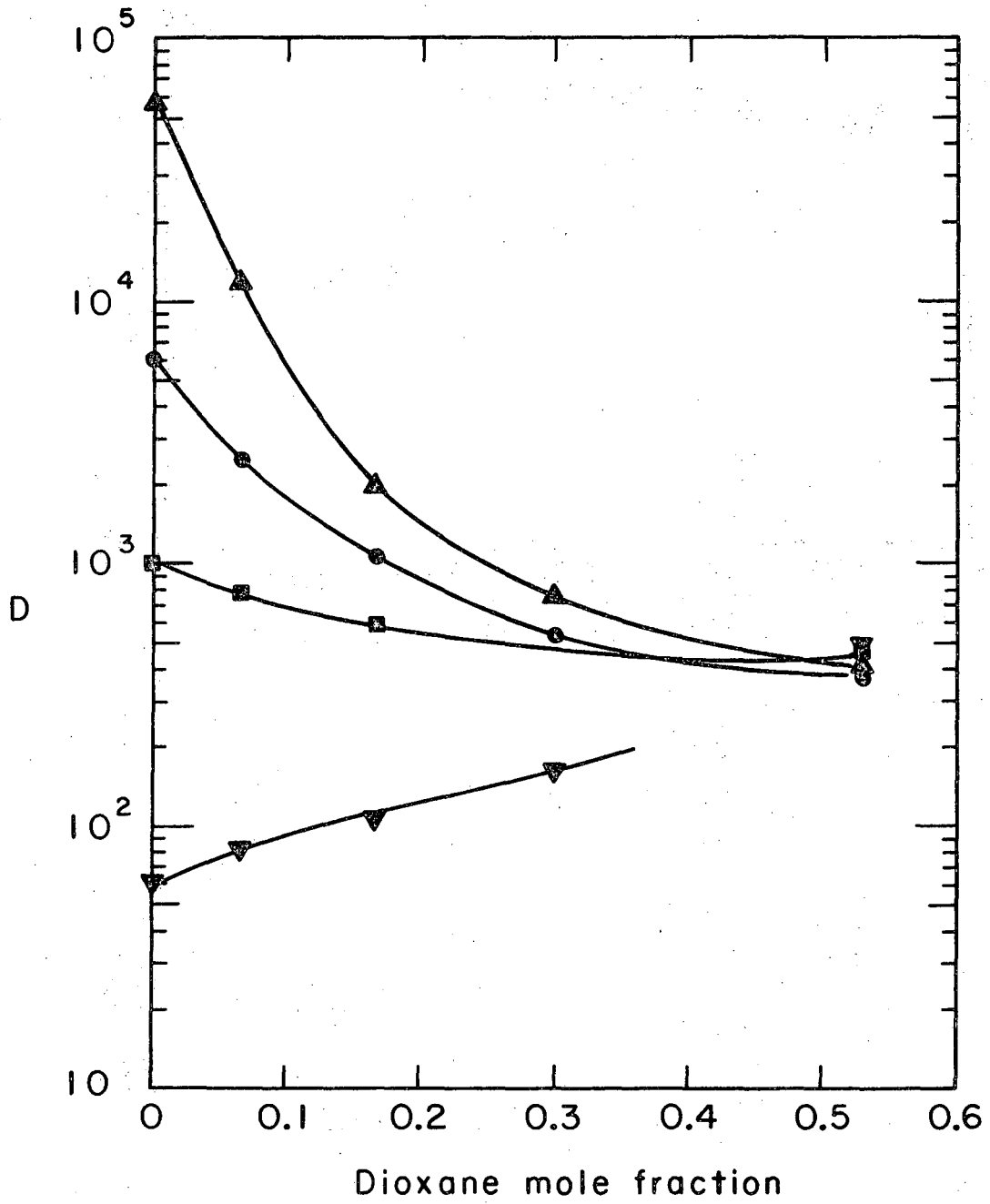
Fig. 4.





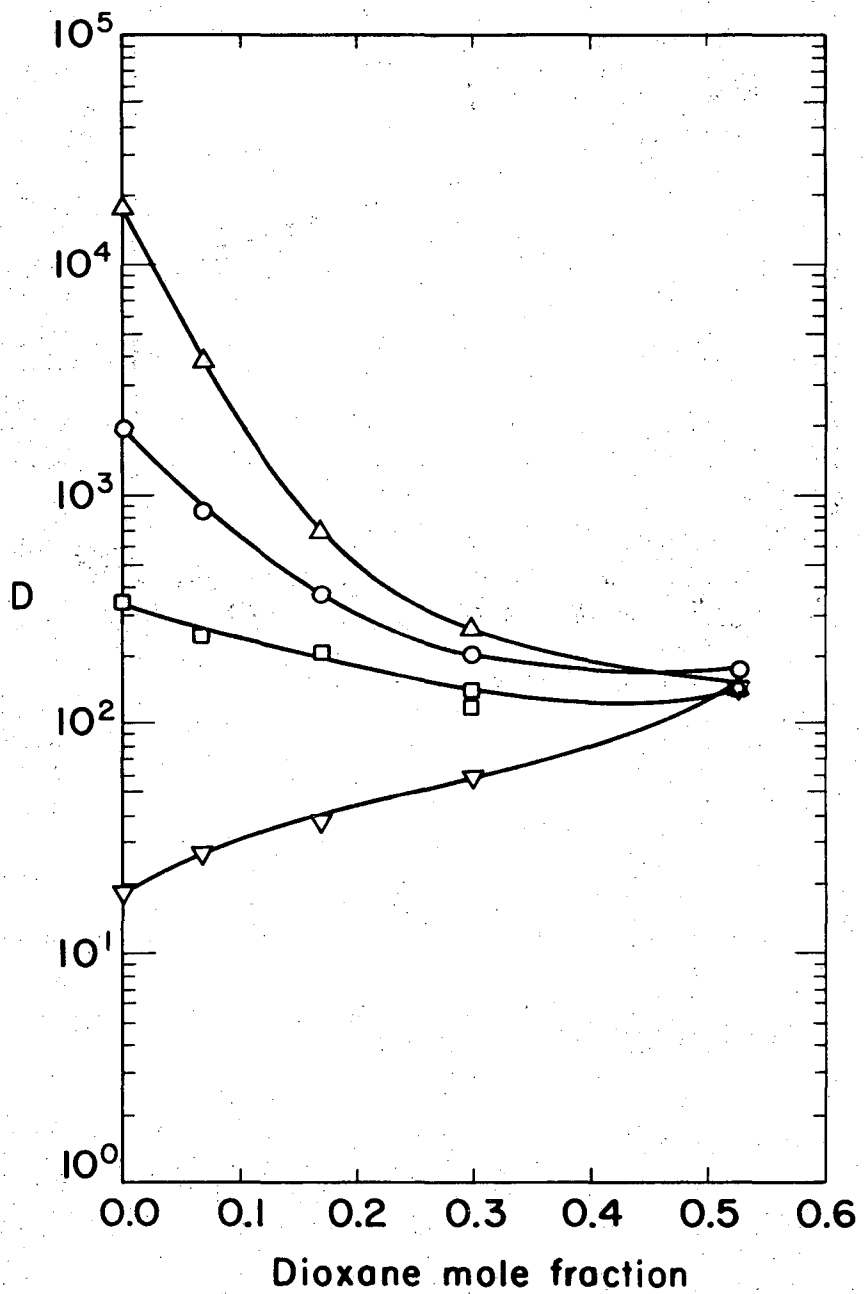
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Fig. 5.



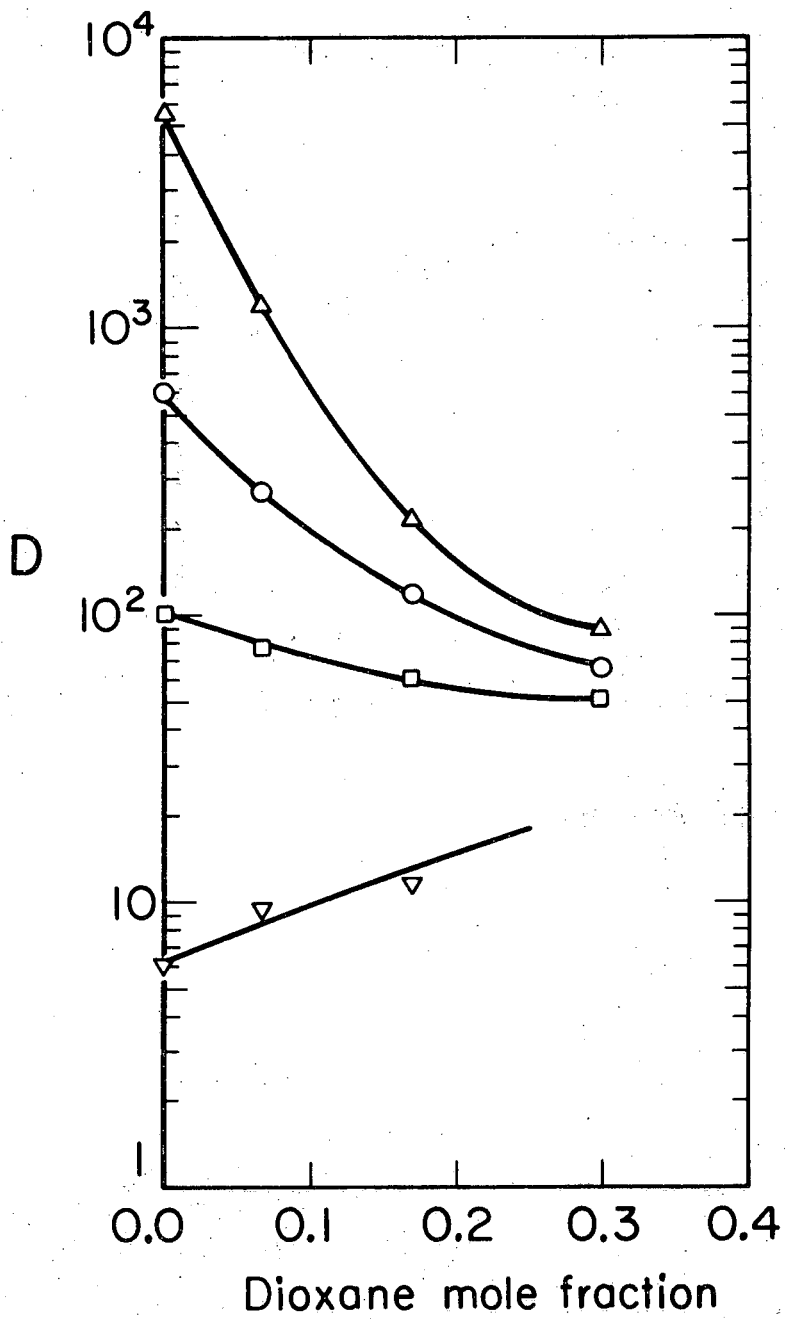
XBL678-3701

Fig. 6.



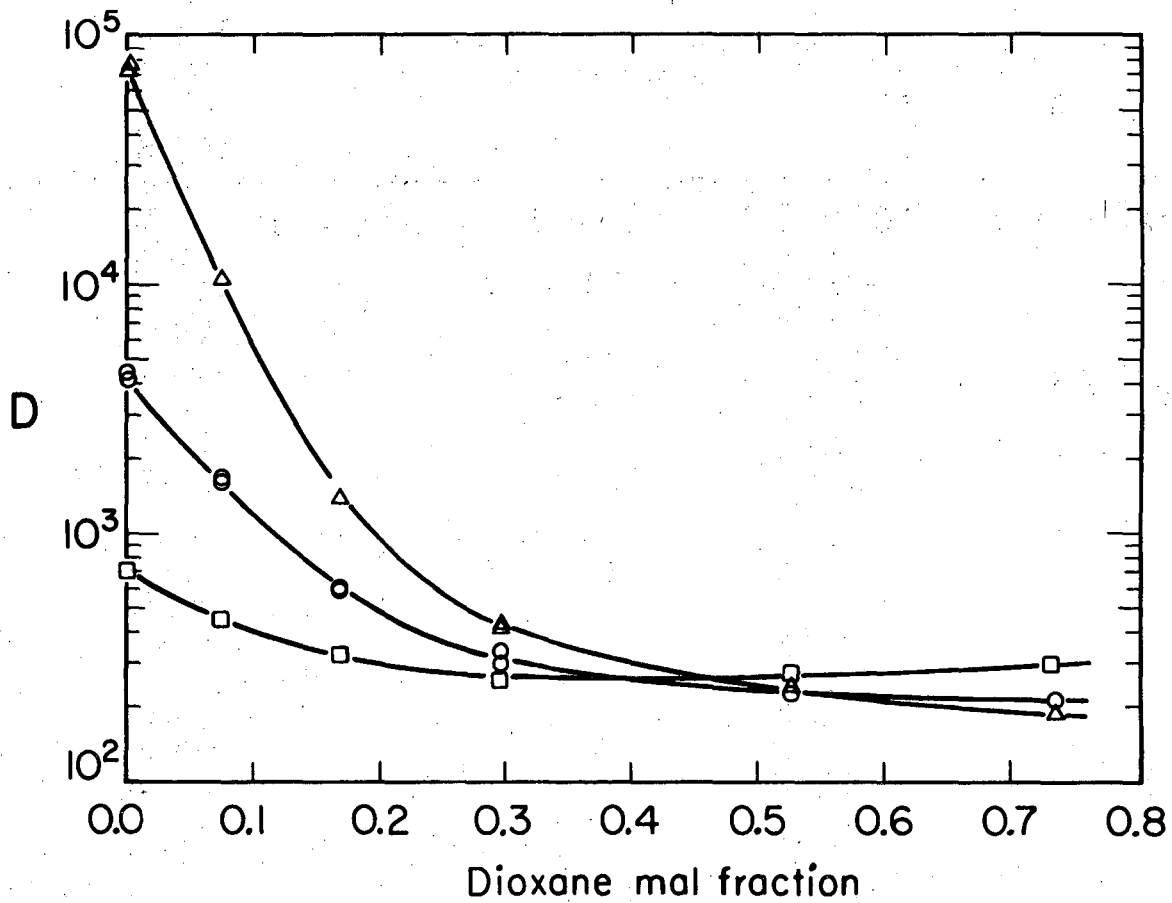
XBL701-2080

Fig. 7.



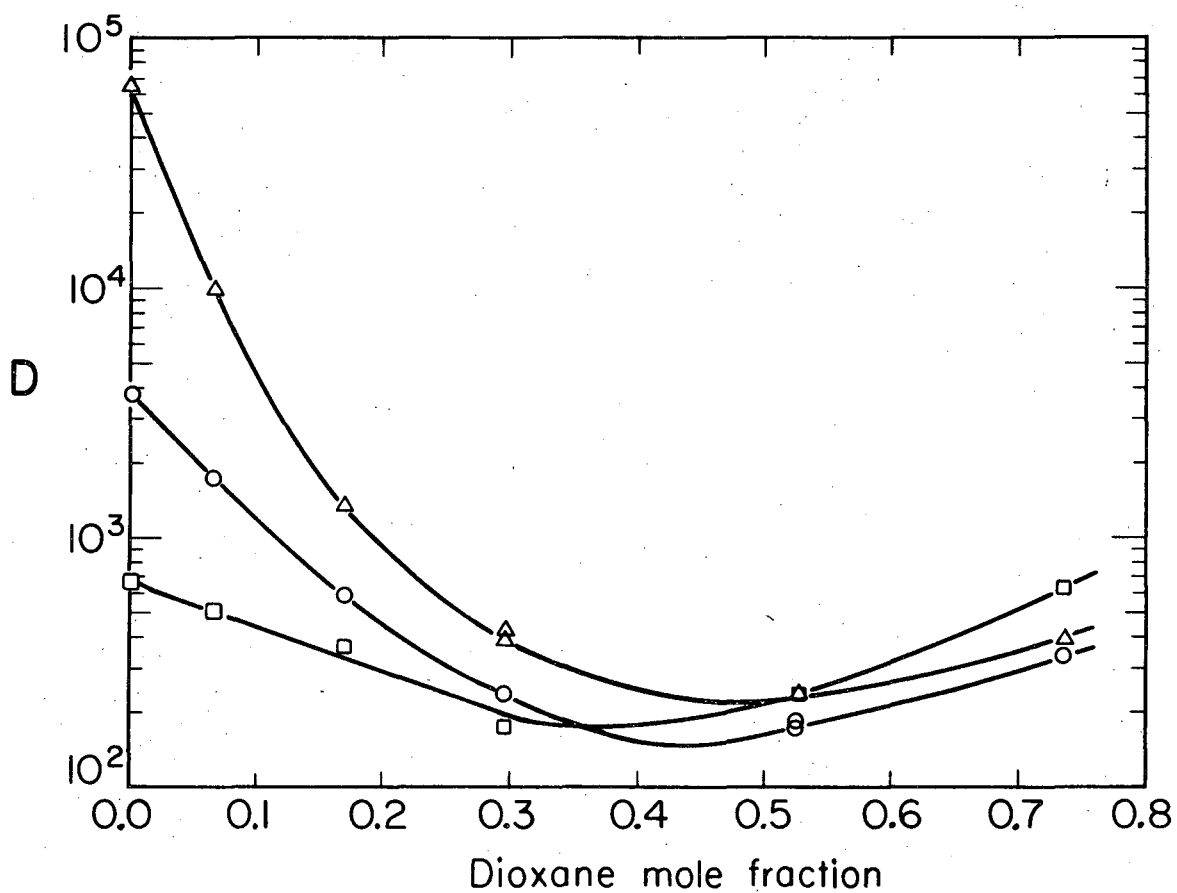
XBL702-2388

Fig. 8.



XBL702-2392

Fig. 9.



XBL702-2391

Fig. 10.

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