Lawrence Berkeley National Laboratory
Recent Work

Title
ANION EXCHANGE IN CONCENTRATED SOLUTIONS

Permalink
https://escholarship.org/uc/item/2tb273f1

Authors
Jensen, C.H.
Diamond, R.M.

Publication Date
1965-04-01

eScholarship.org Powered by the California Digital Library
University of California

UCRL-11806 Rev.

University of California

Ernest O. Lawrence Radiation Laboratory

ANION EXCHANGE IN CONCENTRATED SOLUTIONS

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UCRL-11806-Rev.

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

ANION EXCHANGE IN CONCENTRATED SOLUTIONS

C. H. Jensen and R. M. Diamond

April 1965

ANION EXCHANGE IN CONCENTRATED SOLUTIONS[1]

C. H. Jensen[2] and R. M. Diamond

Lawrence Radiation Laboratory
University of California
Berkeley, California

April 1965

ABSTRACT

The resin selectivity of tracer halide ions has been discussed as a function of the nature of the anion, of the resin-group cation, and of the macro-electrolyte. In dilute solution, interactions between ions and water and between the anions and resin-group ions are dominant, but with concentrated solutions, anion-cation interactions play an important role. Experimental confirmation of the ideas presented was obtained with Dowex 1 and Dowex 4 resins, containing a quaternary ammonium and a tertiary amine group, respectively, and employing KOH, LiCl, and tetramethyl ammonium chloride (NMe_4Cl) solutions as the eluting agent.

Introduction

In a recent pair of papers the dilute-solution elution orders of the alkali[3] and alkaline earth[4] metal cations have been explained as a competition between the water molecules and resin-group anions for solvating the cations. In going to concentrated external solutions, the effect of the aqueous anion must also be included, and the decrease in water activity in such solutions makes the interactions of the cations with both the aqueous anion and resin anion increasingly important. Depending upon the relative strength of these interactions, the elution order may invert with concentrated electrolyte solutions, and the conditions necessary for such selectivity reversals are consistent with the type of model suggested.

It seemed of interest to extend these considerations to the case of anion-exchange resins. A corresponding model for the dilute-solution exchange of anions has already been presented[5] which, however, makes use of an additional feature for large monovalent ions such as ClO_4^-, $AuCl_4^-$, $FeCl_4^-$, ReO_4^-, etc. (and NMe_4^+, NEt_4^+, etc. in cation exchange). Such large, lowly-charged ions do not coordinate the neighboring water molecules into a first hydration shell and are squeezed by the hydrogen-bonded water structure out into the less structured (less hydrogen-bonded) resin phase. If the resin group itself is also a large, lowly-charged and relatively hydrophobic ion, e.g., the quaternary ammonium ion of a strong-base resin, the residual water structure in the resin phase pushes the two oppositely charged ions together to associate as a water-structure-enforced ion-pair.[6] The result for the halide ions is the dilute-solution elution order observed, i.e., $F^- < Cl^- < Br^- < I^-$.

But more important to the present discussion is whether such considerations can explain the elution behavior of the halide (and other) anions with a change in the nature of the resin group, and in the presence of concentrated external solutions. If so, this might lead to the systematic tailoring of conditions to yield desired types of behavior, as, for example, an inverted selectivity sequence for the halide ions.

Experimental

Reagents. The anion-exchange resins used were Dowex 1-X8, a strong-base resin with a polystyrene matrix, and Dowex 4, a tertiary amine resin derived from the condensation of epichlorohydrin and ammonia. The capacity and water uptake of the Dowex 1 were 3.46 meq. and 0.72 g, respectively, per gram of dry Cl-form resin, and the corresponding figures for the Dowex 4 were 2.99 meq. and 0.89 g per gram of dry, Cl-form resin. The solutions of KOH, LiCl, and $N(CH_3)_4Cl$ (NMe_4Cl) were prepared by volumetric dilution with conductivity water of analyzed stock solutions of reagent-grade materials. The ^{18}F tracer was prepared at the Lawrence Radiation Laboratory HILAC from reagent-grade Li_2SO_4 by the nuclear reaction, $^{16}O(\alpha,d)^{18}F$. The $^{36,38}Cl$ and ^{82}Br were prepared by neutron irradiation of reagent-grade LiCl and LiBr at the Livermore Reactor. The ^{131}I tracer (carrier-free in Na_2SO_3) was purchased from Oak Ridge National Laboratory. The ^{22}Na (carrier-free) was purchased from Nuclear Science and Engineering Corp., Pittsburgh, Pa.

Procedure. Batch measurements were made with the I^- tracer by placing weighed samples (0.0150-0.1000g) 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 8 hours. Two 2.00 ml aliquots of solution were then removed through fritted glass filters and gamma counted using a well-type NaI(Tl) scintillation counter with single-channel analysis. Two 2.00 ml samples of the stock solution were also counted to give the initial tracer activity. After correction for background, the distribution coefficient was calculated in the usual way.[3] Column elution measurements were made for the Br^-, Cl^-, and F^- tracers; several polyethylene columns were used. The resulting elution volumes were converted to distribution coefficients by means of a proportionality factor determined for each column by calibrating them with I^- against the batch measurements with I^- tracer. The free column volume was determined for each column using the tracer ^{22}Na, and this volume was subtracted from the peak elution volumes of the halide ions before they were converted to D's. A polyethylene thimble was placed at the top of each column to prevent floating of the resin in concentrated solutions and to keep the total volume of the column a constant. All experimental work was done at room temperature, 23 ± 2°C.

Results

The results are recorded as log-log plots of D vs aqueous salt molarity in Figs. 1-4. Figure 1 is for the halide tracers vs KOH on Dowex 1; Fig. 2 has the tracers vs LiCl on Dowex 1; Fig. 3 has the tracers vs LiCl on Dowex 4; and Fig. 4 is for the tracers vs NMe_4Cl on Dowex 4.

Discussion

The equation for the exchange of a halide tracer ion, A^-, with a univalent macro-ion, B^- on an anion-exchange resin can be written

$$A + \overline{B} = \overline{A} + B \qquad (1)$$

where charge and ion hydration have been omitted for simplicity, and the superscript bar denotes the resin phase. Choosing the standard state to be the same in both phases, and in particular to be the usual hypothetical state of unit activity with the properties of the infinitely dilute solution leads in the usual way to the expression

$$1 = \frac{(\bar{A})(B)}{(A)(\bar{B})} = \frac{[\bar{A}][B]}{[A][\bar{B}]}\,\frac{\bar{\gamma}_A\gamma_B}{\gamma_A\bar{\gamma}_B} = K_{A/B}\Gamma_{A/B}\ . \qquad (2)$$

When this is combined with the definition of the distribution coefficient

$$D \equiv \frac{[\bar{A}]}{[A]} \qquad (3)$$

we obtain

$$D = \frac{[\bar{B}]\bar{\gamma}_B\gamma_A}{[B]\bar{\gamma}_A\gamma_B}\ . \qquad (4)$$

For dilute solutions, where resin invasion is negligible and the activity coefficient ratios are essentially constant, eq. (4) reduces to the well-known form, $D \propto [B]^{-1}$. As can be seen in Figs. 1-4, this is obeyed in dilute solution for all of the tracers with the types of resins and eluting solutions studied.

Furthermore the elution order is the same in all cases, $F^- < Cl^- < Br^- < I^-$. We believe this sequence is due mainly to the better hydration available to the (crystallographically) smaller halide ion in the dilute external phase over that possible in the concentrated resin phase solution, and not due to electrostatic ion pairing with the large quaternary ammonium resin group.[5] For example, the extraction order of the halides by tertiary ammonium ions in organic solvents (the so-called "liquid exchangers") is the same,[7] $F^- < Cl^- < Br^- < I^-$, and yet here there is infra-red and NMR evidence[8] that the halides are ion paired to the ammonium cation in the inverse order, $Cl^- > Br^- > I^-$. It is obviously necessary to account for the order of extraction in a different way than by ion pairing explanations.

We further feel that some recent thermodynamic measurements on ion-exchange reactions are in agreement with, although they certainly do not prove, this viewpoint. In particular, the sign of the free energy change for the exchange of Cl^- by Br^- on Dowex 1-X10 has been shown to be determined by the enthalpy change;[9] both ΔH and $T\Delta S$ are negative but the former is the larger quantity. This is what would be expected if the reaction involved an increase in the hydration of the (ions in the) system. That is, there is an enthalpy decrease due to the additional hydration and a smaller decrease in $T\Delta S$ due to the increased ordering of the water molecules around the ion, just as in the much more energetic hydration of bare, gaseous ions. The same changes in ΔH and $T\Delta S$ have also been found in the exchanges of the alkali cations on a strong-acid sulfonic resin,[10] where again we believe changes in ion hydration mainly determine the selectivity order rather than resin-group ion pairing. But this is not the case for the Cs^+-Li^+ exchange on a weak-acid carboxylate resin where bonding to the resin group does determine the (inverse) selectivity order,[11] $Li^+ > Cs^+$. In this exchange the binding of the Li^+ to the carboxylate group lowers the unfavorable enthalpy change enough so that the entropy increase of releasing some of the lithium ion's water of hydration can dominate ΔF, as is observed.

But it can be seen that the degree of separation of the halide tracers varies with the nature of the macro-anion and of the resin group. Figures 1 and 2 compare the use of OH^- and Cl^- as eluants with the Dowex 1 resin. The 1750-fold increase in D from F^- to I^- with OH^- as the macro-anion is compressed to a 250-fold increase when Cl^- is the macro-anion. This type of behavior was earlier noticed in the cation exchange case when substituting the more tightly held Cs^+ for Li^+ as the macro-cation in the ion exchange of alkali metal tracers with Dowex 50.[3]

A more dramatic compression of the halide separation factors occurs if a tertiary amine rather than a quaternary ammonium ion is used as the resin group. An obvious result is that the selectivity for OH^- is increased enormously, but halide exchange is also affected. Dowex 4 is such a weak-base resin, and so in slightly acid solutions has R_3NH^+ as the exchange group. The resulting ammonium ion is still a large ion, but it has a special site, the hydrogen, which probably carries much of the ion's charge, and which can hydrogen-bond to water and to other bases. That is, it has the possibility of (hydrogen-) bonding, even though weakly, to small basic anions such as F^-, and so making the resin phase more attractive to such ions than is the case with strong-base resins. Furthermore, the tertiary ammonium ions cannot participate in water-structure-enforced ion pairing as well as can the quaternary ion, thereby decreasing its attraction for large ions like I^-. For both reasons, the halide elution sequence should be compressed over that with a quaternary ammonium resin, and Figs. 3 and 4 show only a ten-fold spread in D from F^- to I^- with Dowex 4 and eluting solutions of LiCl or NMe_4Cl below a few hundredths molar in concentration compared to the 250-fold range in D with Dowex 1.

That this compression of the halide separation is due to the presence of the hydrogen on the ammonium group and not to the fact that Dowex 4 has a different lattice structure than Dowex 1 (polystyrene structure) was shown by the similar behavior observed with Dowex 3, a polystyrene-base resin containing a mixture of primary, secondary, and tertiary amine groups; the ratio of the distribution coefficients of tracer Br^- to tracer F^- with LiCl as the macro-electrolyte is 5.5, compared to 50 with the quaternary ammonium resin, Dowex 1. The differences in the exchange capacity and cross-linking of these resins certainly influence their behavior, as has been amply shown in other anion resin systems (cf. references 12 and 13), but the similar compression of the selectivity of the two quite different amine resins with respect to the selectivity of the quaternary ammonium resin leads us to believe that it is the amine group itself which is responsible. A conclusion, then, for dilute solution exchange, is that the largest separation factors will be obtained using a quaternary ammonium resin with a not too strongly held macro-anion.

As can be seen in Figs. 1-4, all of the tracers deviate from the mass-action slope of -1 as the external salt solution concentration is increased. These deviations indicate a breakdown in the dilute solution assumptions made in the derivation of eq. 4. One effect is the entrance of non-exchange electrolyte into the resin phase at high external solution concentration. This resin invasion electrolyte acts, to a first approximation, as additional cationic sites for the anions (increase of $[\bar{B}]$ in eq. 4), and so contributes to a gradual increase above the ideal mass-action line of slope -1 for all the tracer anions, but with some leveling of the selectivity. More important, however, are the increasingly stronger interactions of the anions with the aqueous cations and with the resin groups as the amount of water available to hydrate each ion decreases. That is, as the external aqueous phase concentration is increased, ion hydration gradually tends to become replaced by solvation (complexing) by the aqueous phase macro-cation and by the resin group. With the halide anions and simple cations such as the alkali metal ions, these interactions are not chemical complex-ion formation, but more transient types of electrostatic association.

Two such types, a temporary contact ion pairing of the bare ions and an association through one, or more, polarized water molecules (localized hydrolysis) have been discussed in an earlier paper on cation exchange.[3] The strength of such electrostatic associations depends upon the crystallographic size of the ions, decreasing from Li > Na > K > Rb > Cs and from F > Cl > Br > I. It should be remembered that the very different type of water-structure-enforced ion pairing has precisely the opposite behavior, becoming more important the larger the ion, and occurring noticeably only with ions as large as NMe_4^+ (possibly Cs^+) and I^- (Br^-).

If, as the aqueous phase concentration increases, the interactions of the tracer anion of interest with the resin group are stronger than those with the aqueous phase macro-cation, the anion will increasingly prefer the resin phase, and conversely, if the aqueous phase cation interactions are the stronger, the anion will go preferentially into that phase. But in an ion-exchange reaction it must be remembered that both anions are competing for the best solvating medium; the exchange goes in such a direction as to provide the most favorable situation, the lowest free energy, for the system as a whole, and this will usually be determined by the smallest ion, that which needs solvation the most.

With these considerations in mind, we can take up the experimental results in concentrated salt solutions. Figure 1 shows the behavior of tracer F^-, Cl^-, Br^-, and I^- on a quaternary ammonium resin with KOH as the macro-electrolyte. Only the small F^- can compete with the OH^- for solvation by water in the concentrated KOH solutions, and so the larger halide ions are pushed into the resin phase in the exchange, and the more so the larger the halide ion and the lower the water activity. This leads to an increasingly greater separation of the halides in concentrated solution over that in dilute KOH, and together with the effect of the resin invasion electrolyte results in an increase in the value of D above the mass-action line for all the tracer ions.

With LiCl as the eluting agent, one has a more strongly complexing cation (Li^+ instead of K^+), as well as the already mentioned effect of a more tightly held macro-anion (Cl^- for OH^-). As the external solution concentration increases, the aqueous phase remains the more favorable one for solvating the anions, for with decreasing water activity, anion hydration tends to be replaced by complexing with the lithium ion. Fluoride is complexed more strongly than Cl^-, and enough so that it is held in the aqueous phase more strongly relative to Cl^- in concentrated LiCl than in dilute solution; the curve for F^- tracer shows a slight negative deviation from the mass-action slope of -1 in concentrated solutions (Fig. 2). Furthermore, the dilute solution selectivity order $F < Cl < Br < I$ is greatly enhanced in concentrated LiCl solutions, as the larger halides are pushed out of the aqueous phase into the resin in order to permit the smaller anions to achieve their solvation by complexing with the Li^+ in the concentrated external solution.

However, it should be possible to greatly change this selectivity order by changing the nature of the resin group and of the macro-cation. Obviously, as already mentioned for the dilute solution case, the replacement of the quaternary ammonium cation of the strong-base resin with a group capable of (hydrogen-) bonding to the (smaller) anions would more nearly equalize the distribution coefficients of the halide ions. And this effect should be even more significant in concentrated solutions, where the anion-cation interactions become more important relative to anion-water solvation, than in dilute solution. A comparison of the results given in Fig. 2 for the quaternary ammonium ion resin and in Fig. 3 for the tertiary amine resin shows indeed this result; the 250-fold range in distribution coefficients from F^- to I^- for Dowex 1 in dilute solution is increased 80 times in going to 10 M LiCl, while the 10-fold spread of D's with Dowex 4 in dilute solution only increases by a factor of ~5 at 10 M LiCl. Furthermore, the ability of the R_3NH^+ resin group to hydrogen-bond to the small electronegative anions means that even F^- can obtain solvation in the resin phase comparable to that available in the aqueous phase (from the Li^+), and so yields a small positive deviation from the ideal mass-action curve in concentrated LiCl.

By going to a still better complexing resin group or to a more poorly complexing macro-cation, a reversal in the elution order of the halides should be possible in concentrated solution. The latter approach was tried, substituting tetramethyl ammonium chloride for lithium chloride, and using Dowex 4 resin. Now, as the water activity falls, the tertiary amine resin group can provide stronger interactions for the smaller anions than does the macro-cation in the aqueous phase, although unfortunately, the water activity does not fall as rapidly with NMe_4Cl concentration as with LiCl. As can be seen in Fig. 4, the distribution curves for F^-, Br^-, and I^- tracers, instead of diverging at higher macro-electrolyte concentrations as in the three previous cases, come together at 6 M NMe_4Cl. (It should be noted that the differences in the behavior of all the distribution curves from those with LiCl solutions extend down to concentrations as low as 0.05 M.) Although no region of inverted selectivity order was actually observed, the behavior found certainly supports the ideas presented, and somewhat more forcing conditions would appear capable of yielding such an inverted sequence

Acknowledgments

The authors would like to thank Mr. J. Bucher and Dr. D. C. Whitney for help with some of the experiments, and Dr. R. Wheaton, the Dow Chemical Company, Midlands, Michigan, for the sample of Dowex 4 resin before it was commerically available.

Footnotes and References

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

2. Summer Visitor, 1962, NSF High School Teachers Research Participation Program. Permanent address: Cabrillo College, Aptos, California.

3. D. C. Whitney and R. M. Diamond, Inorg. Chem. 2, 1284 (1964).

4. D. C. Whitney and R M. Diamond, J. Inorg. Nucl. Chem. 27, 219 (1965).

5. B. Chu, D. C. Whitney, and R. M. Diamond, J. Inorg. Nucl. Chem. 24, 1405 (1962).

6. R. M. Diamond, J. Phys. Chem. 67, 2513 (1963).

7. A. S. Wilson and N. A. Wogman, J. Phys. Chem. 66, 1552 (1962).

8a. W. Keder, A. Wilson, and L. Burger, Amine Systems in Solvent Extraction, Hanford Laboratory Report HW-SA 2959, April 1963;

b. W. Keder and A. Wilson, Nucl. Sci. Eng. 17, 287 (1963).

9. K. A. Kraus, R. J. Raridon, and D. L. Holcomb, J. Chromatog. 3, 178 (1960).

10. G. E. Boyd, F. Vaslow, and S. Lindenbaum, J. Phys. Chem. 68, 590 (1964).

11. S. Lindenbaum and G. E. Boyd, private communication, February 1965.

12. S. Lindenbaum, C. F. Jumper, and G. E. Boyd, J. Phys. Chem. 63, 1924 (1959).

13a. R. H. Herber, K. Tonguc, and J. W. Irvine, J. Am. Chem. Soc. 77, 5840 (1955);

b. J. Aveston, D. A. Everest, and R. A. Wells, J. Chem. Soc. 231 (1958);

c. B. Chu, Ph.D. Thesis, Cornell University, 1959;

d. Y. Marcus and D. Maydan, J. Phys. Chem. 67, 983 (1963).

FIGURE CAPTIONS

Fig. 1. Plot of log D vs. log KOH molarity with Dowex 1 resin for tracer F^-, ▨; Cl^-, ▼; Br^-, ◍; I^-, ▲.

Fig. 2. Plot of log D vs. log LiCl molarity with Dowex 1 resin for tracer F^-, □; Br^-, ○; I^-, △. Dashed line is "ideal" slope of -1.

Fig. 3. Plot of log D vs. log LiCl molarity with Dowex 4 resin for tracer F^-, □; Br^-, ○; I^-, △. Dashed line is "ideal" slope of -1.

Fig. 4. Plot of log D vs. log NMe_4Cl molarity with Dowex 4 resin for tracer F^-, □; Br^-, ○; I^-, △. Dashed line is "ideal" slope of -1.

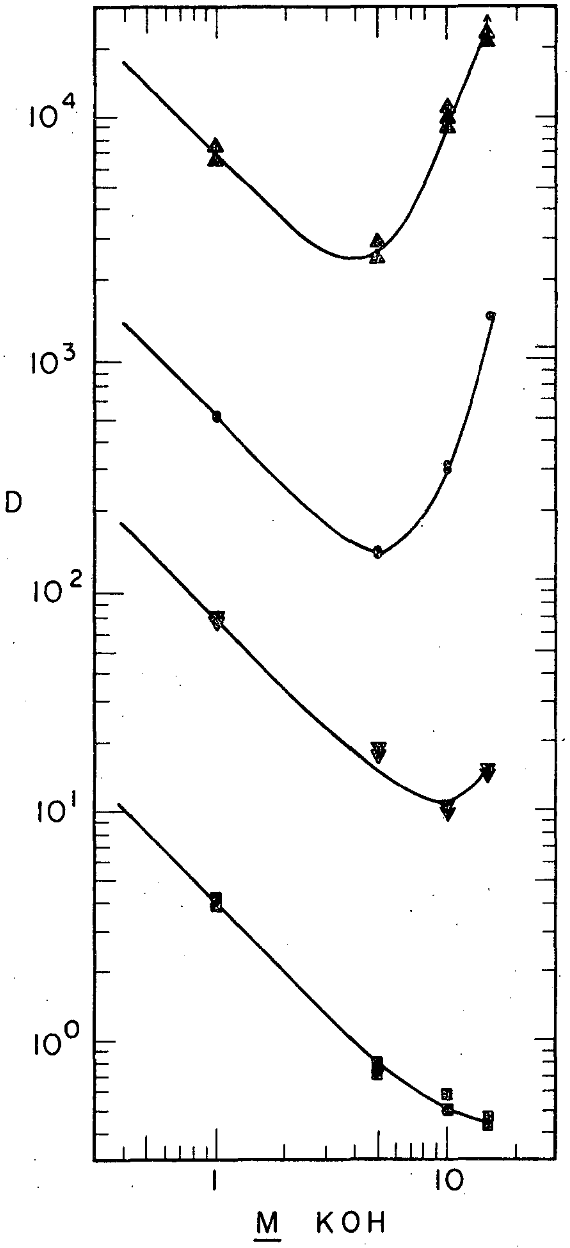
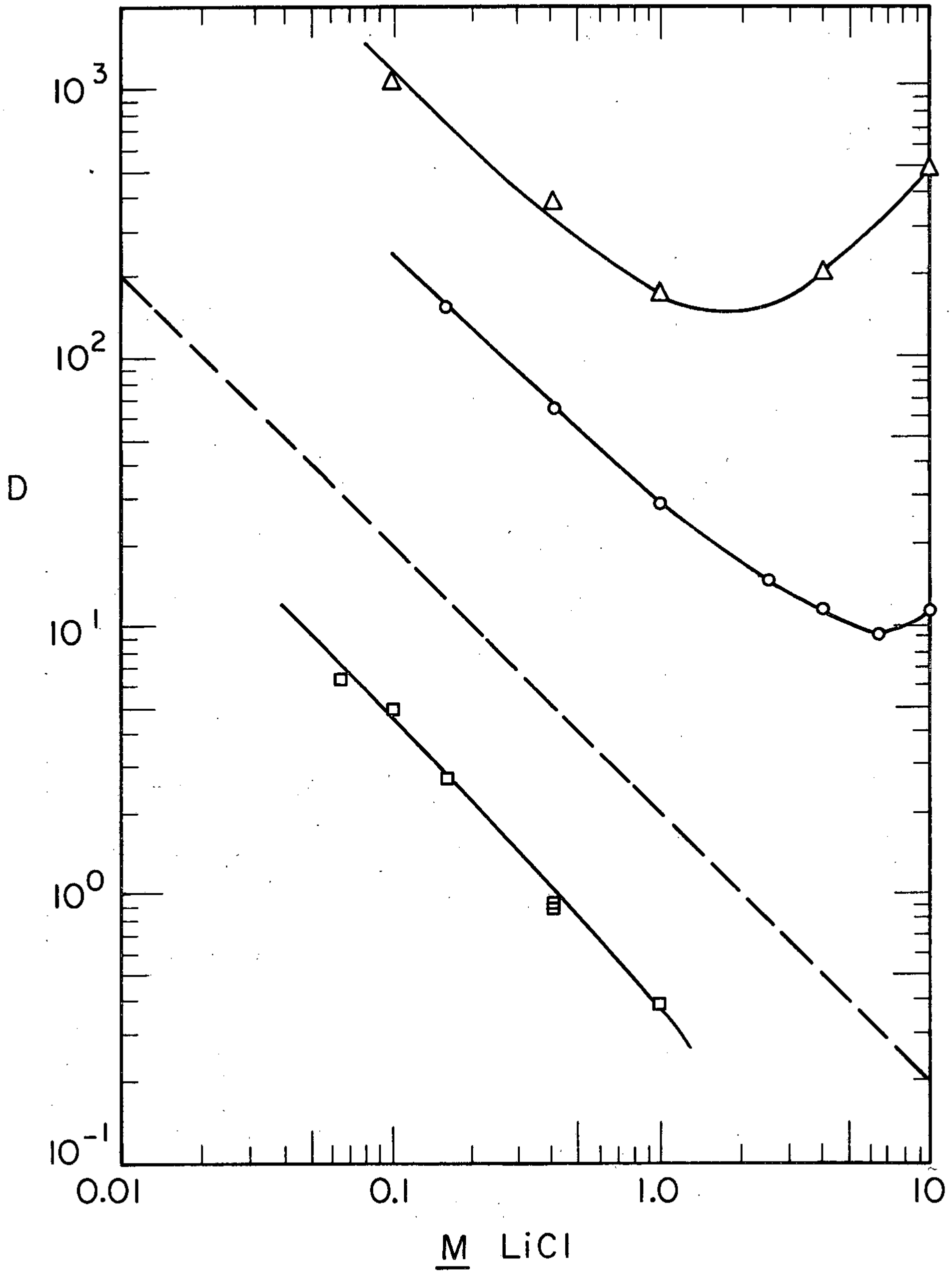


Fig. 1



MUB-4772

Fig. 2

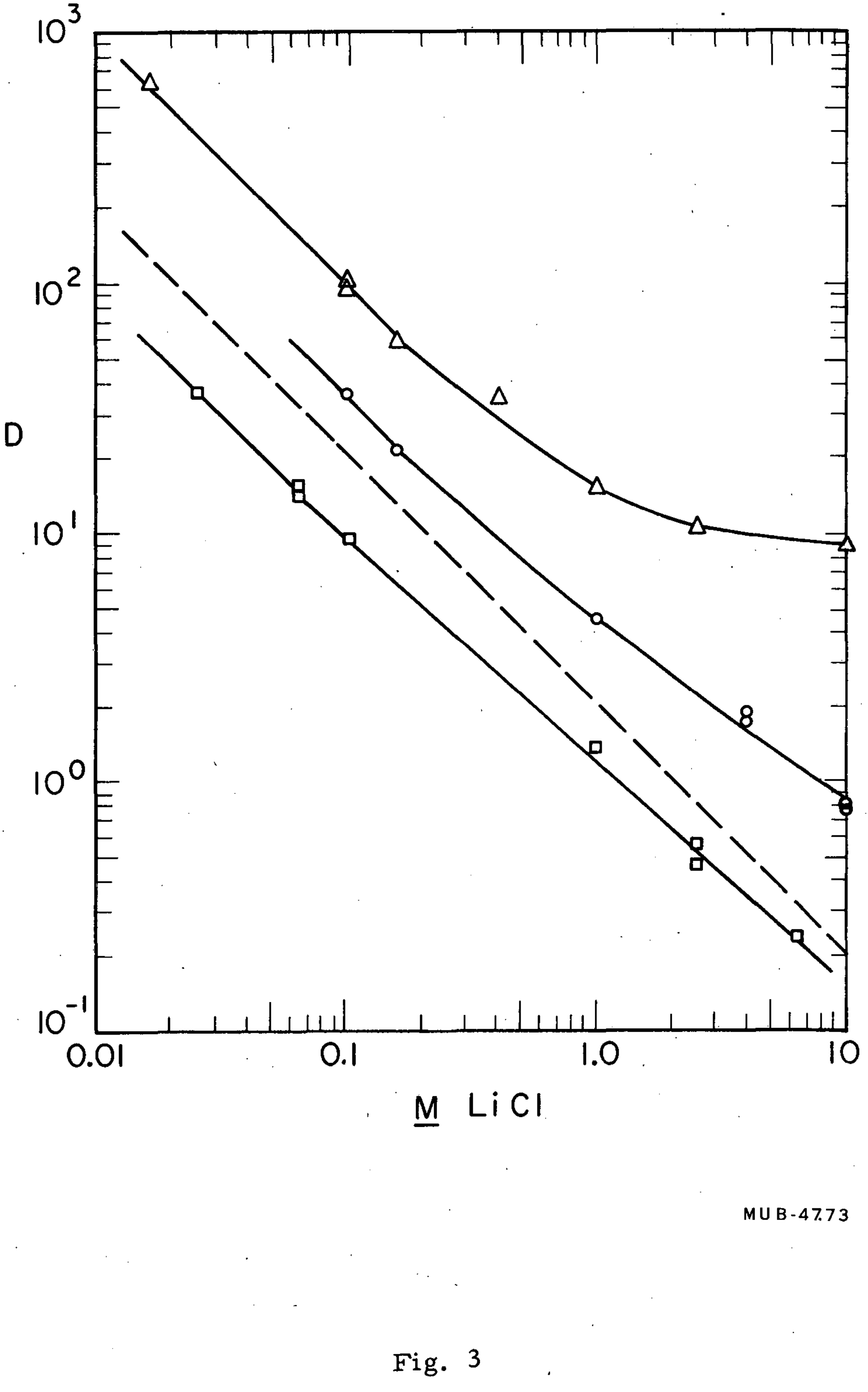
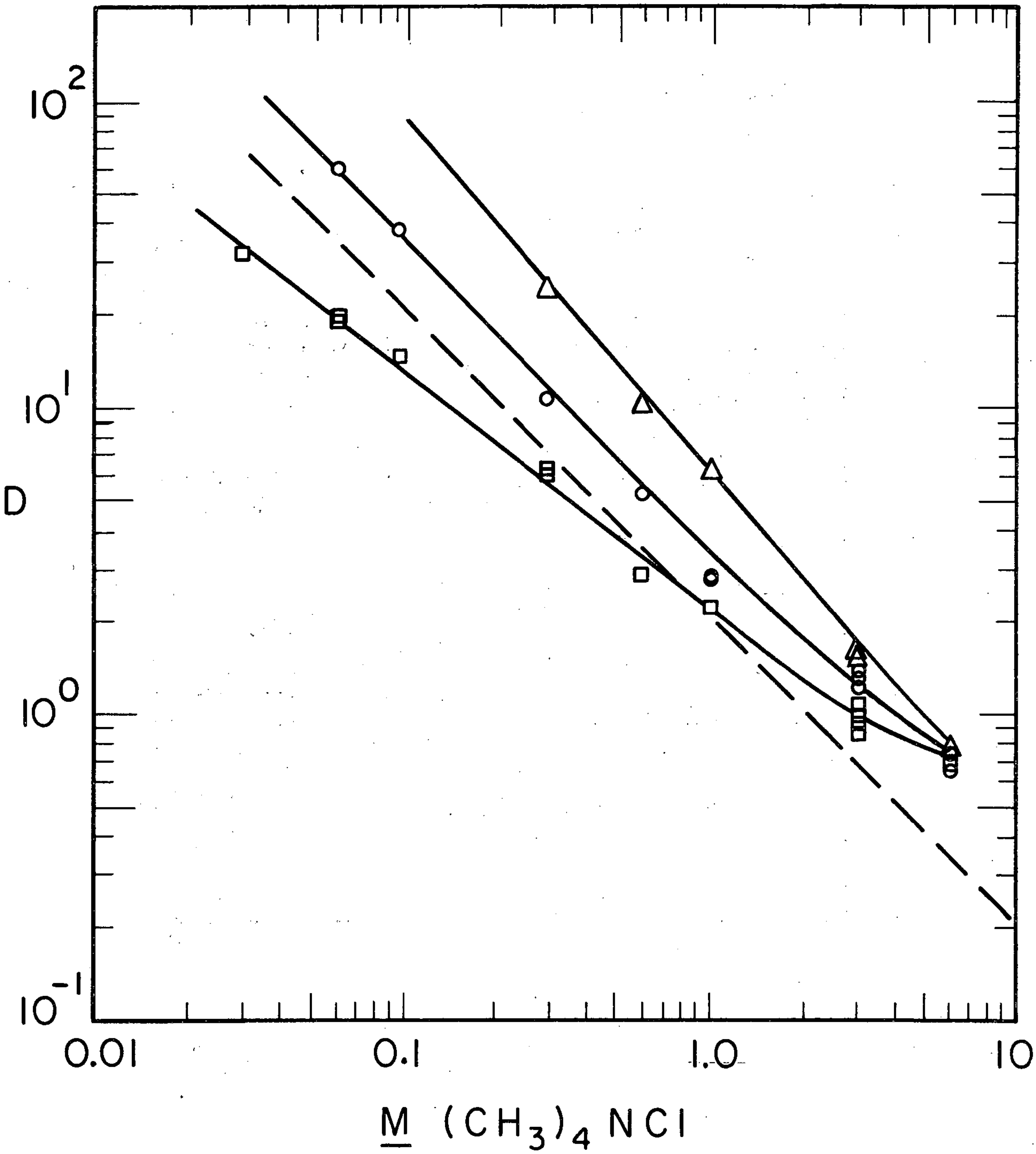


Fig. 3



MUB-4774

Fig. 4

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.