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THE EXTRACTION OF HYDROHALIC ACIDS BY TRILAURYLAMINE

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Abstract

Equilibria between trilaurylamine dissolved in several organic diluents and dilute aqueous solutions of hydrohalic acids (HCl, HBr, HI) and of hydrogen thiocyanate have been studied. In dilute solution in the low-dielectric-constant diluents, the ammonium salts usually exist as ion pairs. With increasing concentration, however, they can aggregate to higher ion associations. This aggregation decreases with increasing polarity or dielectric constant of the diluent, and from hydroiodide to hydrochloride. In nitrobenzene solution, the ion pairs dissociate to free ions at low ammonium salt concentration.

For a given diluent, the equilibrium constants for the extraction to the ion-paired trilaurylammonium salts increase from hydrochloric to hydroiodic acid. These constants also increase according to the following order of diluents: cyclohexane - carbon tetrachloride - benzene - chloroform- nitrobenzene.

The water uptake by the organic phases is proportional to the amine salt concentration and decreases with increasing anion size. The behavior of trilaurylammonium thiocyanate is similar to that of the ammonium iodide.

Introduction

Solutions of high molecular weight ammonium salts in organic diluents are increasingly being used for the extraction of metals from aqueous phases.[1,2] The salts of tertiary amines have been of particular interest in separation and purification steps during the reprocessing of irradiated fuel elements and in the isolation of transplutonium elements.[3,4] In order to understand the factors controlling metal extraction, it is necessary to know how such salt solutions behave in equilibrium with the supporting aqueous acid phase. Such knowledge contributes to the general picture of the extraction of mineral acids by organic bases, and serves as a guide to the extraction of the metallic anions.

Ammonium salts, when dissolved in the common low-dielectric-constant organic diluents, usually exist as ion pairs. Depending on the concentration of the salt, the ion pairs can dissociate, or associate into higher ion aggregates. In the presence of aqueous phases, ammonium salts in organic solution are hydrated. The stability range of the salt is limited by hydrolysis and, if concentrated acidic aqueous phases are present, by the uptake of excess mineral acid. The existence of ion pairs, their dissociation or association, and the stability and the hydration of the ammonium salts all depend on the nature of the anion and of the organic diluent.[5-15]

Previous investigations of the extraction of perchloric acid[13] and of hydrochloric acid[16] by trilaurylamine (TLA) have shown that the nature of the diluent does influence significantly the properties of the salt in solution. It was hoped that a systematic study of the hydrohalic and thiocyanic acid extraction systems using TLA in several types of diluents might cover a large range of ammonium salt behavior. The diluents were chosen so as to furnish a

wide variation in character, e.g.: chloroform, a polar, acidic diluent, providing the possibility of hydrogen bonding to the anion; benzene, a basic aromatic diluent capable of interacting via its π-electrons with the ammonium cation; carbon tetrachloride and cyclohexane, both of them usually considered to be relatively inert; and nitrobenzene, a high-dielectric-constant diluent with some basic nature.

The extraction systems were studied by a back-extraction or hydrolysis technique; organic solutions of the pure ammonium salt were equilibrated with water and the composition of the phases were then determined. By the use of radioisotopes such a study can be extended to very low halide concentrations in both phases. Therefore, radiobromide was used to cover a large concentration range, but, because of the absence of convenient tracers for chloride and thiocyanate ions, the comparison of the different amine hydrohalides was based also on titrations in both phases and on pH measurements of the aqueous phase. The determination of the composition of the organic phase was completed by measurements of the water bound to the ammonium salt. Finally, since the behavior of the ammonium salt was expected to be explained in part on the assumption of association, vapor pressure measurements of the organic phases were used to check independently the results obtained from the extraction studies alone.

Experimental

Reagents. Trilaurylamine "Rhône-Poulenc", qualité nucléaire, contains 99% tertiary amine (TLA) which was determined by titration with perchloric acid in a mixture of glacial acetic acid/acetic anhydride in the presence of crystal violet. The ammonium salts or their solutions were prepared using reagent grade

HCl "Merck"; HBr, HI (1.5% H_3PO_2) and NaSCN "Baker and Adamson". Radiobromide, $^{82}Br^-$, was produced by irradiation of LiBr in the Livermore Pool-type reactor and dissolution in water; before use, the initial radiobromide solution was treated (reduced) with gaseous hydrogen sulfide. Reagent grade "Baker and Adamson" diluents: benzene, nitrobenzene, carbon tetrachloride and cyclohexane were used without further treatment; chloroform was washed five times with equal volumes of distilled water to remove the stabilization alcohol.

Preparation of ammonium salts. Anhydrous amine hydrochloride (TLAHCl) and hydrobromide (TLAHBr) were obtained by neutralizing amine solutions in isooctane with aqueous acid; the salts were recrystallized from isooctane. From the anhydrous salts, solutions of TLAHCl and TLAHBr in the desired diluent were prepared. Solutions of TLAHCl, TLAHBr or TLAHI were also obtained by equilibrating 25 Vol % (~0.4 M) amine solutions in organic diluent with equal volumes of 1.0 M aqueous acid; solutions of lower concentration were prepared by dilution.

Usually, solutions of TLAHSCN were obtained by equilibrating 0.4 M TLAHCl three times with equal volumes of 6 M aqueous NaSCN solution, followed by a further equilibration with 0.5 M NaSCN solution. Because of the low solubility of TLAHCl in cyclohexane, 0.4 M TLAHSCN solutions in this diluent were obtained from 0.4 M TLAHBr or by neutralizing a 0.4 M TLA solution by a mixture of aqueous hydrochloric acid and sodium thiocyanate. The concentrations of the ammonium salt solutions were checked by titration.

Analytical methods. The composition of the aqueous phases was determined by titration with sodium hydroxide and from pH measurements (calomel-glass electrode). When aqueous phases of low acidity were saturated with nitrobenzene, the pH values were found to increase. Therefore, in this system the acid concentrations had to be determined from a calibration curve obtained by measuring the pH values of aqueous phases of known acidity after equilibration with nitrobenzene. This observation may explain why formation constants of ammonium salts in nitrobenzene as reported in the literature[7,17] disagree. The concentration of aqueous hydrobromic acid was determined using radiobromide; this permitted the extension of amine hydrobromide determinations to very low concentrations. If ammonium salt concentrations in an organic phase were higher than 0.01 M, they were determined by titration with sodium methylate in the presence of thymol blue, after dissolving the sample in a mixture of equal volumes of benzene and methanol. The water content of the organic phases was determined by titration with Karl Fischer solution (premixed, stabilized; "Matheson, Coleman and Bell"), after dissolving aliquots of the organic phase in methanol.

Experimental Procedures

Hydrolysis of the ammonium salt. Starting from 0.4 or 0.1 M ammonium salt solutions of exactly known concentration, series of solutions were prepared by dilution. Twenty ml of the salt solution were shaken with (usually) an equal volume of distilled water at room temperature (23±2°C) for two hours. If radiobromide was used, between 20 and 200 μl of the tracer solution were

injected into the aqueous phase before equilibration. If necessary, the phase separation was accelerated by centrifugation. Five- or ten-ml aliquots of a phase were pipetted for titration; for the counting of the radiobromide in a Na(Tl)I well-type crystal, 2-ml samples were taken or smaller samples were taken and adjusted to 2 ml. All pipettes had been treated previously with dimethyl-dichloro-silane.

Vapor pressure measurements. The vapor pressures above water-saturated solutions of amine or ammonium salts at 25°C were determined with a Mechrolab Vapor Pressure Osmometer, Model 301A. Reference solutions were the water-saturated pure diluents.

Results

The hydrolysis, or back-extraction, of the ammonium salts can be represented by the equation

$$nTLA \cdot nHX_o \rightleftharpoons nTLA_o + nH^+ + nX^- \qquad (1)$$

if the salt contains an equal number of mols of amine and of acid, as in the present case. The subscript o stands for the organic phase; no subscript represents the aqueous phase. The results of the hydrolysis are presented as log-log plots of the organic phase acid concentration (corrected for acid solubility in the diluent, when this is significant), $[TLAHX]_o$, vs the product $[TLA]_o\, a_{HX}$. The organic phase acid concentration $[TLAHX]_o$ is determined

directly by titration or radiometric measurement and/or has been calculated from the initial ammonium salt concentration in the organic phase, c_i, and the total acid concentration in the aqueous solution at equilibrium, [HX],

$$[TLAHX]_o = c_i - [TLA]_o$$

$$V_o/V \; [TLA]_o = [HX] \; , \qquad (2)$$

V_o/V is the volume ratio of the organic to the aqueous phase. The acid activity, a_{HX}, was obtained from pH measurements or from the acid concentration, using literature data[17,18] for the activity coefficients. It is assumed that the activity of HSCN equals that of HI at equal concentrations. Figure 1 shows the results obtained by the use of radiobromide. Figures 2 to 6 show the results of the titrations and pH measurements and contain some results taken from Fig. 1 in order to show the agreement between the different analytical methods and in order to indicate the general feature of the experimental curves at low concentrations.

In Figs. 7 and 8 organic-phase water concentrations, $[H_2O]_o$, are given as a function of the total ammonium salt concentration, $[TLAHX]_o$. They have been corrected for the solubility of water in the diluent:

$$[H_2O]_o = [H_2O]_{o,total} - [H_2O]_{Dil} \cdot Vol\%_{Dil} \; . \qquad (3)$$

where $[H_2O]_{Dil}$ is the solubility of water in the pure diluent after saturation with the same aqueous phase as the ammonium salt solutions, and $Vol\%_{Dil}$ is the

volume percentage of the diluent in the solution calculated on the basis that a 0.4 M TLA solution contains 75 Vol% diluent and that no significant volume change is observed upon neutralization.

The solubilities, $[H_2O]_{Dil}$, determined at 25°C in the presence of pure water are listed in Table I.

The results of the vapor pressure measurements are given in Figs. 9 and 10. The ordinates are in arbitrary units (the osmometer readings directly), but are proportional to the vapor pressure difference between the water-saturated solutions and the water-saturated diluents.

Discussion

In the organic phase, the ammonium salt formed by the reaction of the amine and the extracted acid may be in the form of dissociated ions, of ion pairs, or of still higher ion associations. With the restriction that the amount of acid extracted is equal to, or less than, the total amine concentration, a condition fulfilled in the present study, the concentration of extracted acid can be expressed as a sum of terms,

$$[TLAHX]_o = [TLAH^+]_o + [TLAH^+ \cdot X^-]_o + 2\,[2TLAH^+ \cdot 2X^-]_o + \ldots$$

or (4)

$$[TLAHX]_o = y_{\pm o}\sqrt{K_{1/2}[TLA]_o(HX)} + \sum_{n=1} nK_n\,[TLA]_o^n\,(HX)^n$$

where

$$K_{1/2} = \frac{[TLAH^+]_o[X^-]_o\,y_{\pm o}^2}{[TLA]_o\,(HX)} \qquad (5)$$

$$K_n = \frac{[nTLAH^+ \cdot nX^-]_o}{[TLA]_o^n(HX)^n} \qquad (6)$$

and brackets and parentheses indicate molar concentration and activity, respectively. In any given experimental situation, one or two species most likely dominate. From a log-log plot of $[TLAHX]_o$ vs $[TLA]_o(HX)$, the average value of n can be determined from the slope; a constant value over a range of concentration indicates a single species, and allows evaluation of the appropriate K_n. Where the slope is varying, or for isolated data where the value of n is not known, an "apparent" constant may be defined as $K_{app} = [TLAHX]_o/[TLA]_o(HX)$, but this likely will have validity only under this particular set of conditions.

Figure 1 illustrates the role of the diluent in the extraction of HBr. A unique slope of one is observed for solutions in chloroform, indicating ion pairs to exist over the whole concentration range studied. In contrast, for the lower salt concentrations in nitrobenzene, n becomes smaller than unity, which behavior strongly suggests that the ion pairs dissociate. For high ammonium salt concentrations in benzene, and to a still larger degree in carbon tetrachloride and cyclohexane, the slope exceeds unity indicating that the ion pairs are aggregating to higher ion associations.

The behavior of the different amine hydrohalides in a given diluent can be seen in Figs. 2 to 6. In all cases, the order of extraction is $Cl^- < Br^- < I^-$, and the reason has been suggested previously.[19] The smallest, most basic anion is the one most in need of solvation, and since, in the systems studied, water is the best anion-solvating agent, the ions are only able to leave the aqueous phase in the order $F^- < Cl^- < Br < I^- \sim SCN^-$. The logarithms of the equilibrium constants K_1 for the extraction to an ion-paired salt (region of unit slope in the log-log plots) and of the apparent formation constants K_{app}, the latter at a total ammonium halide concentration of 0.1 M, are summarized in Table II.

Since the solubility of TLAHCl in cyclohexane at room temperature is smaller than 0.1 M, the corresponding constant K_{app} has been obtained by extrapolation.

If it is assumed that the difference between corresponding values of K_1 and K_{app} is due to the association of ion pairs, it should be possible to determine the extent to which the salts are aggregated from the equilibrium measurements as well as from the vapor pressure determinations. Considering the simplest case of dimerization, to ion quadrupoles, the constant

$$K_D = [2TLAH^+ \cdot 2X^-]_o / [TLAH^+ \cdot X^-]_o^2 \qquad (7)$$

can be determined in the following manner. The difference between any total ammonium salt concentration and the corresponding amount of single ion pairs, as calculated from the value of K_1, is taken to be twice the dimer concentration, $[2TLAH^+ \cdot 2X^-]$. A slope of 2 in a plot of $\{[TLAHX]_o - [TLAH^+ \cdot X^-]_o\}$ vs $[TLAH^+ \cdot X^-]_o$ indicates the range in which dimers exist. Dimerization constants taken from such a plot (Fig. 11) for the ammonium salts dissolved in benzene are listed in Table III.

From the osmometric measurements an independent check can be made on these values. The pure amine appears to be monomeric in solution over the whole concentration range studied. At any given total concentration, the average association number, $\bar{p}$, of the ammonium salt equals the ratio of the vapor pressure lowerings for amine and ammonium salt solutions of the same concentration, and hence equals the ratio of the osmometer readings of corresponding

amine and ammonium salt solutions (Figs. 9 and 10). Table IV summarizes such average association numbers, $\bar{p}$, determined from vapor pressure measurements at total concentrations of 0.1 M.

From Figs. 9 and 10 and from this table the following conclusions can be drawn: 1) there is essentially no association beyond the ion pair with chloroform as the diluent, at least up to 0.1 M total salt concentration; 2) association or aggregation increases from the chloride to the iodide salt; and 3) for each ammonium salt, association increases in the order chloroform, benzene, carbon tetrachloride, and cyclohexane. What explanations can be suggested to account for these results? Consider the order of aggregation of the halides. On simple Coulombic grounds, the interaction in the organic phase between the ammonium cation and the anion should decrease from Cl^- to Br^- to I^-. There is ample evidence for this. In the infrared absorption spectra of the ammonium, or deuterated ammonium, salts, the wave numbers of the bands attributed to $\overset{+}{N}H$- or $\overset{+}{N}D$- bonds increase as a result of decreasing cation-anion attraction from chloride to iodide[21]; furthermore, the absorption bands narrow in the same sense because of the decreasing hydrogen bonding. Similarly, NMR studies show a chemical shift of the ammonium hydrogen which can be correlated in the same order with a decreasing interaction from chloride to iodide.[22] But the stronger the cation-anion hydrogen bonding, the less the resulting ion-pair needs further (electrostatic) solvation through aggregation into higher ion associations. So in all cases, we would expect association beyond the ion pair to increase in the order $Cl^- < Br^- < I^-$, as is observed.

The differences in behavior from one diluent to another clearly show that the diluents themselves are not "inert", but interact in various ways with

the amine and with the ammonium salts. With the uncharged, but basic, amine molecule, this interaction can only be a short-range chemical one, but with the salts there is, in addition, the possibility of long-range Coulomb effects, that is, a general electrostatic solvation of the ions by the diluent molecules' dipole moments, both static and induced. The higher the dielectric constant of the diluent, the better, in general, the extraction, as the smaller the (positive) electrostatic free energy of transfer of ions from the aqueous to the organic phase. If, in addition, the diluent interacts more strongly chemically with the ammonium salt than with the amine, compared to a relatively "inert" solvent, the extraction will be increased further. Conversely, if the chemical interaction of the diluent is greatest with the amine, the effect will be noticed in poorer extraction (a smaller value of K_1).

Consider as a first example the cyclohexane systems. Cyclohexane is chemically the most inert of the diluents studied, and has the lowest dielectric constant. It cannot very effectively solvate the ammonium salts (nor probably the amines, either). The order of salt solubilities in the diluents reflects to some extent the salt-diluent interactions; the solubilities of a given ammonium salt decrease from chloroform to cyclohexane and parallel the solubilities of water or of molecular hydrogen halides in the diluents.[16] Furthermore, the low dielectric constant of cyclohexane also works against the formation of charged species in the organic phase, so that the extraction of acids (values of K_1) into cyclohexane is the poorest of the diluents studied. In a situation where the diluent is such a poor solvating agent, the ions themselves help solvate each other: chemically, by forming hydrogen bonds between the hydrogen of the ammonium ion and the anion, if basic enough; and electrostatically, through association into ion pairs and higher ion aggregates.

Thus, for cyclohexane it might be expected that the degree of aggregation at a given concentration would be larger than for any of the other diluents studied, and that this is indeed so is indicated by the values of $\bar{p}$ in Table IV and by the differences between K_1 and K_{app} in Table II.

Carbon tetrachloride is also relatively inert, but apparently not as much so as cyclohexane, and it has a slightly higher dielectric constant (Table II). The values of K_1 with it are larger for all the ions studied than with cyclohexane, and the degree of aggregation is lower. The molecule of CCl_4 presents a more polarizable surface of higher electron density than does the hydrocarbon, and this may interact more favorably with the positively-charged ammonium cation of the salt than can the hydrogenic exterior of cyclohexane.

Certainly with benzene, where the π-electrons of the aromatic ring give a weakly basic character, significant interactions with the hydrogen of the ammonium cation help stabilize the cation, and hence salt formation. This should be especially true for salts with large, very weakly basic anions, such as I^-, SCN^-, ClO_4^-, as these ions hydrogen-bond the least to the cation, give it the least solvation, and so require the greatest help from the diluent. The result, as shown in Table II, is that the values of K_1 for all salts are still larger than for CCl_4, and the increase is greatest for the large anions.

In contrast to benzene, the fourth diluent studied, $HCCl_3$, has a slightly acidic hydrogen, and also a larger dielectric constant, Table II. Because of its somewhat acidic nature, $CHCl_3$ might be expected to stabilize the amine through weak hydrogen-bonding, and so depress the extraction of the acids, as has been found to occur with the less basic extractant, trioctylphosphine oxide (TOPO).[23] But in fact, the opposite was observed; the hydrohalic acids have larger K_1's with $HCCl_3$ than with the other diluents already

described. It appears that the greater proton affinity of the amines over the $\geq$PO containing extractants cannot be generalized to include better coordination with small, weakly acidic, uncharged molecules. Another example of this is the extraction of water; dilute solutions of TLA in the usual diluents extract a negligible amount, whereas dilute solutions of TOPO extract from 30% to almost 100% their molarity of water.[24]

But $HCCl_3$ can interact with the smaller halide anions, and this coordination or solvation of the anion, and also the greater electrostatic solvation of both cation and anion because of the higher dielectric constant of the diluent, are factors in the better extraction. The halide-$HCCl_3$ interactions also spread the anionic charge and make the ion effectively bulkier, and so both types of solvation, chemical and electrostatic, reduce the importance of the higher ion-ion interactions and thus the degree of ion aggregation. (Table IV). But both types of solvation become less important, the larger the anion (the charge density on the anion becomes less, and the basicity is less, c.f., the acid strength of the hydrogen halides), and so there should be less difference among the values of K_1 for the ammonium halides in $HCCl_3$ than in cyclohexane, CCl_4, or benzene. Another way of saying this is that $HCCl_3$ should be a better diluent for the smaller, more basic anions, relative to the larger ones, than a neutral or weakly basic solvent, and it is, as can be seen in Table II.

The last diluent studied, nitrobenzene, illustrates the extraction behavior in a weakly basic, but high-dielectric constant, medium. The electrostatic solvation represented by the high dielectric constant greatly reduces the positive electrostatic free energy change involved in transferring charged ions from the aqueous to the organic phase, and so greatly helps the extraction; nitrobenzene was the best diluent studied. The ion-ion attractions are also so

weakened that at low, but experimentally accessible, concentrations of the ammonium salts, the ion pairs dissociate to free ions. In Fig. 3, the complete dissociation of TLAHI is indicated when $[TLAHI]_o \leq 10^{-3}$ M (log-log slope of 1/2 in the figure), and dissociation appears to occur below 10^{-5} M for $[TLAHBr]_o$. Furthermore, up to the highest concentrations studied, 0.1-0.2 M, there was no indication of ion association beyond the ion pair, even for HI, in contrast to the situation with the other diluents of lower dielectric constant. Clearly, the dielectric constant of the diluent plays a very important, although not all-powerful, role in determining the magnitude of extraction and degree of aggregation of the salts.

Since the aggregation of the ammonium salts is a characteristic feature of extraction with most diluents of low dielectric constant, unless they contain functional groups capable of coordinating with the anion or cation, e.g., $CHCl_3$, let us consider this process further. In Fig. 11 is plotted logarithmically the concentration of extracted acid in excess of that for the ion pair, as calculated from the value of K_1 determined at lower concentrations, vs the concentration of ion pair. Benzene is the diluent. The observed range of slope 2 in the log-log plot indicates dimerization (ion quadrupoles) as a prominent form of association at total amine hydrochloride and bromide concentrations up to almost 0.04 M in benzene. At this concentration, average association numbers of 1.34 and 1.44 are calculated from the dimerization constants $K_D = 20$ for TLAHCl and $K_D = 40$ for TLAHBr as obtained from the extraction data, Table III. Vapor pressure measurements (Fig. 10) give $\bar{p} = 1.33$ and 1.47, respectively, under the same conditions. This agreement indicates that at least for benzene solutions up to the concentrations studied, the variation of the apparent formation constants of

the ammonium salts as reflected by the increasing slopes in Fig. 4 can be explained by ion aggregation, and initially by ion-quadrupole formation.

However, the high (and even negative) slopes shown in Fig. 5 and Fig. 6 for concentrated solutions in CCl_4 and in cyclohexane cannot be understood on the basis of association alone; an infinite slope would indicate complete aggregation to a colloidal phase, and negative slopes are physically unacceptable on this picture if all deviations are to be ascribed to ion aggregation. Furthermore, and perhaps most importantly, the vapor pressure measurements of the corresponding organic phases give smaller average aggregation numbers (Table IV). It appears to us that a possible explanation of this discrepancy is a change, an increase, in the value of the extraction constants K_1, K_2, etc., in more concentrated solutions. That is, these were defined as concentration "constants", not thermodynamic constants, and the activity coefficients for the ionic species in the organic phase do not remain constant, as is generally assumed, but become smaller. This is not unexpected, nor too hard to explain. A 0.2 M solution of TLAHX has a high concentration of ionic charges, and even though the charges are associated, the solution has quite different physical and chemical properties from the diluent itself which dominated the system in more dilute cases. Now the diluent is effectively the solution of the ammonium salt. For example, Table V lists the room temperature dielectric constants measured for solutions of TLAHBr in benzene and in cyclohexane as a function of concentration. It can be seen that the dielectric constant increases markedly above 0.1 M TLAHBr. (Why it does so more effectively in benzene than in cyclohexane is not clear), although no significant changes are observed for comparable concentrations of the pure amine in the diluent. Clearly the presence of the ions changes the

nature of the phase, and the increase in the dielectric constant is itself a change in the nature of the organic phase which makes extraction of ionic species much easier (this can be seen from the Born charging expression as applied to the transfer of ions from one medium to another). This is not presented as the sole cause for the change in organic phase activity coefficients (furthermore, it is difficult to know what relation exists, if any, between the measured macroscopic dielectric constant and the effective value at the ion itself), but only as an indication that the nature of the solvent has changed.

In any case, the conclusion is that although in dilute organic solutions extraction and vapor pressure measurements give the same and presumably correct values for ion association, in more concentrated solutions the two methods may give differing results. Although both methods may be in increasing error, it is most likely that the extraction method will give the more greatly over-exaggerated degree of ion aggregation, for the reason given in the previous paragraph, and so such results should be carefully considered in this light.

In the presence of aqueous phases, ammonium salts in organic solution are hydrated. The amount of hydration of a given salt (e.g., TLAHCl, Fig. 7) depends on the diluent, decreasing in the order cyclohexane, benzene or toluene, carbon tetrachloride, chloroform. The gross features of this order can be explained. Cyclohexane is chemically the most inert of the diluents used, and so offers the extracted ions the smallest degree of chemical solvation, as already mentioned. This leads to the poorest extraction, and to the largest amount of water bound to the ionic complex as solvating agent. At the other extreme, $HCCl_3$ is acidic enough to solvate the anions (and possibly in so doing the Cl atoms become basic enough to interact with the hydrogen of the ammonium

cation) and so leads to very good extraction and the minimum amount of water carried along to solvate the extracted ions.

In the same diluent (cyclohexane, Fig. 8), the ratio water:/ammonium salt decreases from chloride to iodide and thiocyanate. The reason for this order follows from the previous paragraph. The smaller the halide ion, the greater its need for solvation, and so the greater the amount of water co-extracted. It should be mentioned that for higher salt concentrations—where aggregation occurs—more water appears to be bound by the ammonium salt than in the range where mainly ion pairs exist.

Table VI contains the ratios of water:ammonium salt (corrected for the solubility of water in the diluent itself) determined in the concentration range where the amount of water is directly proportional to the salt concentration (slope 1 in Figs. 7 and 8). This water does not significantly affect the vapor pressure measurements nor the aggregation of the ammonium salt, as was seen by a comparison of solutions of anhydrous and of hydrated ammonium salt. From the values of the vibrational stretching frequencies, infrared spectra show the water to be bound, but all experimental data so far obtained do not allow for an unambiguous decision between the possibilities that 1) the anion is hydrated, or 2) the ion pair is linked together by a water molecule; although we favor the first possibility. We can rule out that the ammonium cation alone is hydrated. Exactly the same conclusions have been reached by Mohr, Wilk, and Barrow[25] from an infrared absorption study of solutions of the tetrabutylammonium halides in CCl_4.

In conclusion, it can be said that both the dielectric constant and the chemical nature of the diluent affect the degree of extraction of the acid and the extent of aggregation of the resulting ammonium salt. In general, the

higher the dielectric constant and the stronger the chemical interaction of the diluent with one or both of the ions of the salt, the better is the extraction and the smaller the degree of aggregation, at least for ammonium salt concentrations below a few tenths molar. When, in a "poor" diluent of low dielectric constant, the salt concentration becomes appreciable, determinations of the degree of aggregation by extraction methods, whether by radioactive tracer, pH determinations, or two-phase titrations, yield impossibly high results. A reason for this behavior has been suggested, and indeed, direct osmometric measurements do give lower and more reasonable values, which, however, are still subject to the errors inherent in such measurements at concentrations in the tenths molar region.

Footnotes and References

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Table I

Water Solubility at 25°C.

Diluent	$[H_2O]_{Dil} \times 10^2$ M^{-1}
Benzene	3.3
Toluene	2.4
Carbon Tetrachloride	0.9
Cyclohexane	0.4
Chloroform	7.4

Table II

Ion Pair and Apparent (0.1 M) Extraction Constants

	TLAHCl		TLAHBr		TLAHI		TLAHSCN		Dielectric Constant[a]
	$\log K_1$	$\log K_{app}$	$\log K_1$	$\log K_{app}$	$\log K_1$	$\log K_{app}$	$\log K_1$	$\log K_{app}$	
Nitrobenzene	6.78	6.78	7.70	7.70	9.00	9.00			34.8 (25°)
Chloroform	6.85	6.90	7.60	7.70	8.48	8.65	8.70	9.00	4.81 (20°)
Benzene	4.26	4.70	5.08	5.70	6.34	7.18	6.96	7.78	2.28 (20°)
Carbon Tetrachloride	3.40	4.11	4.00[b]	5.30	5.30	7.55	<5.48	7.00	2.24 (20°)
Cyclohexane	<1.30	3.08	2.18[b]	4.04	<3.90	5.48	<4.40	6.18	2.02 (20°)

[a] A. Weissberger and E. Proskauer, Techniques of Organic Chemistry, Vol. VII, "Organic Solvents", revised by J. Riddick and E. Topps, Jr., 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1955.

[b] Determined with radiobromide.

Table III

Dimerization Constants in Benzene

Salt	K_D M^{-1}
TLAHCl	20
TLAHBr	40
TLAHI	80
TLAHSCN	80

Table IV

Average Association Numbers at 0.1 M

Diluent	TLAHCl	TLAHBr	TLAHI	TLAHSCN
Chloroform	1.00	1.01	1.02	1.01
Benzene	1.47	1.65	1.74	1.65
Carbon Tetrachloride	2.20	2.20	2.87	2.20
Cyclohexane	2.85	3.56	4.50	3.85

Table V

Static Dielectric Constants of Solutions

	Benzene	Cyclohexane
Pure diluent	2.28	2.02
0.4 M TLA	2.28	2.02
0.1 M TLAHBr	2.90	2.22
0.2 M TLAHBr	4.30	2.75
0.4 M TLAHBr		4.35

Table VI

Water:Salt Ratio in Various Diluents

Diluent	Salt	Ratio water:salt (corrected for diluent water)
Cyclohexane	TLAHCl	1.15
Benzene	TLAHCl	0.95
Toluene	TLAHCl	0.95
Carbon Tetrachloride	TLAHCl	0.50
Chloroform	TLAHCl	0.33
Cyclohexane	TLAHBr	0.50
Cyclohexane	TLAHI	0.25
Cyclohexane	TLAHSCN	0.20

Figure Captions

Fig. 1. Total ammonium bromide concentration, $[TLAHBr]_o$, versus $[TLA]_o\ a_{HBr}$ for various diluents. The composition of both phases has been determined by titration and by use of radiobromide. The acid activity was calculated from Ref. 18.

Fig. 2. Total ammonium salt concentration, $[TLAHX]_o$, versus $[TLA]_o\ a_{HX}$ for chloroform diluent. The composition of both phases was determined by titration and from pH measurements. Acid activities were calculated from Refs. 18 and 19 assuming equal activity coefficients for HI and HSCN.

Fig. 3. Total ammonium salt concentration, $[TLAHX]_o$, versus $[TLA]_o\ a_{HX}$ for nitrobenzene diluent. The filled triangles indicate determinations with radiobromide.

Fig. 4. Total ammonium salt concentration, $[TLAHX]_o$, versus $[TLA]_o\ a_{HX}$ for benzene diluent.

Fig. 5. Total ammonium salt concentration, $[TLAHX]_o$, versus $[TLA]_o\ a_{HX}$ for carbon tetrachloride diluent. The filled triangles indicate determinations with radiobromide.

Fig. 6. Total ammonium salt concentration, $[TLAHX]_o$, versus $[TLA]_o\ a_{HX}$ for cyclohexane diluent. The filled triangles indicate determinations with radiobromide.

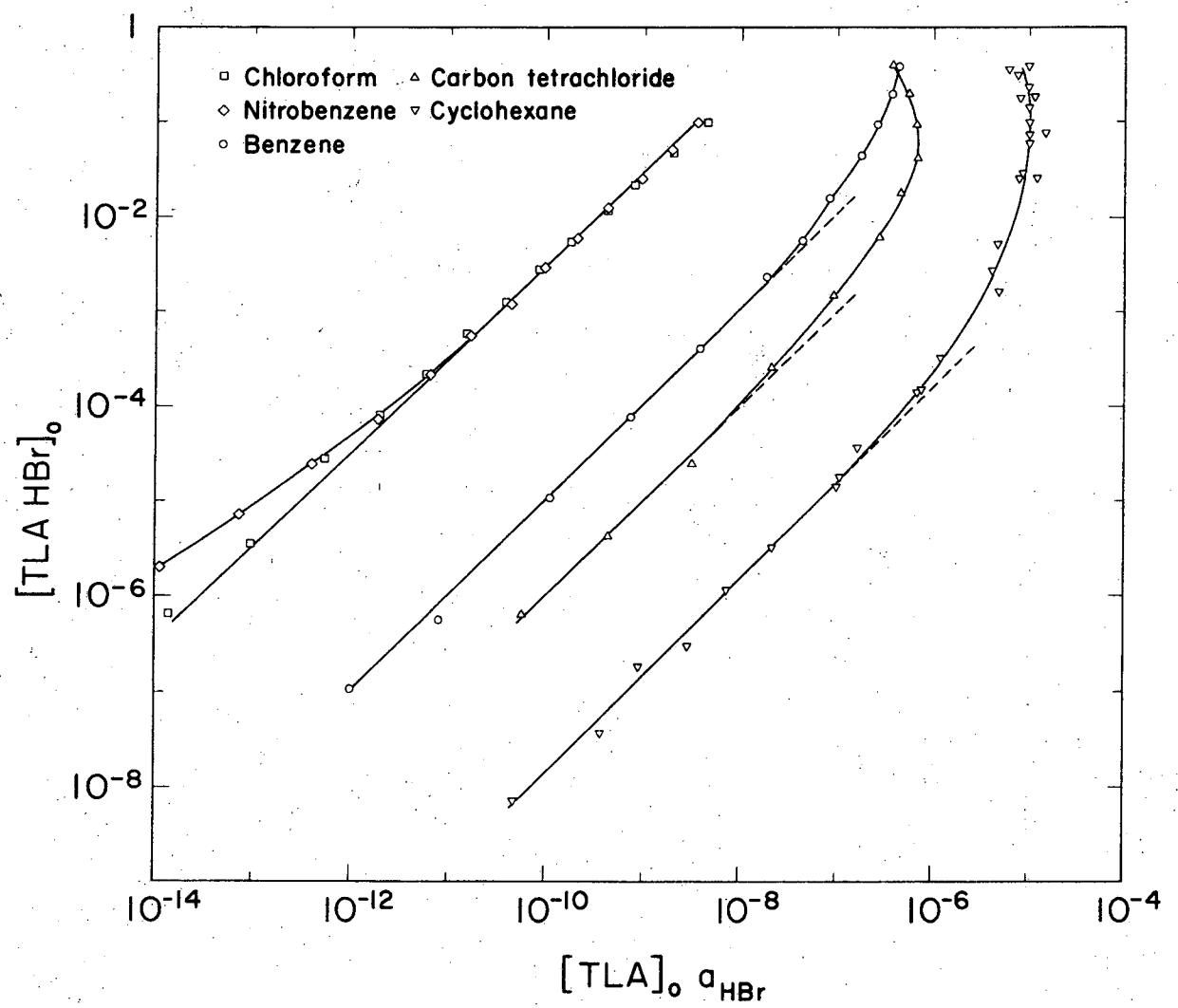
Fig. 7. Water content of water-saturated trilaurylammonium chloride solutions in various diluents. The values for toluene diluent are from Refs. 14, 16. The results are corrected for the solubility of water in the diluent itself.

Fig. 8. Water content of water-saturated ammonium salt solutions in cyclohexane, corrected for solubility of the water in the diluent itself.

Fig. 9. Vapor pressure measurements of amine and ammonium salt solutions in chloroform at 25°C. The ordinate is proportional to the vapor pressure differences between the water-saturated solution and the water-saturated diluent as determined with a vapor pressure osmometer.

Fig. 10. Vapor pressure measurements of amine and ammonium salt solutions in benzene at 25°C.

Fig. 11. Plot of the ammonium salt in excess of the (calculated) ion pair concentration $[TLAHX]_o - [TLAH^+..X]_o$, versus the ion pair concentration, $[TLAH^+ \cdot X^-]_o$, in benzene solution. The lines are drawn with a slope of 2.0.


Chloroform
Carbon tetrachloride
Nitrobenzene
Cyclohexane
Benzene
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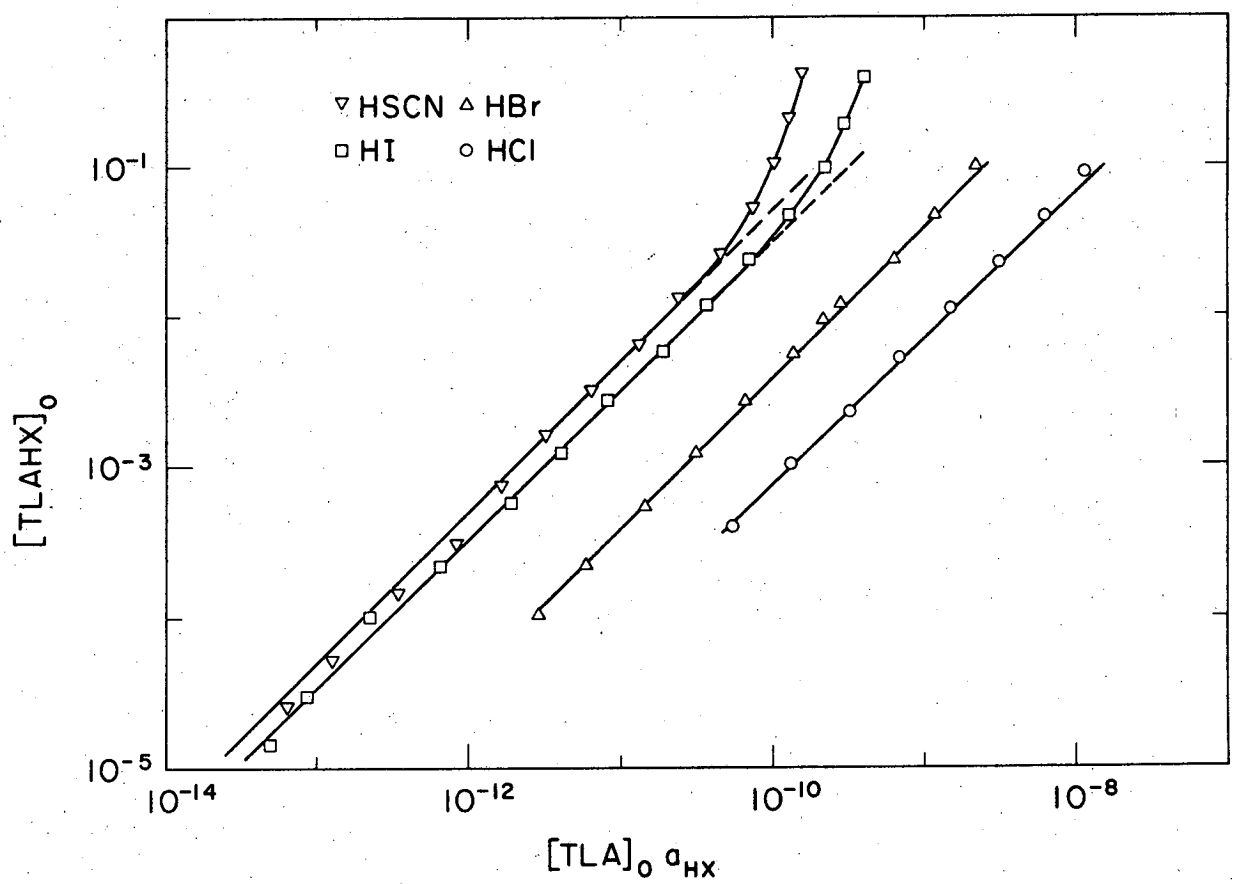
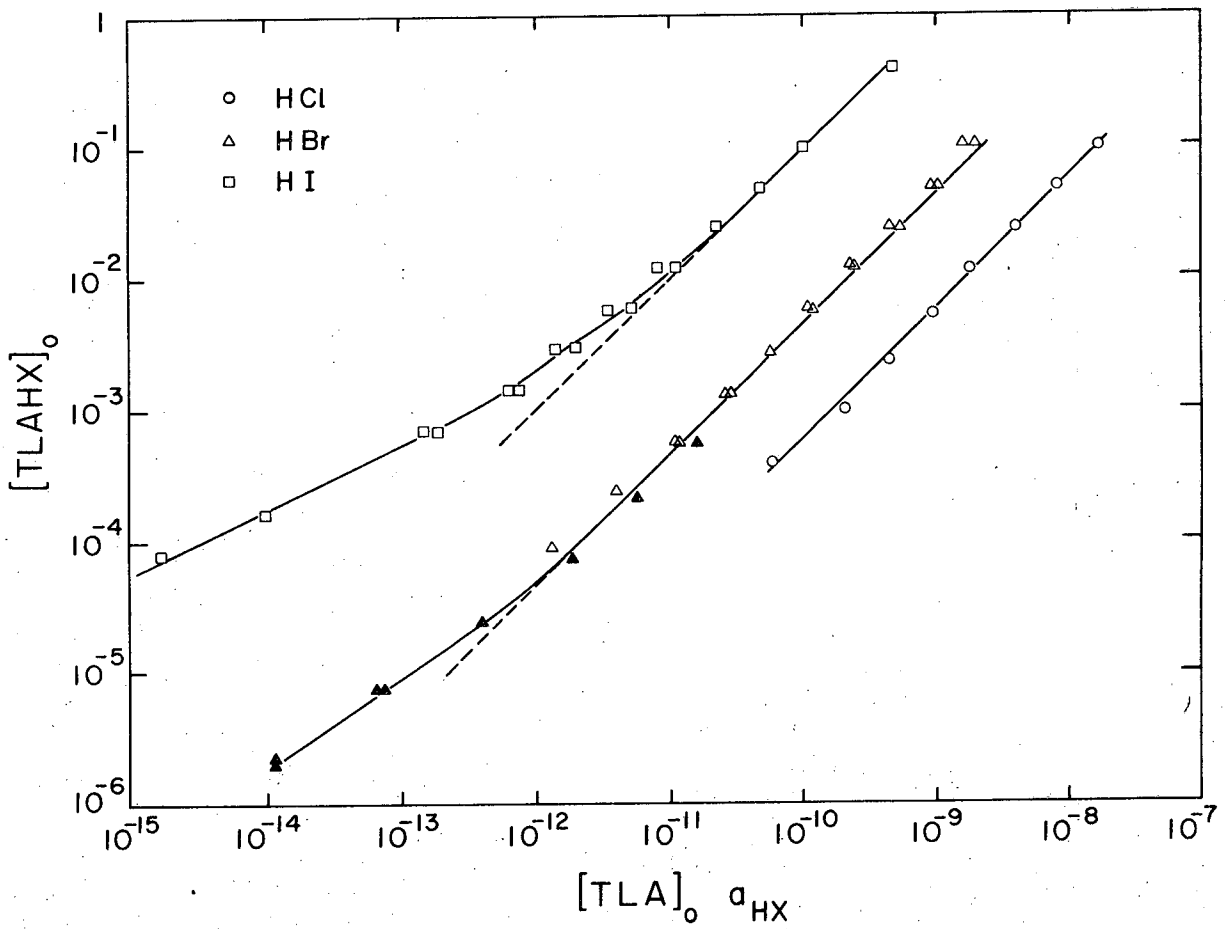
10^{-2}
10^{-4}
10^{-6}
10^{-8}
$[TLA\ HBr]_o$
10^{-14}
10^{-12}
10^{-10}
10^{-8}
10^{-6}
10^{-4}
$[TLA]_o\ a_{HBr}$
MUB-6917

Fig. 1



MUB-6918

Fig. 2



MUB-7129

Fig. 3

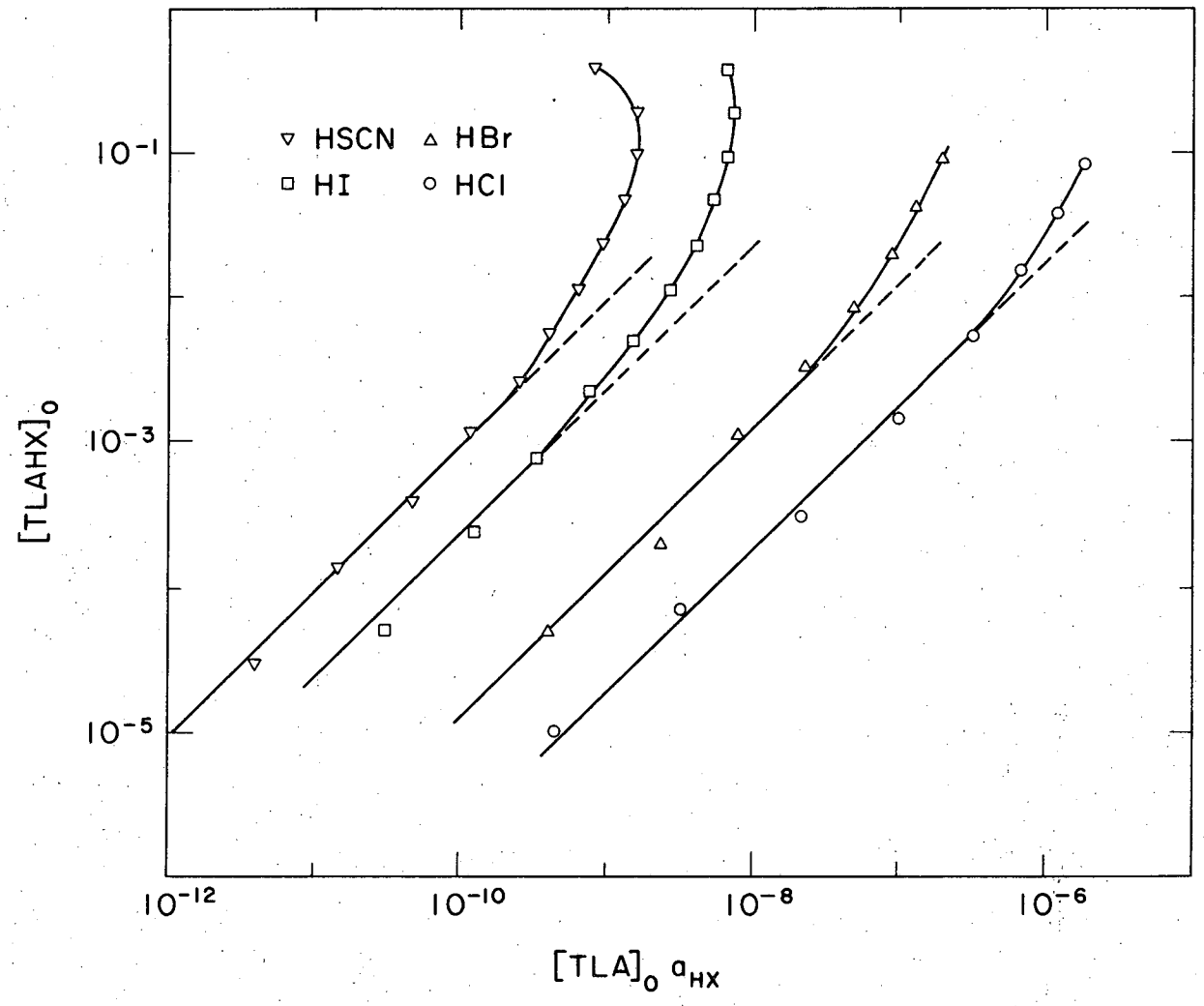


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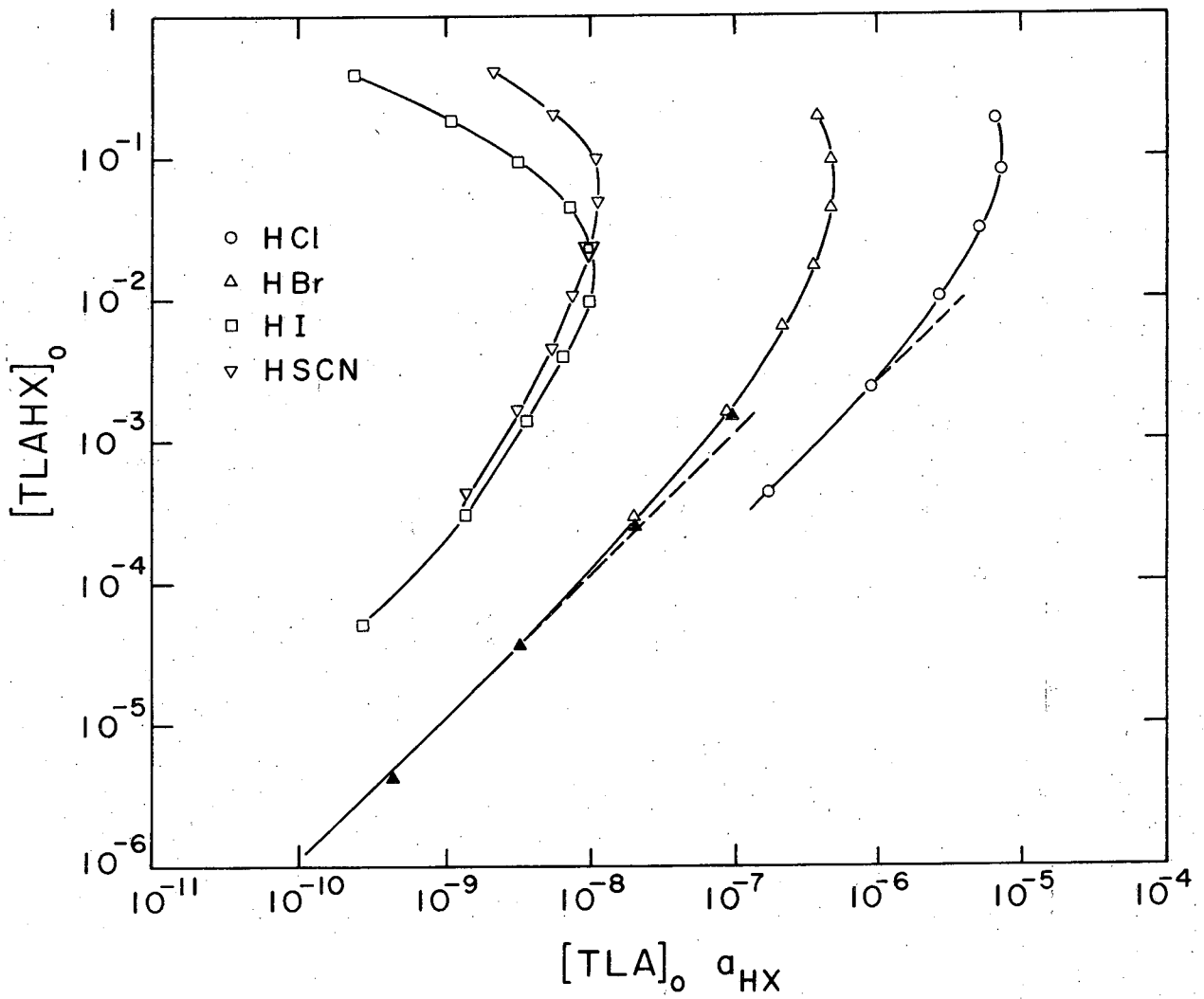
Fig. 4



MUB-7130

Fig. 5

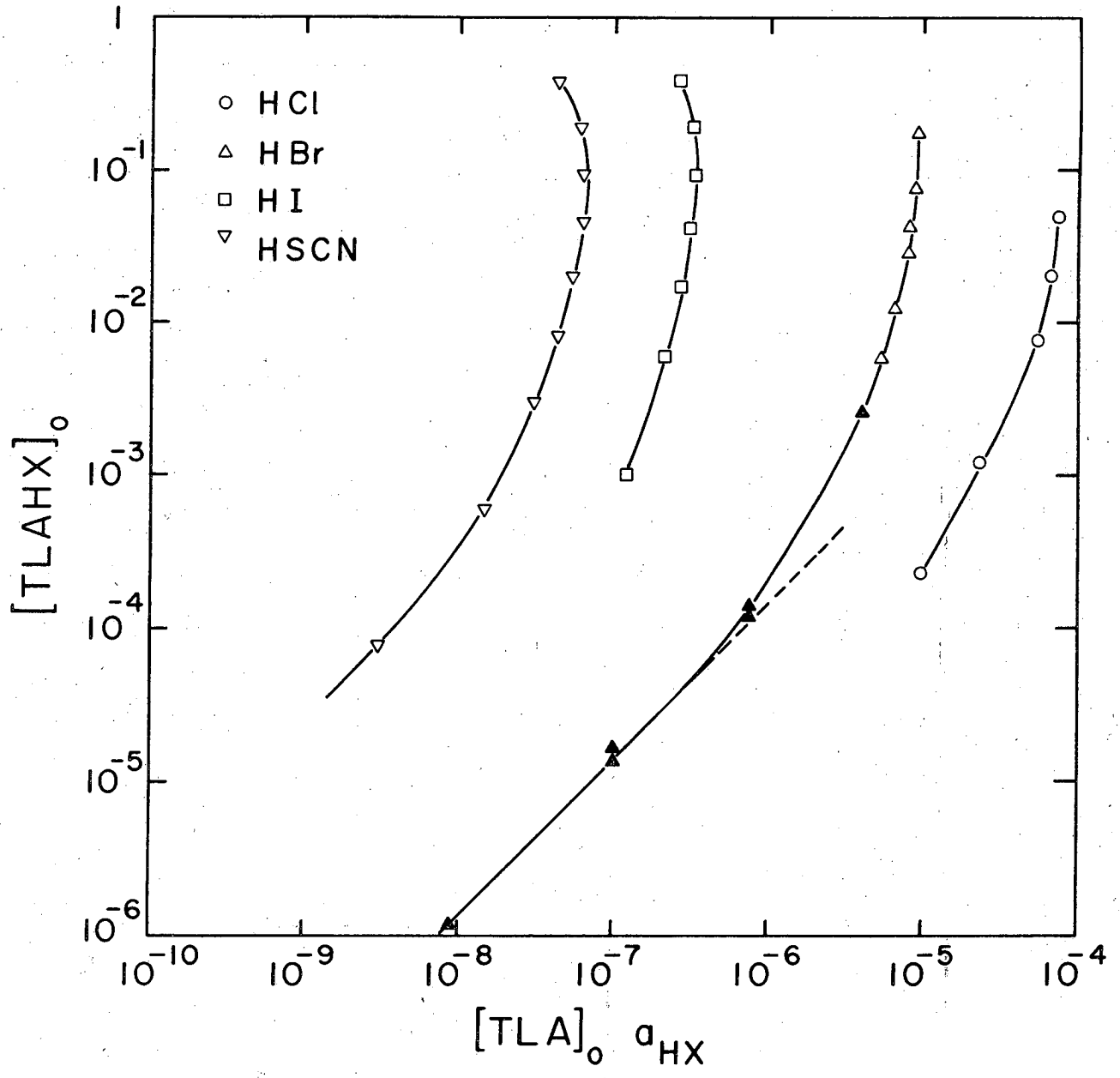


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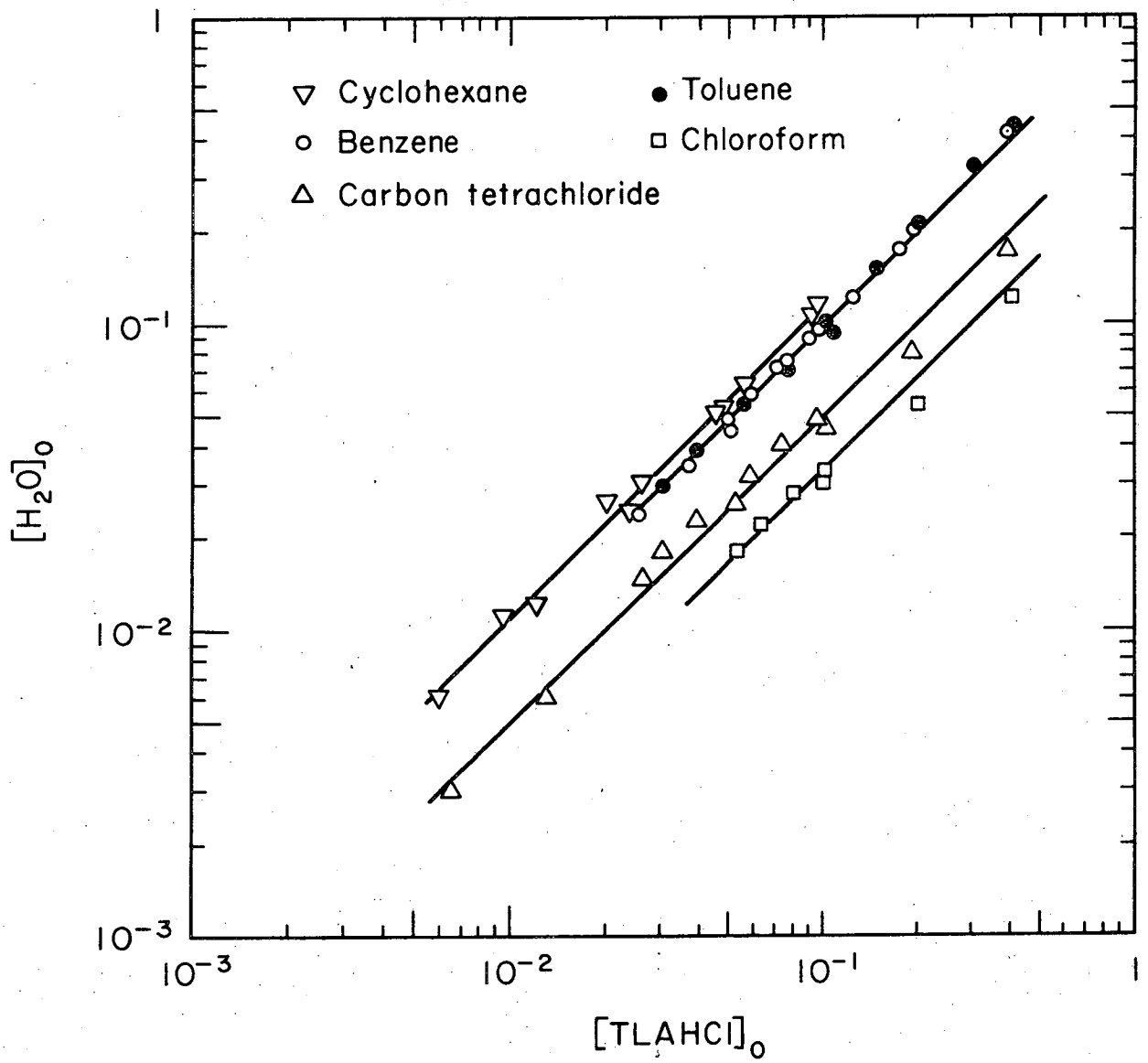
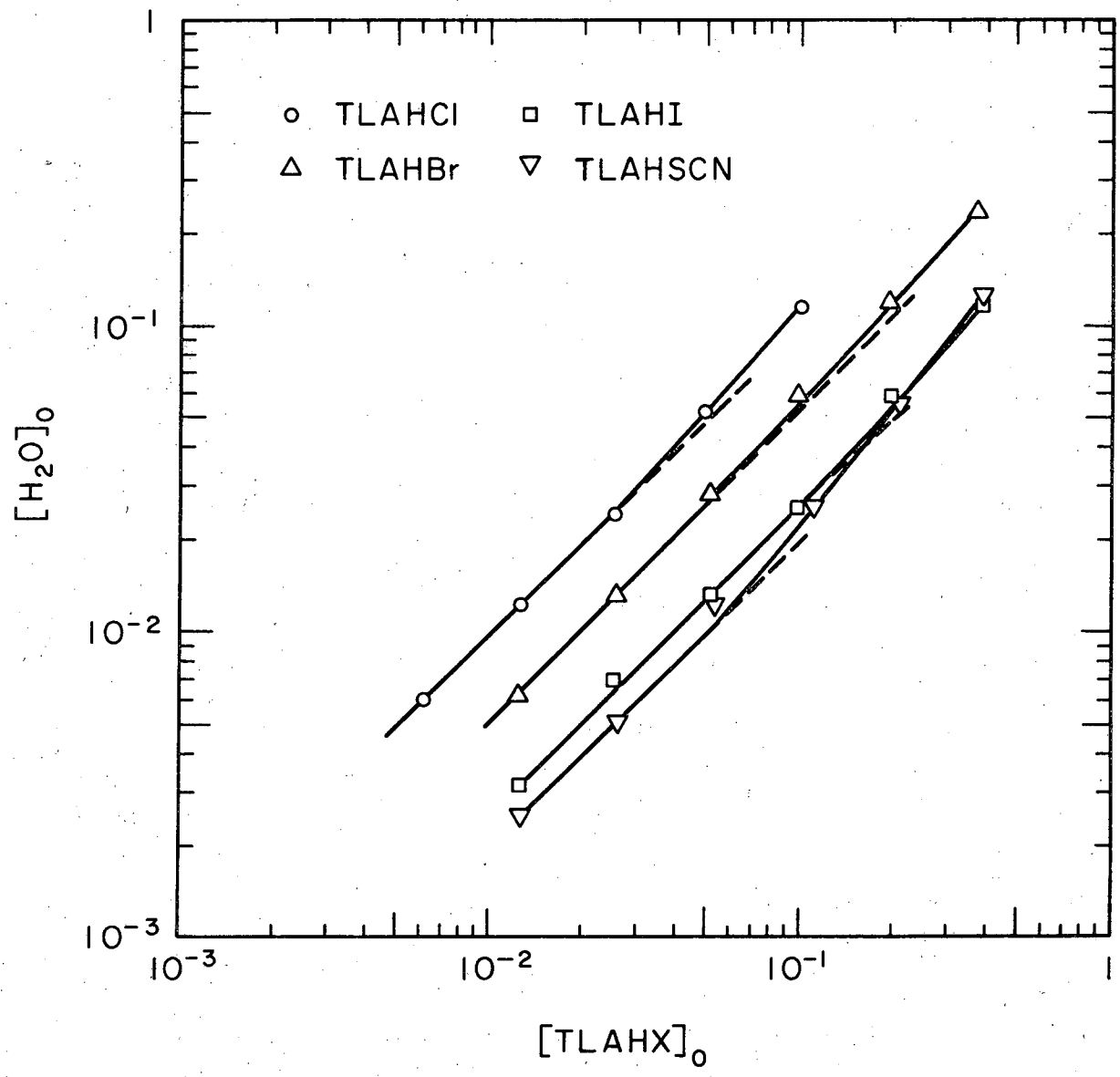
Fig. 6



MUB-6922

Fig. 7



MUB-6924

Fig. 8

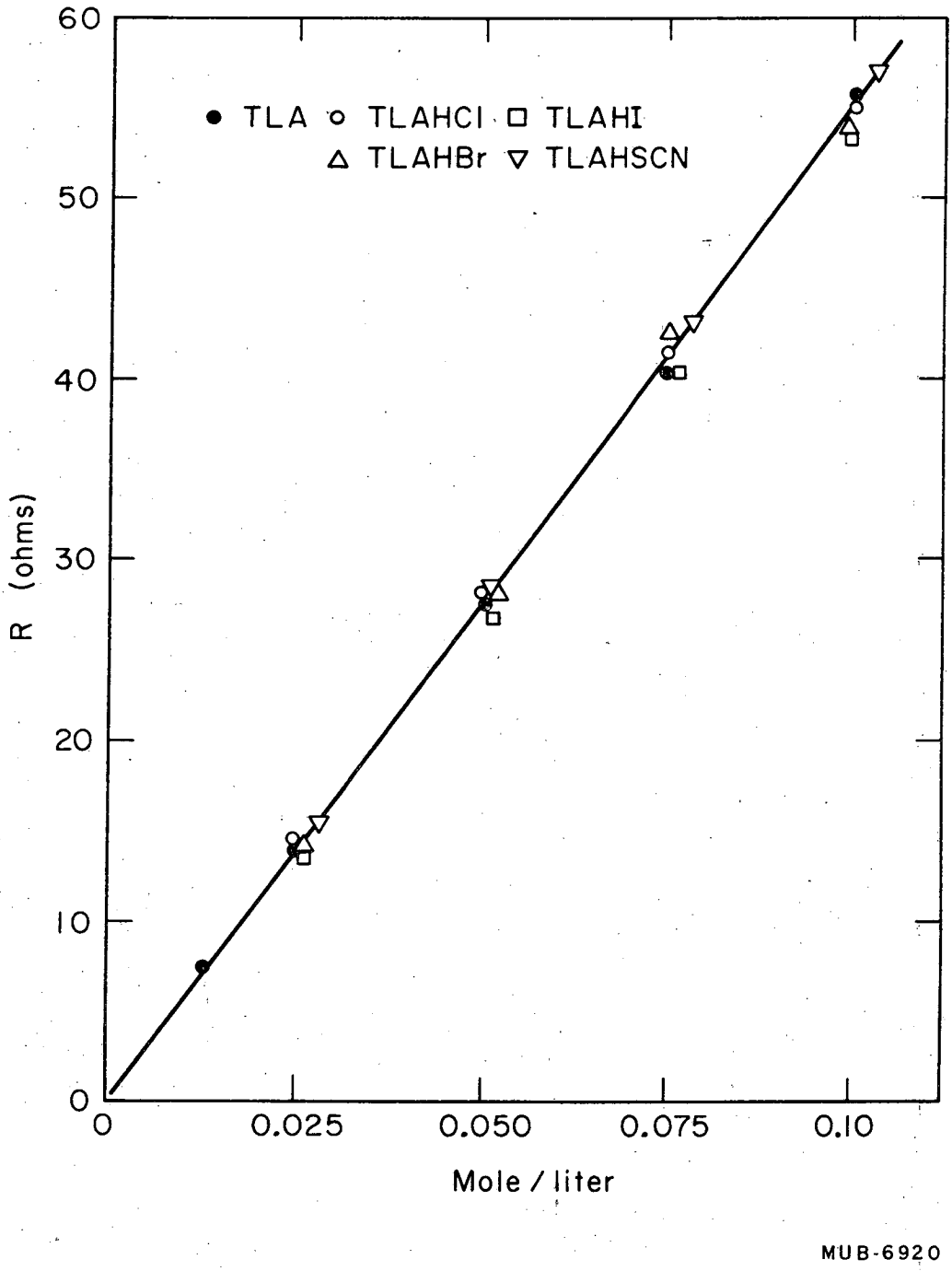
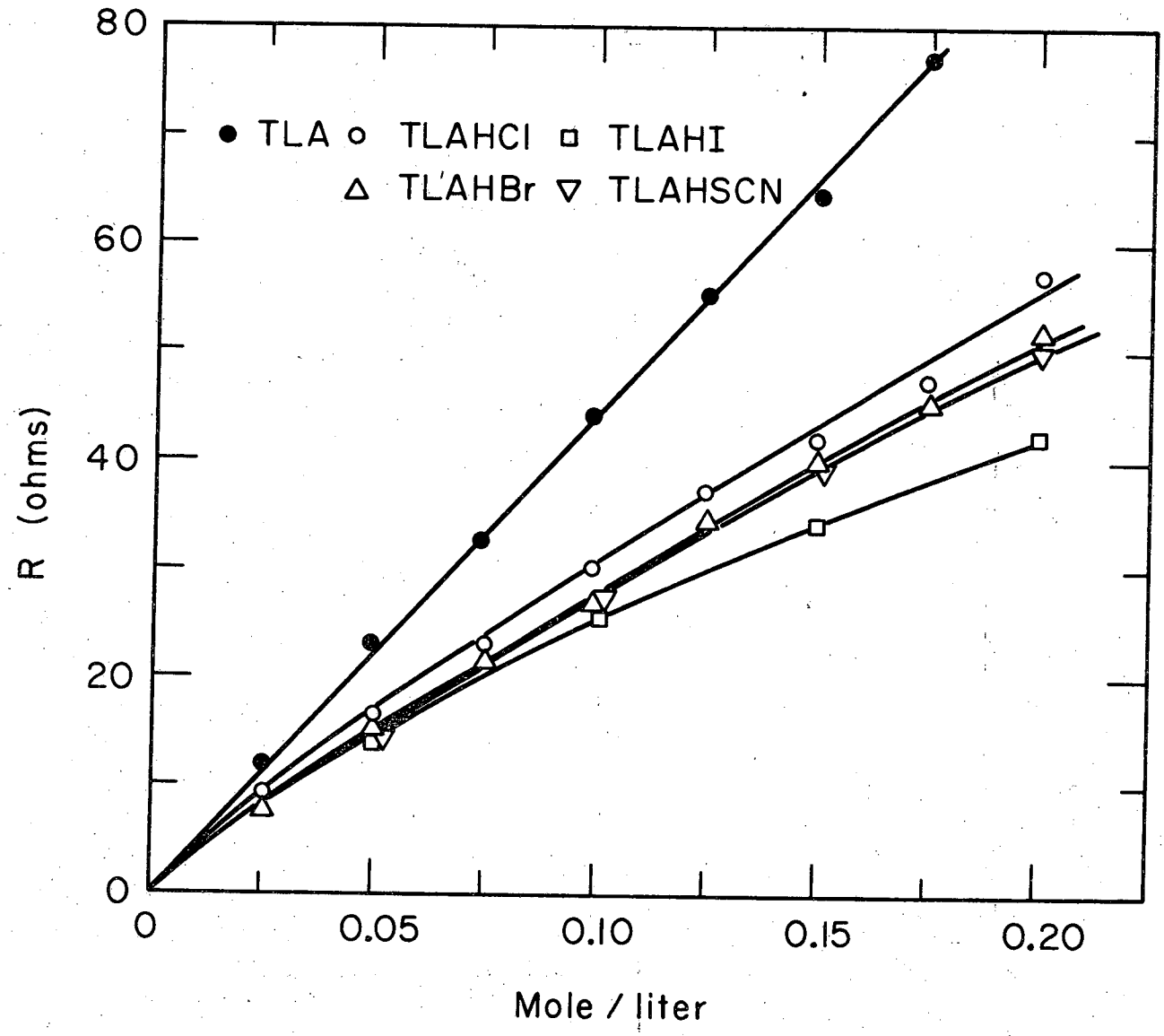
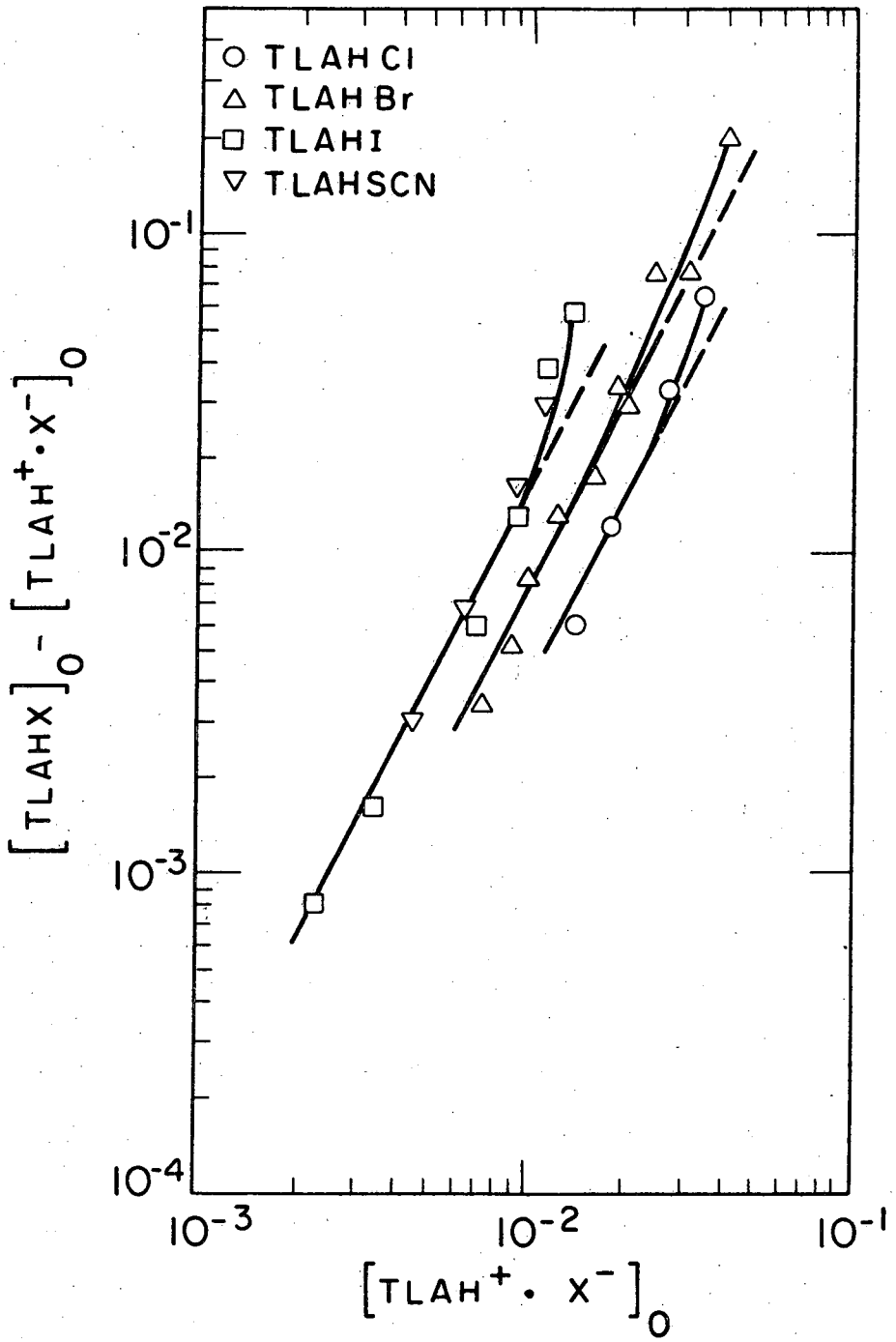

60
50
40
30
20
10
0
R (ohms)
● TLA ○ TLAHCl □ TLAHI
△ TLAHBr ▽ TLAHSCN
0
0.025
0.050
0.075
0.10
Mole / liter
MUB-6920

Fig. 9



MUB-6921

Fig. 10



MUB-9315

Fig. 11

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