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ABSTRACT

The use of slope analysis for interpreting extraction data is usually coupled with the assumption that the activity coefficients of the new chemical species that yield the changes in slope are ideal. This assumption is shown to be wrong in several extraction systems that are described. In particular, the phenomenon of "backbending" in certain tertiary ammonium salt systems is completely inexplicable under such an assumption, and incorrect extractant coordination numbers are obtained for trioctylphosphine oxide-strong acid species in poor solvents. As a result of this assumption literature values for aggregation numbers determined for alkylammonium salts in poor solvents may be too large.

Introduction

Slope analysis is an often-used method for interpreting and analyzing data from extraction equilibria in order to obtain information on the nature of the extracting species.[1] Central to the application of this method is the assumption that any deviation from the law of mass action is due to the formation of a new chemical species, e.g., a higher complex of the extraction reagent, if the latter's concentration is being increased, or a higher ion association or aggregate, if the concentration of an extracted ionic species is being increased, But as has been pointed out,[2-7] it is unreasonable to ignore all non-specific non-idealities of the extracted species and blame all deviations on new chemical species. For example, with amine salt systems, the strong electrical interactions between ions in low dielectric-constant media that cause association to ion pairs and ion quadrupoles, etc., surely lead to non-constant activity coefficients for these same ion aggregates. The importance of the analog of the solubility parameter term of regular solution theory has been described in the literature for these same systems,[3] and use of such an activity-coefficient correction was shown to lead to more "chemically sensible" results than unrestricted computer fitting to a large number of oligomers.[8-11]

Some years ago one of the present authors[4] described extraction behavior of a half-dozen amine-salt systems that was clearly incompatible with the usual slope analysis procedure of ignoring the activity coefficients of the amine-salt aggregates and blaming all deviations from ideal (ion-pair) behavior on higher ion aggregation. In these examples the log-log plots of $[\mathrm{TLA \cdot HX}]_o$ vs. $[\mathrm{TLA}]_o(\mathrm{H^+X^-})$ not only deviated upwards away from the ion-pair slope of unity observed at low concentration, but went beyond the limiting asymptote of mass-action law theory for aggregation into a colloid, namely a vertical line. They actually bent backwards so that $[\mathrm{TLA \cdot HX}]_o$ became a double-valued function of the product $[\mathrm{TLA}]_o(\mathrm{H^+X^-})$, Figure 1 . Since this indicated a complete breakdown of the assumptions usually used for slope analysis, and because it posed an interesting problem to explain in its own right, we have examined the origin and generality of such behavior further in this work. We have also considered another type of organic-phase activity coefficient variation arising in certain trioctylphosphine oxide-strong acid extraction systems.

Experimental

Reagents:

The trilaurylamine (TLA), Rhône-Poulenc, qualité nucléaire-99% pure tertiary amine, was used as received. A comparison using this material and TLA that was further purified (by repeated recrystallization of the TLA·HCL salt from petroleum ether, b.p. 30-65°C) indicated no significant difference in the equilibrium data. Trioctylphosphine oxide (TOPO) was obtained from the Carlisle Chemical Corp., Reading, Ohio. The technical grade TOPO was washed with mild base and distilled water and recrystalized five times from pentane. The $\mathrm{HClO_4}$ solutions were prepared by diluting a stock solution of reagent grade acid (G. F. Smith) with distilled water. Standardization of the stock $HClO_4$ solution was by titration with sodium hydroxide, using bromothymol blue as an endpoint indicator. Reagent grade 57% hydroiodic acid (Merck)(without the usual 1.5% H_3PO_2 as a preservative) was further purified by saturation with H_2S gas and subsequent distillation. The stock solution of HI was stored in amber-glass bottles. Iodide tracer, $Na^{131}I$ in 0.1 M NaOH solution, was obtained from New England Nuclear Corp. and used as received. $HReO_4$ solutions were made by dilution from a stock prepared by dissolving Re_2O_7 (Varlacoid Corp. 99.5% purity) in distilled water. The isooctane and cyclohexane were "spectro grade" reagents from Matheson, Coleman and Bell. CCl_4 and 1-bromooctane were obtained from J. T. Baker. The 1-bromooctane was purified to a colorless reagent by distillation.

Solutions of the particular ammonium salt were prepared by taking ~0.5 M TLA in a diluent and shaking it fairly vigorouly with ~0.6 M HX for several hours. After separation with the aid of centrifugation, the organic layer was washed with ~0.01 M HX to remove, or to prevent any possibility of having, excess acid in the amine salt (i.e., ratio of TLA/HX <1.0). For CCl_4 solutions two methods of preparation were attempted: the one outlined above and another in which a solution of TLA·HCl in CCl_4 was repeatedly washed with an aqueous solution of 0.01 M $HClO_4$ (to prevent premature hydrolysis) and ~2 M $NaClO_4$. Complete conversion to the amine perchlorate salt was judged by testing for the lack of a visual precipitate with $AgNO_3$. It is known that aliphatic amines may react with CCl_4 or nearly any halocarbon,[12] but in this instance the amine salt from either procedure gave the same extraction results.

The amine·HI salt was made as described above. But because of the sensitivity of acidic iodide to air oxidation, both the organic and aqueous solutions were carefully purged with argon. This removal of oxygen gave amine·HI solutions that were stable for >1 week (no visual formation of brownish I_3^-, etc. observed) instead of <1 hour with exposure to air. Details for the preparation of the TOPO solutions can be found elsewhere.[13]

Procedures:

The amine extraction systems were studied by a back-extraction or hydrolysis technique. Starting from standarized ~0.5 M trilauryl ammonium salt solutions in the organic solvent, a series of solutions were prepared by dilution. These salt solutions (5 or 10 ml) were then shaken for >18 hrs. with 50 ml of distilled water for the TLA·$HClO_4$ systems and with an equal aqueous volume (10 ml) for the TLA·HI systems. Before equilibration of the TLA·HI systems, radio-iodide (<10^{-5}M) was added to the aqueous phase. After equilibration, phase separation was accelerated by centrifugation. (If the shaking during the equilibration process is done too vigorously, at least for the most concentrated salt solutions, a cloudy aqueous layer is obtained. This phase is then quite resistant to clearing even with prolonged centrifugation.) For the counting of the tracer iodide in a Na(Tl)I well-type crystal, 3 ml samples of each phase were taken, or smaller samples of a particular phase adjusted to 3 ml if the count rate was too high. Conventional acid-base titrations were made to analyze the aqueous equilibrium acid content. Except for the lowest initial amine-salt concentrations, the aqueous acid concentration is by far the most sensitive parameter to be determined. This is due to the relatively small amount of amine salt that is hydrolyzed over most of the concentration range considered. Subtraction of this quantity from the well established initial amine salt concentration is, in most instances, a minor perturbation upon the latter. That is, the equilibrium organic-phase salt concentration is little different from the initial value.

Procedures that were used to obtain the distribution data for the $TOPO \cdot HReO_4$ system are similar to those already outlined elsewhere.[13] Distribution measurements for all systems were at room temperature, $24 \pm 2^{\circ}C$.

Results and Discussion

The extraction of a strong acid, H^+X^-, by a solution of trilaurylamine, TLA, in a low dielectric-constant medium that induces association of the resulting salt to an ion pair or higher aggregate can be described by the reaction,

$$nTLA(org) + nH^+ + nX^- \rightleftarrows nTLA \cdot nHX(org) \qquad (1)$$

with an equilibrium constant,

$$K = \frac{[nTLA \cdot nHX]_o \; y_{nTLA \cdot nHX}}{(H^+X^-)^n \; [TLA]_o^n \; y_{TLA}^n} \; . \qquad (2)$$

Brackets indicate concentrations, parentheses are activities, and y is a molar activity coefficient. Taking logarithms, eq. 2 can be written,

$$\log[\mathrm{nTLA \cdot nHX}]_o = \log K + n \log[\mathrm{TLA}]_o(H^+X^-) + \log \frac{y^n_{\mathrm{TLA}}}{y_{\mathrm{nTLA \cdot nHX}}} . \qquad (3)$$

Thus, a log-log plot of the stoichometric concentration of the organic-phase amine salt $[\mathrm{TLA \cdot HX}]_o$, vs. the product $[\mathrm{TLA}]_o(H^+X^-)$ should yield a curve whose tangent is the value of n at that point, if the activity-coefficient ratio is a constant. This condition is usually assumed in slope analysis work.

The results of the present study of the extraction by TLA of $HClO_4$ into 1-bromooctane and into CCl_4 and of $HClO_4$ and HI into cyclohexane are shown as log-log plots of $[\mathrm{TLA \cdot HX}]_o$ vs. $[\mathrm{TLA}]_o(\mathrm{HX})$ in Figure 1, curves 1 to 4, respectively. Where determined to low amine-salt concentrations, as for curve 1 (and other examples not shown), the log-log plots are straight lines with unit slope, indicating predominantly ion pairs for the salt in this region and the validity of the assumption that the organic-phase activity-coefficient ratio is constant. This constancy is due to the very low concentrations of the salt and of the amine in the organic diluent, so that the nature of the organic phase is essentially unchanged.

But at higher concentrations, the curves deviate upward from a line of unit slope. This is the region that has been of most interest in the literature,[14] and this behavior has almost always been ascribed to a further association of the ion pairs to higher ion aggregates in the low dielectric-constant medium.[15] As just described, the average value of this aggregation, $\bar{n}$, at any point can be determined by the tangent of the curve, or the whole curve can be fitted to a small number of oligomers, by hand or by computer, to yield the changing nature of the amine-salt species, if the activity-coefficient ratio of the various oligomers are assumed constant. As the concentration is increased, the slopes become steeper, indicating the predominance of still higher and higher species. The limiting slope for such a system of ideal amine-salt aggregates is a vertical asymptote, corresponding to infinite aggregation, the formation of a colloid. But as can be seen in Figure 1, and less conclusively in the earlier work,[4] with "poor" diluents the curves for these TLA salts actually "backbend" for concentrations above ~ 0.1 M, yielding negative values for the slope.

This behavior is completely unexplainable in the context of an aggregation model with ideal activity coefficients for the salt associations. It does not appear to be a non-equilibrium effect. In the TLA-$HReO_4$ system in CCl_4 (not shown), for instance, the same results are obtained either by starting with $HReO_4$ tracer in the aqueous phase or by titrating the macro-concentrations of $HReO_4$ in the aqueous phase which is hydrolyzed from the salt. The simplest, and we believe the correct, explanation is still that given earlier,[4,5] namely, that at these large concentrations of amine salt we are dealing with a new diluent. Instead of the original solvent phase, we now have a more polar phase consisting of the amine salt (25-30% by volume at 0.4 M TLA·$HClO_4$) in the solvent. This new organic phase has properties more favorable for extraction of the salt; for example, it has a higher dielectric constant, due to the presence of the ion aggregates themselves. In an earlier paper the origin of the backbend was similarly stated as being due to a change in the nature of the diluent leading to enhanced extraction; the increase in dielectric constant was measured[4] but explicitly stated as being only one example of the type of change occurring, rather than the sole cause of the increased extraction as quoted in the English translation of ref. 6. As a result, the value of the organic-phase-coefficient $y_{nTLA \cdot nHX}$ decreases with the increase in amine-salt concentration. But there are thermodynamic limits to the rate of decrease of $y_{nTLA \cdot nHX}$ refs. 16-17. Considering a three-component system of diluent, amine salt, and amine, the condition $\partial \mu_{(nTLA \cdot nHX)} / \partial n_{(nTLA \cdot nHX)} > 0$ must be satisfied. This limitation on the decrease of $y_{nTLA \cdot nHX}$ led the authors of ref. 6 to state that to explain the backbending behavior one must take into account the activity of other components of the system, and, in particular, the water in the organic phase.[18]

Indeed, no amount of tinkering with the amine-salt activity coefficient alone can yield the results of Figure 1, and we, too, believe that one must take into account another component. But we think it is the amine that is important, and not the water. For just as the introduction of macro amounts of the amine salt ($\geqslant 0.1$ M) changes the nature of the solvent from the original diluent to a mixed one whose properties (more polar nature, higher dielectric constant[19], etc.) should lower the activity coefficient of the amine salt,[21,20] these changes in the diluent make it less suitable for the non-polar and relatively inert trilaurylamine itself. That is, the activity coefficient of the TLA should increase with increasing salt concentration in the mixed diluent, and both activity-coefficient changes should cause a very marked lowering in the ratio $y_{nTLA \cdot nHX}/y^n_{TLA}$. In fact by inspecting eq 2 or 3, it can be seen that for backbending to occur, the value of y_{TLA} must increase sufficiently to overcome the decrease in the product $[TLA]_o(H^+X^-)$ with increasing amine-salt concentration. Even though the concentration of amine in the organic phase is small (10^{-2} -10^{-3} M) so that one might think its activity coefficient would not vary much, the change in the nature of the diluent from a pure hydrocarbon or halogenated hydrocarbon to an amine-salt solution can cause large changes in the amine activity. Some support for the suggested amine activity-coefficient behavior appears in the solubility pattern of tertiary amines[22]. In general they are completely miscible with non-polar diluents, but only sparingly soluble in alcohols and other polar solvents. Since the concentrated amine-salt solutions are certainly more polar than the initial diluent,[4,19,23] an increase in the amine coefficient is thus suggested.

While it is not possible to determine the changes in the individual organic-phase activity coefficients in the backbending region (only the change in the ratio of the coefficients is measured), limits can be set on the change in y_{TLA} using eq. 1 and the experimental data shown in Figure 1. For even if $y_{nTLA \cdot nHX}$ falls as steeply as permitted by thermodynamics without third-phase formation, the value of y_{TLA} must increase with increasing amine-salt concentration at least enough to account for the decrease in $[TLA]_o(H^+X^-)$ from its maximum value. For a change in the amine-salt concentration from 0.1 to 0.5 M, the four curves in Figure 1 suggest a minimum increase in y_{TLA} of 1.3-4.5, a reasonable set of lower limits.

We have described how it is impossible to explain the backbending behavior of a number of concentrated amine-salt systems using the usual slope analysis method which attributes all deviations from simple ion-pair behavior to the formation of higher ion associations, all of which behave ideally (have activity coefficients = 1). Instead we suggest that the increasing proportion of amine salt in the organic phase changes the nature of that phase so much that the activity coefficients of various ion aggregates of the amine salt decrease and that of the amine increases. To a smaller degree this behavior is also true below the concentration of amine salt at which backbending commences, so that all of the deviation from a straight line of unit slope (pure ion-pair behavior) in that region may not be due to the formation of higher ion associations. Some of the increased extraction is because of the change in the solvent, and so the true degree of aggregation is smaller than that determined by the usual slope analysis methods, whether graphical or by computer. This feature probably explains the rather unusual series of oligomers usually determined by slope analysis of amine-salt systems in "poor" diluents, in which the ion pair is followed by a dimer and then a much higher oligomer, or where even the dimer is skipped and the next smallest ion association is a trimer.[8-11] The irregularities are probably false; the true aggregation is less than the apparent value, and the appearance of high oligomers or of a trimer without passing through a dimer species is likely due to the neglect of the non-idealities of the ion dipoles and quadrupoles, in particular of their (attractive) electrostatic interactions with each other in the increasingly concentrated organic phase. If the ideas presented are correct, the irregularities in the series and the degree of aggregation would become more marked, the more inert and less polar the initial diluent and the higher the charge on the anion, for then the changes in the activity coefficients of the salt species and of the amine would be the larger.

Actually one of the early examples in the literature where simple alope analysis of an amine-salt system led to completely unexplainable results was the extraction of H_2SO_4 by trioctylamine in benzene.[24] Although the extraction of the normal sulfate salt appeared well behaved at low salt concentrations and followed the mass-action expression for an ion triplet, $(TOAH^+)_2SO_4^=$, the extraction increasingly deviated upwards from an ideal slope above a salt concentration of ~ 0.025 M. The explanation given at that time was that the salt was aggregating to a colloid.[24] But later light-scattering studies by the same author[25] showed that the sulfate salt remained essentially monomeric, leaving the extraction behavior unexplained. We would like to suggest that the enhanced extraction of the amine sulfate in concentrated benzene solution is due, not to ion association, but to a more non-specific interaction of the salt with itself through changing the nature of the medium from the original benzene to a mixture of salt in benzene (a more polar, better-extracting solvent).

Other than by light-scattering studies, it is not easy to unambiguously determine the state of aggregation of an amine salt in the range of concentrations being considered. The (non-specific) interaction of the amine-salt species with themselves brings into question the accuracy of the determination of aggregation numbers of amine-salt solutions by osmometric methods, as again ideal activity coefficients are usually assumed for the associated species. In this case the effect of the change in the amine activity coefficient is not important, but the changes in the salt species' activity coefficients still play a role and would again make the true aggregation smaller than that derived assuming all deviation from ideality comes from association alone. Marcus has discussed a rough quantitative way to take part of the non-idealities into account,[3] and has shown that his treatment does lead to simpler, more chemically reasonable aggregation behavior. The effect is noticeable in the examples he uses of aromatic solvent solutions of trilaurylammonium salts from 0.010 → 0.10 M in concentration, but the differences with simple association calculations would become much larger with less polar diluents and more concentrated salt solutions.

A variation of this process where the presence of an amine salt decreases its own activity coefficient is the solubilization of an amine salt, which is difficult to dissolve even in a relatively polar solvent, by the addition of a more soluble amine salt. For example, the salt $(R_3NH^+)_2(CoCl_4^=)$ in p-xylene is solubilized by appreciable concentrations of the extractant salt, $R_3NH^+Cl^-$,[26] and there are other examples in the literature.[27] In fact, the activity coefficient of $(R_3N^+)(FeCl_4^-)$ has been shown to decrease with an increase in $R_3NH^+Cl^-$ concentration,[28] exactly as expected from the present discussion.

Are there other types of extraction systems that do not allow for simple slope analysis, and, if so treated, lead to wrong conclusions? The answer appears to be yes. Consider the extraction of $HReO_4$ by trioctylphosphine oxide (TOPO) solutions in isooctane. The extraction to an ion-paired product can be expressed:

$$H^+ + ReO_4^- + n\text{TOPO(org)} \rightleftarrows H^+\cdot n\text{TOPO}\cdots ReO_4^-\text{(org)} \qquad (4)$$

with the corresponding equilibrium constant

$$K_n^a = \frac{[H^+\cdot nTOPO\cdots ReO_4^-]_o \; y_{nTOPO\cdot HReO_4}}{(H^+ReO_4^-)[TOPO]^n \; y_{TOPO}^n} \quad . \qquad (5)$$

Thus a log-log plot of the organic-phase $HReO_4$ concentration vs. the aqueous-phase acid activity for a constant TOPO concentration should yield a straight line of unit slope if the organic-phase species is an ion pair and the ratio of activity coefficients is constant. This result is indeed obtained for fixed TOPO concentrations from 0.0020 to 0.10 M and for aqueous $HReO_4$ activities ranging from 10^{-8} to 10^{-1} M (except at the highest $HReO_4$ activities and lowest TOPO concentrations). Then to determine the value of n, the number of TOPO molecules coordinated to the extracted acid, one can study the dependence of the extracted acid on the TOPO concentration. To exclude the possibility of aggregation beyond the ion pair, tracer concentrations of $HReO_4$ can be used. Figure 2 shows the distribution of 1×10^{-6} M $HReO_4$ in 1.0 M HCl with TOPO in isooctane. The initial slope drawn is two (n = 2), but the raw data show deviations from this line even at TOPO concentrations as low as 2-3 × 10^{-3} M. The organic-phase $HReO_4$ concentration at these TOPO concentrations is ~10^{-8} M, so no aggregation beyond the ion pair is expected. Extension of the line of slope two is shown by a dashed line, and the subtraction of this line from the raw data is indicated by the dashed line connecting the filled triangles. This resultant line has a slope three. By all the normal rules of slope analysis this indicates that at the initial low TOPO concentrations there are two TOPO molecules coordinated per extracted acid, but that over most of the TOPO concentration range studied the slope of three indicates a three-to-one complex.

Figure 3 shows the extraction of 0.10 M and 0.010 M $HReO_4$ (macro amounts of perrhenic acid) as a function of TOPO concentration. Curve 2, for 0.010 M $HReO_4$, is almost a duplicate of the tracer distribution study in Figure 2. A dashed line of slope two is drawn in to match the apparent concentration quotient, K_2^a, obtained from line 1. The open triangles are the result of subtracting the slope-two line from the raw data, and they give a line with a slope of three. The upper end of these data must be corrected for TOPO complexed by acid. Square symbols indicate correction assuming a 2TOPO complex, but there is little difference between a choice of 2TOPO or 3TOPO for curve 2. However, in the set of data illustrated in curve 1, for 0.10 M aqueous $HReO_4$, the choice of 2 or 3 TOPO molecules in the complex leads to much more divergent results after subtraction of the slope-two line. If one assumes a $2TOPO \cdot HReO_4$ complex, the points indicated by squares are obtained, and fall surprisingly upon a line of slope three. If one assumes a 3TOPO per acid correction (the inverted triangles), a line with a slope considerably steeper than three is obtained. The result for a 3 to 1 complex would be possible if aggregation were occurring, but a similar degree of aggregation ought to have been observed in the set of data for 0.010M $HReO_4$ curve 2, where a similar range of $[HReO_4]_o$ concentrations were examined. It is not; nor is there any indication for a large degree of aggregation from the log-log plots of organic-phase $HReO_4$ vs. aqueous acid described earlier.

Thus there is a problem. Is the extracted species at the top of curve 1 a 2:1 or a 3:1 complex, and, whichever it is, why is it not well behaved? In an earlier publication we took this type of extraction results at higher TOPO concentration to indicate a 3:1 complex.[29] But infra-red spectroscopic results[30] over the whole TOPO range studied indicate that the species is a 2TOPO·$HReO_4$ complex like the one known in other diluents, and water analyses show that it is essentially anhydrous and so not based on a hydronium-cation[31] (which has three possible positive sites for a 3:1 complex), but on a bare proton, which is unlikely to permit coordination to more than two close TOPO molecules.[13,30]

So in this case, dependence on simple slope analysis leads to the wrong result (although there are warning inconsistencies); the TOPO·$HReO_4$ species in isooctane is only a 2TOPO·$HReO_4$ species with no evidence for the 3:1 complex suggested by the log-log plots in Figures 2 and 3. What can be the cause of this error in the simple mass-law analysis, especially since deviations from the line of slope two appear at extremely low values of the $HReO_4$ concentration in the organic phase (10^{-8} M in Figure 2 and $<10^{-6}$ M in Figure 3)? These concentrations are too low to suppose that the presence of the TOPO·$HReO_4$ species changes the nature of the solvent, so that, in contrast to the amine situation, we must look elsewhere for the origin of the deviations. It is certainly an organic-phase effect, as this behavior does not occur under the same aqueous conditions but with other "better" diluents.[13] We believe it is due to the presence of the polar TOPO molecules when dissolved in very inert ("poor") diluents. That is, the addition of the very polar TOPO molecules makes the inert dilutent isooctane into a new and more polar solvent, a mixture of isooctane and TOPO. This explains why the deviations occur similarly for both tracer and macro amounts of acid (Figures 2 and 3) but at the same TOPO concentration. It is surprising, however, at least to us, what a small amount of TOPO is necessary to cause deviations from the line of slope two. Figures 2 and 3 show significantly enhanced extraction at as low as $2\text{-}3\times10^{-3}$ M TOPO. At such a concentration there is only one TOPO for approximately 4000 isooctane molecules; to have any marked effect the TOPO must selectively solvate (be in the vicinity of) the even rarer $H^+(TOPO)_2ReO_4^-$ species. This process leads to a lowering of the activity coefficent of the extracted acid but not the formation of a higher TOPO complex or aggregation of the $H^+(TOPO)_2ReO_4^-$ species.

Summary

In this paper we have described several examples of systems that do not follow the behavior expected for extraction models based on the simple application of mass action to stepwise equilibria. In the usual application of slope analysis to extraction systems, all deviations from the behavior at low concentrations are considered to be due to the stepwise formation of higher complexes but with ideal activity coefficients for all of the species involved. Types of studies included are the formation of higher complexes with the extractant molecule, as the extractant concentration is increased, and stepwise aggregation of the extracted amine salt, as the salt concentration is increased. In the former case, neglect of possible organic-phase activity-coefficient variations in applying slope analysis leads to the suggestion of higher complexes than actually exist or make sense chemically. In the latter case, ignoring possible activity-coefficient variations in the analysis yields a greater degree of ion aggregation and higher types of ion aggregates than really

exist. This leads us to question the accuracy of the determinations of such ion aggregation properties in the literature from extraction studies or even osmometric methods, when all deviation from ideal behavior are blamed on aggregation alone, especially with "poor" solvents.[8-11] For tertiary amine salts in such solvents, there may appear the very interesting phenomenon of "backbending" in the log-log plot of extracted acid concentration vs. the product of aqueous acid activity and amine concentration. This result is completely inexplicable in the simple slope analysis formulation, and is excellent proof that the activity coefficients of both the amine salt and the amine are changing with amine-salt concentration. We believe that the origin of this change comes from the change in properties of the diluent as it goes from the initially pure solvent to a mixture of amine salt and solvent.

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Figure Captions

Figure 1. Total ammonium salt concentration $[TLA \cdot HX]_o$, versus $[TLA]_o(H^+X^-)$ for various diluents. Curve 1 is the $TLA \cdot HClO_4$, 1-bromooctane system; curve 2 is the $TLA \cdot HClO_4$, CCl_4 system; curve 3 is the $TLA \cdot HClO_4$, cyclohexane system; and curve 4 is the $TLA \cdot HI$, cyclohexane system. The dashed lines indicate unit slope. The square symbols, ■ , (curve 4) indicate acid-base titration data from ref 4.

Figure 2. Variation of distribution ratio, D, with TOPO in isooctane for 1×10^{-6} M $HReO_4$ in 1.0 M HCl. The dashed lines are drawn with either slope two or three (▲).

Figure 3. Variation of acid content of the organic-phase with TOPO in isooctane for aqueous $HReO_4$ concentrations of 0.10 M (line 1) and for 0.010 M (line 2). ●, uncorrected data; △ , resultant of subtracting slope two component from raw data; □ , data corrected assuming 2:1 $TOPO:H^+$ complex; ▽ , data corrected for used-up TOPO assuming a 3:1 $TOPO:H^+$ complex. Dashed lines are drawn with either slope two or three.

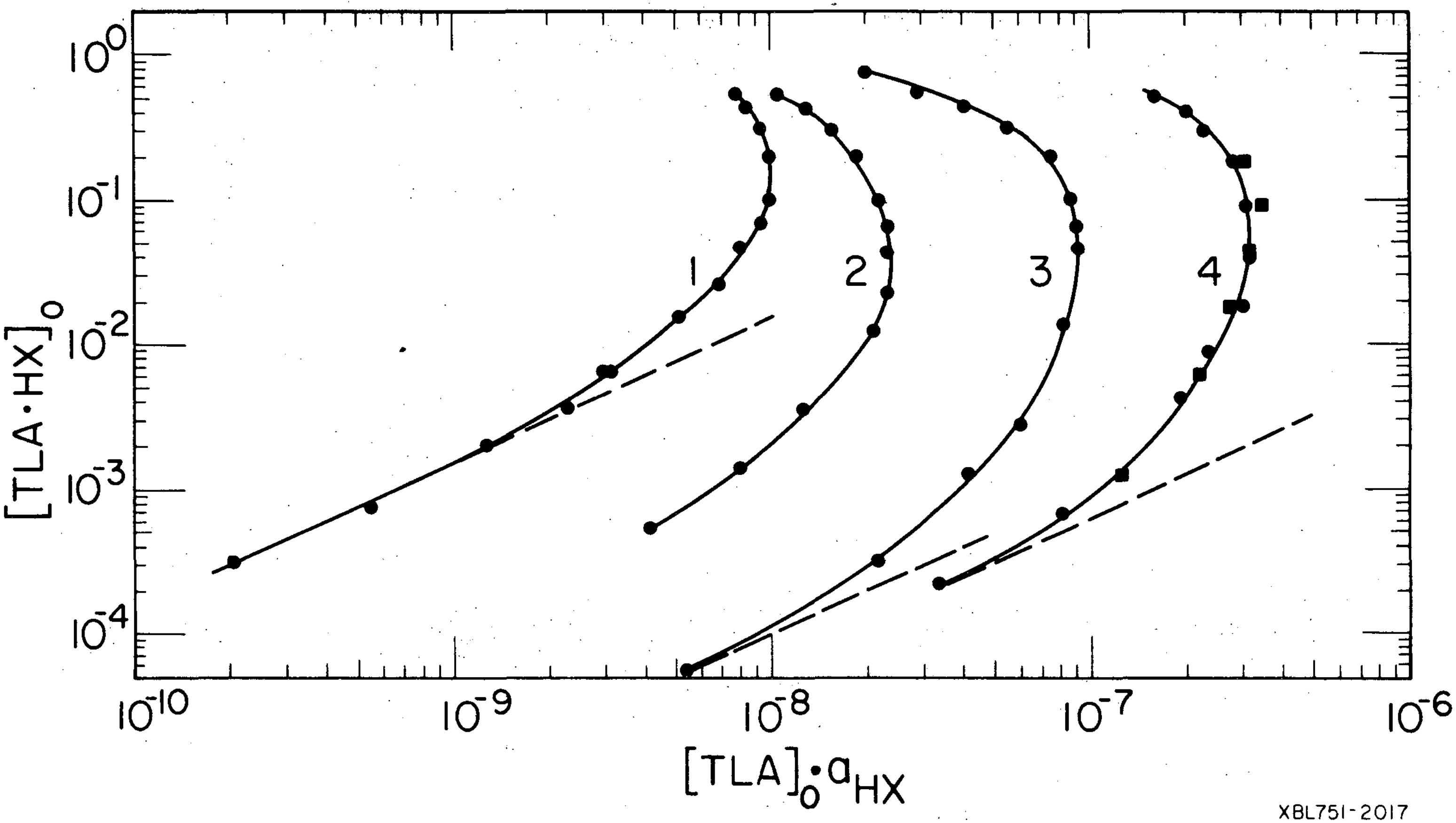

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Fig. 1

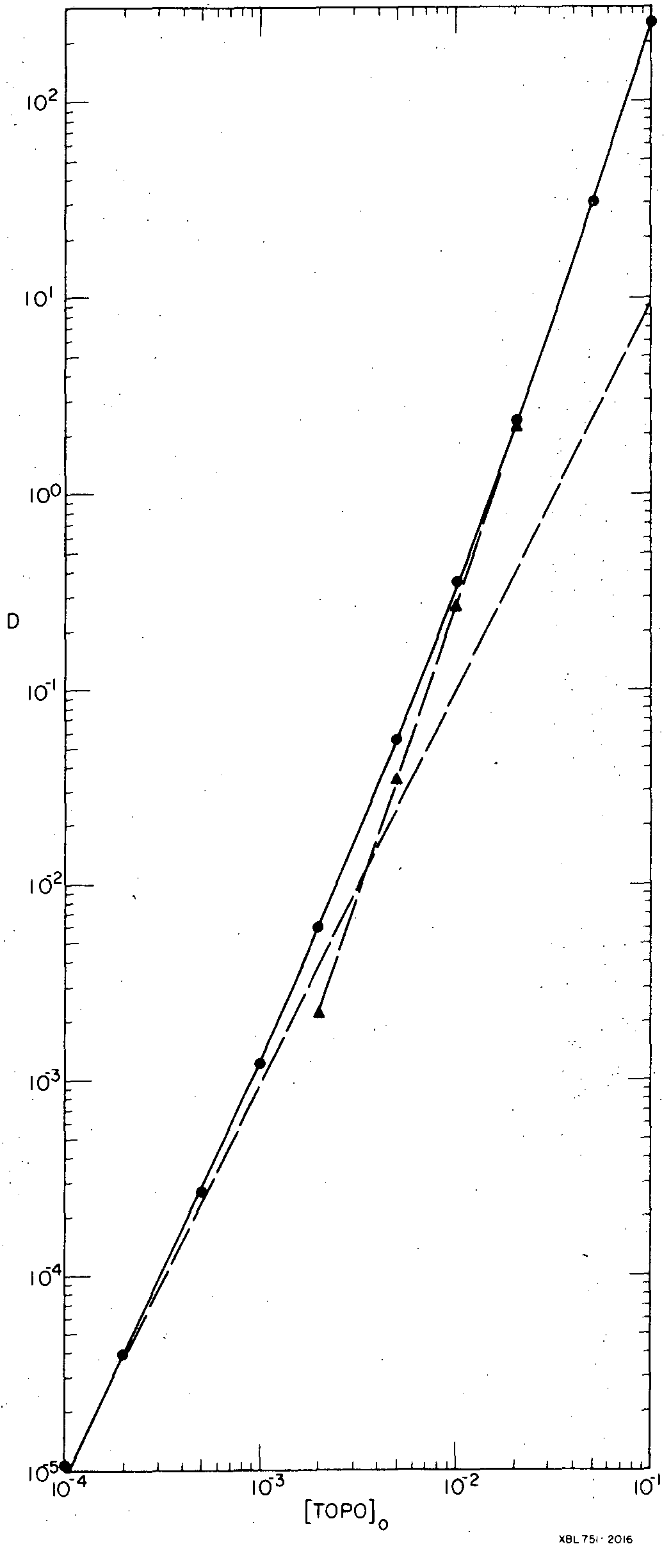
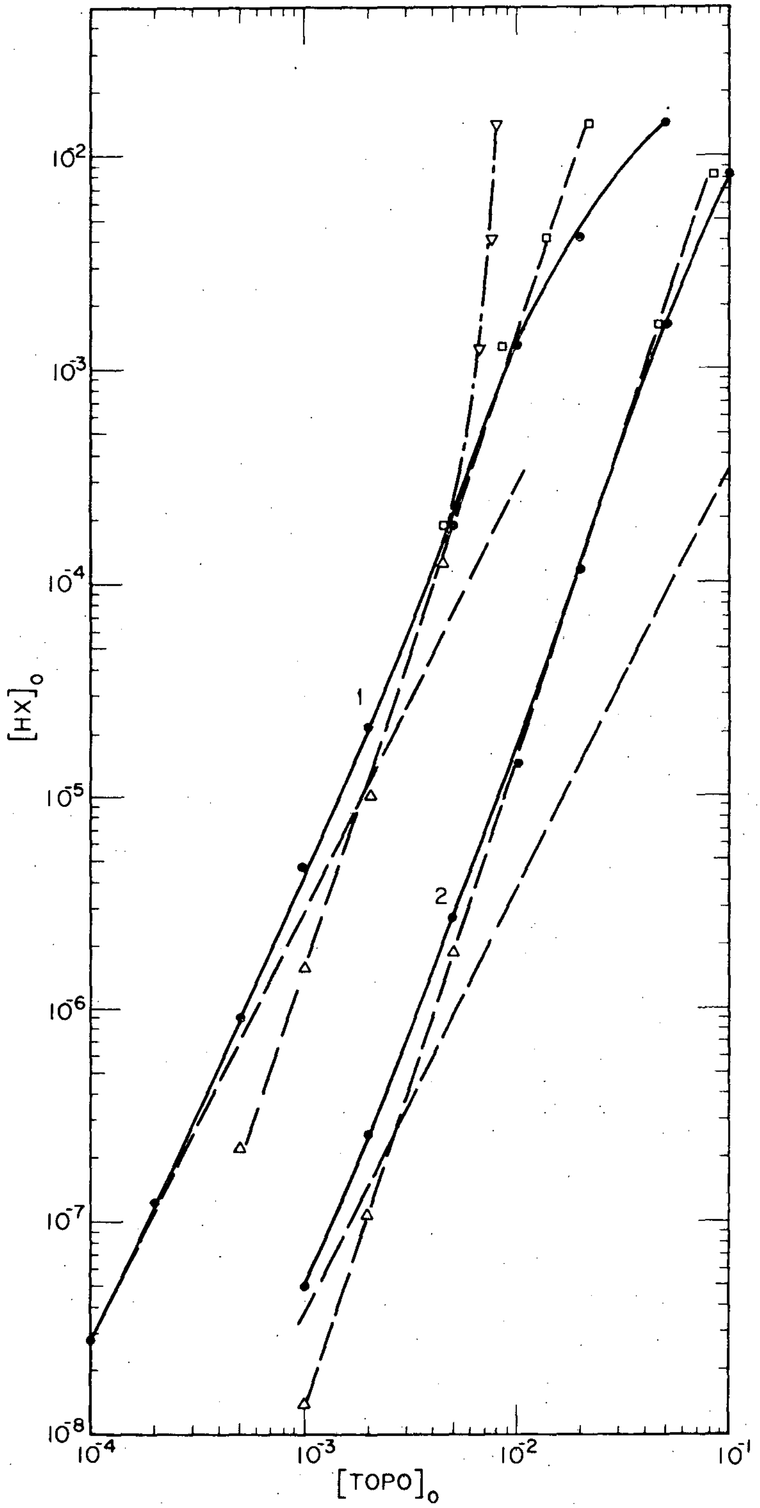

D
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
$[TOPO]_o$
XBL 751- 2016

Fig. 2



$[HX]_o$
$[TOPO]_o$
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
1
2
XBL718-4016

Fig. 3

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