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The simplest expression we can write for the reaction between an amine dissolved in an organic diluent and an aqueous solution of acid is

$$\overline{R_3N} + H_3O^+ \rightleftharpoons \overline{R_3NH^+} + H_2O \tag{1}$$

where the superscript bar indicates the organic phase, and a secondary or primary amine can be substituted for the tertiary amine. Although this is too simple to account adequately for all the complications occurring in the extraction of acids by amines, it is a good starting point, as it emphasizes the acid-base nature of the reaction. The amine binds the proton more strongly than does a water molecule, and that is the main driving force for the extraction.

However, different acids show very different degrees of extraction under similar conditions, and so extraction also depends upon the anion. It must therefore be included in eq. (1). Exactly how this should be done depends upon the nature of the ammonium species in the organic phase and upon the diluent. In dilute solution in the usual low dielectric constant diluent, the salt will be ion paired [1,2] so eq. (1) becomes

$$\overline{R_3N} + H_3O^+ + X^- \xrightleftharpoons{} \overline{R_3NH^+X^-} + H_2O \tag{2a}$$
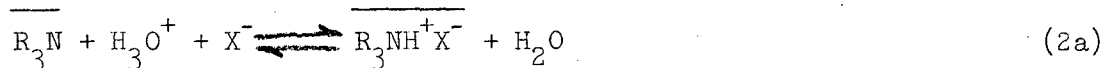
$$K_1 = \overline{[R_3NH^+X^-]}/\overline{[R_3N]} \; a_{HX} \tag{3a}$$

The ion pairing is not purely electrostatic, but may involve a weak hydrogen bond between the ammonium cation and the anion. This interaction is stronger, the smaller and the more basic the anion, but the ease of extraction shows just the opposite order, e.g., $Cl^- < Br^- < I^- < ClO_4^-$, fig. 1. This is because it is the aqueous phase interactions of the ions, and not the organic phase ones, which dominate in determining the sequence. Water is the best anion-solvating agent present, and so the ions leave the aqueous phase inversely with the order of increasing hydration [3].

When considering the extraction of a given acid under varying conditions, however, differences in the organic phase interactions readily show up. For simple acids the order of extraction by amine class is usually primary > secondary > tertiary [4,5,6]. An explanation is that the increasing number of alkyl groups sterically hinder the approach of the anion to the ammonium hydrogen, as well as cutting down the number of interacting hydrogens on the nitrogen. The cation-anion interaction is weakened for both reasons, and so the extraction decreases. For the same reason, the spread in selectivity among anions should be expected to increase in going from primary, secondary, tertiary, to quaternary ammonium salts. The cation-anion interactions partially neutralize or oppose the order of extraction dictated by the dominant aqueous phase hydration behavior, and so the latter shows its maximum effect with the quaternary salts and a minimum selectivity with the primary ammonium cations.

The role the organic diluent plays in the extraction must also be
considered [7,8,9,10,11]. The diluent is not "inert," but interacts with
both the amine and the ammonium salt through its functional groups (chemical
properties) and with the salt through long-range Coulombic effects (dielectric
properties). Differences in the magnitude of extraction due to diluent
interactions may become very large, as illustrated in fig. 2, where is shown
the extraction of hydrogen bromide by solutions of trilaurylamine, TLA, in
various diluents. There is a change of more than 10^5 in extraction between
chloroform and cyclohexane as diluents. In general, the higher the dielectric
constant of the diluent, the better the extraction, table 1, and this is easy
to understand. A positive electrostatic free energy obstructs the transfer
of ions from a medium of high dielectric constant (water) to one of lower
value. An order-of-magnitude estimate of this term can be obtained by apply-
ing the Born charging expression [12] to the transfer of a pair of dissociated
spherical monovalent ions from water $(\epsilon_a \approx 80)$ to an organic diluent (ϵ_o)

$$\Delta F_{a \to o} = N_o e^2 (1/2r_+ + 1/2r_-)(1/\epsilon_o - 1/\epsilon_a) \tag{4}$$

If the ions associate to a pair in the low dielectric constant medium, the
(positive) free energy of transfer is reduced by the energy of ion pairing.
With $1/\epsilon_o \gg 1/80$, the most favorable case is for two ions of equal radius,
and the value of $\Delta F_{a \to o}$ is reduced to one-half the value for dissociated ions.
So even for ion pairs the long-range Coulombic interactions with the diluent
provide a positive free energy of transfer whose magnitude depends on the
dielectric constant of the diluent. This term must, of course, be overbal-
anced by the acid-base reaction for extraction to occur.

But the parallelism between the ion-pair extraction constant, K_1, and the dielectric constant of the diluent, ϵ, in table 1 is not very good. For example, anisole, with $\epsilon = 4.33$, has a larger K_1 than chlorobenzene, with $\epsilon = 5.62$. Besides "electrostatic" solvation of the ions, a short-range "chemical" interaction with the diluent must also be considered. If the diluent is somewhat basic, there may be an interaction between it and the weakly-acidic hydrogen of the ammonium cation. This is most likely the explanation for the surprisingly good extraction with anisole (considering only the value of ϵ), as the methoxy group provides such a basic site. It is also probably the explanation for the better extraction with benzene over cyclohexane. The π-electrons of benzene are weakly basic, and the interaction with them helps stabilize the ammonium cation. An indication that such an interaction of aromatic diluents is possible is given by a comparison of the extraction of perchloric acid into TLA solutions in benzene, trimethylbenzene, and triethylbenzene. The substituted rings might be expected to show some steric hindrance to such a π-electron interaction, and, indeed, the value of the ion-pair extraction constant falls almost an order of magnitude from benzene to mesitylene, and again to triethylbenzene (table 1), although all three diluents have about the same dielectric constant.

If, on the other hand, the diluent molecule is slightly acidic, one might expect it to interact with the basic extractant molecule, effectively reducing the latter's concentration, and so decreasing the extraction. For example, such behavior is observed with the phosphoryl bases, the trialkyl phosphates, phosphonates, phosphine oxides, etc., where extraction of acids is poorer in the slightly acidic diluent chloroform than in carbon tetra-chloride [13,14,15]. But as shown in fig. 2, this is not true of tertiary

amine extraction. For some reason, not obvious to me, but probably involving both the different steric availability and the different electronic configuration of the amine vis-a-vis the phosphoryl bases, the former does not interact as strongly with small uncharged molecules, such as chloroform, as might be expected from its greater basicity. (Another example is the interaction with water; the trialkyl phosphine oxides extract of the order of a mol of water per mol of base, while the more basic amines are essentially unhydrated.) But the chloroform molecules may (hydrogen-) bond with the anion of the ammonium salt, thus helping the extraction, and do so the more strongly, the smaller and more basic the anion. For such anions, chloroform, or other such weakly-acidic solvent, becomes one of the best possible diluents for extraction.

One of the most important and interesting features of amine extraction systems is the degree of association of the ammonium salt in the organic phase. The properties of the diluent, and the natures of the ammonium cation and of the anion, and their concentrations determine whether the salt is dissociated, ion paired, or still more highly aggregated in the organic phase. In a high dielectric constant medium, such as nitrobenzene, an ammonium salt with a large anion may be completely dissociated over a wide range of concentration. The expression for this type of behavior is

$$\overline{R_3N} + H_3O^+ + X^- \rightleftharpoons \overline{R_3NH^+} + \overline{X^-} + H_2O \qquad (2b)$$
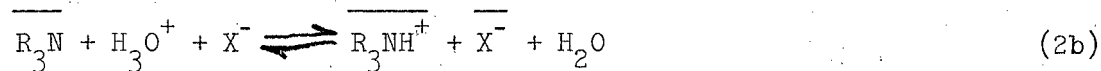
$$K_{1/2} = \overline{[R_3NH^+]}\,\overline{[X^-]}/\overline{[R_3N]}\,a_{HX} \qquad (3b)$$

An example of such extraction is shown by perchloric acid with TLA in

nitrobenzene, fig. 3, where $\log [\overline{X^-}]$ has been plotted against $\log [R_3N] \, a_{HX}$

and yields a slope of 1/2 over the whole range of concentrations studied

(after application of a relatively small Debye-Hückel type correction). The

dissociation has been confirmed by freezing-point measurements [9]. But

with smaller anions the interionic attractions are larger, and the salts,

although dissociated at very low concentrations, ion pair at higher concen-

trations. This is shown in fig. 4, where the similar log-log plots for

TLAHI and TLAHBr show a change in slope from 1/2 (dissociated ions) to 1

(ion pairs) at an increasingly lower organic-phase salt concentration.

Ion pairing is a form of self-solvation, and such association will

occur whenever the diluent itself cannot provide the ions with sufficient

electrostatic or chemical solvation to remain as free ions. If, in fact,

the diluent has a very low dielectric constant and little chemical solvating

ability, the ammonium salt may associate to still larger aggregates beyond

the ion pair, to ion quadrupoles, etc. [16,17].

Such behavior can be represented as

$$n\overline{R_3N} + nH_3O^+ + nX^- \rightleftharpoons \overline{R_3NH_n^+X_n^-} + nH_2O \qquad (2c)$$
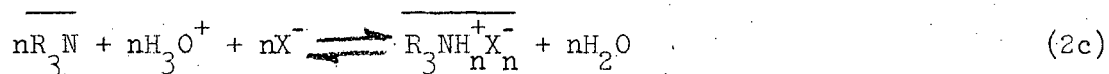
$$K_n = [\overline{R_3NH_n^+X_n^-}]/[\overline{R_3N}]^n \, a_{HX}^n \qquad (3c)$$

A log-log plot of the organic phase acid concentration vs. the product

$[\overline{R_3N}][H_3O^+][X^-]$ yields the average value of n at any point as the slope.

From the previous discussion, a poorly solvating diluent will be expected

to give reduced extraction and enhanced aggregation. Consider fig. 2 again,

where are given log-log plots of the extraction of TLAHBr by various diluents

vs. the product of the unreacted amine concentration times the aqueous acid

activity. Nitrobenzene and chloroform show the best extraction. The curve

for the former indicates free ions at low salt concentration and ion pairs

above about 10^{-5} to 10^{-4} M, while that for the latter shows only ion pairs

from 10^{-6} to 10^{-1} M. The good extraction and small degree of association

with nitrobenzene as diluent occurs because of its high dielectric constant,

and with chloroform because of its chemical (hydrogen-bonded) interaction

with the bromide anion. Benzene, carbon tetrachloride, and cyclohexane, with

low dielectric constants and progressively weaker chemical interactions with

the ammonium bromide show progressively poorer extraction and, at a given

moderately high organic-phase concentration (but below about 10^{-1} M) show

progressively steeper slopes in fig. 2, and hence greater aggregation.

The degree of aggregation should also correlate with the nature of

the anion. For if the anion-cation pair can hydrogen bond, and thus solvate

each other, they will more readily form ion pairs from the free ions, but they

will have less need to aggregate further. Consider the halide systems. There

is good evidence that the halide anions interact with the ammonium hydrogen,

e.g., the lowering of the NH bond frequency as observed in the infra-red, and

the chemical shifts found in NMR spectra [18]. The order of this interaction

is as expected from the size of the ions, $Cl^- > Br^- > I^-$. Then these anions

should show the opposite tendency to aggregate beyond the ion pair, and they

do, as shown in fig. 5 for their extraction into benzene as diluent. Quater-

nary ammonium salts, which are incapable of such hydrogen-bonded cation-anion

interactions, should undergo more extensive association than the tertiary

ammonium salts. It is harder to predict the behavior of the secondary and

primary salts, as their greater number of hydrogens might allow for a more

extensive hydrogen-bonded network, and so greater aggregation, than the

tertiary salts. ·

Quantitatively, the degree of aggregation of the ammonium salt can

be determined from the shape of the extraction curve, whether measured by

the use of tracers or by two-phase titrations [19], from light scattering

studies [20], from vapor pressure or freezing point measurements [10,21,22,

23,24,25], etc.   There are restrictions and possible dangers in using each

method, but one of the most convenient and general methods is interpreting

the extraction curves by slope analysis, either graphically or by means of a

computer program [19].   I would like to point out a possible difficulty.

Consider fig. 6, showing the extraction of the hydrogen halides by TLA

solutions in cyclohexane.   The extraction curves for TLAHI and TLAHSCN

actually turn back on themselves at high concentrations, giving negative

slopes.   This is a completely unphysical result if all deviations from a

straight line of unit slope are to be ascribed to the equilibrium build-up

of aggregates larger than ion pairs.   The limiting slope for complete aggre-

gation to a macro-colloid, or to a new phase, is a vertical asymptote.   I

believe this "unphysical" result merely reflects the fact that the ion pair,

ion quadrupole, etc. concentration constants, K_n, are not constant at high

(> 0.1 M) concentrations of ammonium salts.   One way of saying this is that

the organic phase activity coefficients are not constant.   A more physical

picture is that the diluent is no longer pure cyclohexane, but is a solution

of ammonium halide ions in cyclohexane.   The presence of such a large concen-

tration of ions, even though highly associated, changes the properties of

the diluent from those of cyclohexane to those of an entirely new substance

with better extraction characteristics. As an example, table 2 lists the

dielectric constants of benzene and cyclohexane solutions of TLA and of

TLAHBr. The dielectric constant increases with increasing concentration of

the salt solutions, but not of the pure amine, and is considerably higher in

a 0.4 M salt solution than in the pure diluent. This increase in the dielec-

tric constant alone makes for better extraction of ions by the reasoning

given earlier, but is probably not the sole cause for better extraction. It

is presented only as an indication that the properties of the diluent have

changed. The conclusion is that the concentration constants calculated in

dilute solution do not necessarily hold in the more concentrated regions above

0.1 M ammonium salt where one desires to study aggregation.

This question of the state of aggregation of the organic phase salt

is important when trying to determine the nature of an extracted metal com-

plex anion from the dependence of its distribution ratio, D, on the ammonium

salt concentration. For then one is really measuring the ratio of the number

of ammonium cations in the metallo-complex aggregate to the number in the

initial ammonium salt aggregate. A number of such studies have been made on

halo-metallic complex anions of tripositive metals such as Fe(III), Ga(III),

and In(III) [8,26,27,28,29]. Frequently, a second-power dependence of D on

the ammonium salt concentration is found. Such results have often been

interpreted to mean that $(R_3NH^+)_2MX_5^{-2}$ is the organic phase species, but in

at least some of these systems the extracted anion is really MX_4^-. In partic-

ular, this has been shown for the Fe(III)-HCl case [25,30,31,32]. Thus the

origin of the second-power dependence remains a mystery. I believe it

results from the production of a mixed Cl^- - $FeCl_4^-$ aggregate, but it is hard

to see why the mixed aggregate should always have twice the number of $TLAH^+$

ions as the starting TLAHCl salt when, over the range of concentration

studied, the latter is a monomer in chloroform, and varies from monomer to

dimer in benzene, and from dimer to tetramer in cyclohexane, etc. [10].

Clearly more work must be done on such systems and on their state of aggre-

gation.

A few comments about the order of extraction of halometallic complex

anions as a function of amine class, of increased branching of the amine

alkyl groups, and of diluent, are in order. The sequences will usually not

be the same as for the simple hydrohalic acids; they will tend to be the

opposite. This is because in the halometallic acid systems the hydrogen

halide is present and is in competition with the metallic complex for

extraction; one is dealing with ion exchange. Consider the order with amine

class. As has already been mentioned, the order of (hydrogen-bonded) inter-

action of Cl^- with the ammonium cation is primary > secondary > tertiary >

quaternary, and extraction follows the same sequence. This means that a

weakly interacting anion (ClO_4^- or MX_4^-), which does not depend as much on

such hydrogen bonding to help its extraction as does Cl^-, will compete best

with Cl^- in extraction with a quaternary cation, next best with the tertiary,

and so on, yielding an order opposite to that for HCl extraction itself. A

similar argument holds for the inversion in extraction order between the

hydrohalic acids and the (monovalent) halometallic complex acids with change

in diluent. The halide interacts more strongly with chloroform than do the

larger, less basic anions, so that when both are present, the larger anion is

relatively less strongly favored and extracted than with a chemically more

inert diluent such as cyclohexane. As a result, chloroform is a good diluent

for hydrochloric acid extraction, but poor for the (ion exchange) extraction

of halometallic complex anions, while cyclohexane or the aromatic solvents have the opposite behavior. Such inversions in extraction order become more marked the greater the disparity in size and basicity of the anions involved.

Now a word about the role of water in the extracted salts. As has already been mentioned, the large amines themselves do not seem to be very much hydrated in the common diluents. But with most anions, appreciable water is co-extracted with the ammonium salt [9,10,19,22,32,33,34]. Furthermore, the presence of the water usually increases the solubility of the salt in the diluent. This water is bound in the ammonium salt; it is not osmotically active. This has been indicated by vapor pressure measurements of the extracted species where, if the water were free, impossibly large molecular weights would obtain, and by infra-red measurements in which the water involved shows a broadened and intensified stretching band at a lower frequency than "free" water, behavior characteristic of bound water. But it is not bound solely to the cation, as the amount of water is a function of the nature of the anion, and varies as the need for solvation of the anion, e.g., $Cl^- >$ $Br^- > I^- \geq ClO_4^-$. So the water either acts as a bridge between the cation and anion, or is hydrogen-bonded solely to the anion [10,35]. These two possibilities are also indicated by the behavior in chloroform. Salts in this diluent show significantly smaller hydration than in the other common diluents, since the chloroform also (hydrogen-) bonds with the anions, partially solvating them, and diminishing their need for water. On the other hand, for non-acidic diluents as different in their interactions with the ammonium cation as benzene and cyclohexane, the hydration of an ammonium salt is relatively constant.

Mention should be made of still another well-known phenomenon in some amine extraction systems, the extraction of acid beyond the amount necessary to neutralize the amine [11,19,33,36,37]. I believe this is related to the water problem just mentioned, in that the excess acid is solvating the anion in the same manner. The arguments, though not over-whelming, are as follows. A molecule of an acid such as HCl is a polar molecule which can hydrogen-bond to an anion just as can water. Only acids relatively easily capable of forming and distributing as molecular entities are involved, e.g., hydrochloric, nitric, acetic, but not perchloric or even hydriodic. Infra-red studies show that the excess acid is in a molecular state, and for HCl, such studies indicate the presence of the HCl-solvated Cl^-, the bichloride ion [38,39]. Only anions which greatly need solvation should couple with excess acid, and the amount of excess acid might be expected to vary roughly with this need. A measure of this need is given by the basic strength of the anion, $OAc^- > F^- > NO_3^- > Cl^- > Br^- > I^- > ClO_4^-$. Extraction of excess acid goes in this order, and for the first of these anions, the number of excess acid molecules per ion may go beyond one, rising to two or three for OAc^- and F^-. The ease of solvating ions with molecules of acid varies with the diluent in just the same manner as does the hydration of the anion itself, and presumably for the same reason. Chloroform par-tially solvates the anion, decreasing its need for water or excess acid, while cyclohexane yields the greatest amount of hydration and of excess acid, as is shown in fig. 7.

The extraction of complex metallo-anions from aqueous hydrochloric or nitric acid solutions may be greatly influenced by the formation of these molecule-ions, as the latter are less highly hydrated and more readily

extractable than the simple chloride or nitrate anion, and so compete much

better than the latter in anion exchange. Thus for a complex metallo-anion,

such as $FeCl_4^-$, $GaCl_4^-$, or $CoCl_4^{2-}$, the distribution curves for dilute HCl solu-

tions are almost identical with those for LiCl, but they increasingly fall

below the LiCl values as the concentration rises into the region where HCl_2^-

and $H_2Cl_3^-$ can form and extract. This is the "HCl effect," known earlier from

solid ion exchange resin studies, and due there to the same cause [40,41].

Finally, I would like to come back to the simple equation we started

with

$$\overline{R_3N} + H_3O^+ \rightleftharpoons \overline{R_3NH^+} + H_2O \qquad (1)$$

and consider a possible consequence of decreasing the basicity of the amine.

The extraction should become much poorer, but there is also the possibility

that the nature of the reaction might change. If the amine becomes weak

enough, one molecule may not provide enough solvation for the proton. Two

may be required, yielding the complex $(R_3N)_2H^+$. The amine may even become

too weak to take the proton away from the water molecule, and then must form

a complex with two or three amine molecules bound to the H_3O^+ ion, as does

occur with the weaker phosphoryl bases, such as TBP [42].

In actual fact, the substitution of an aromatic group for an alkyl

one in a tertiary amine causes a considerable reduction in its basicity and

a marked drop in extraction, about a factor of 10^5 per aromatic group [43].

The mono-aryl and di-aryl amines thus roughly span the extractive strength

from TOPO to something less than TBP, but extraction of perchloric acid into

benzene diluent still seems to be that of a simple ammonium salt. Again we

see a difference in behavior between the amines and the phosphoryl bases.
The former appear to bind small neutral molecules such as water and chloro-
form more weakly, but the charged proton, more strongly, relative to the
latter. However, by picking a favorable system and using a poorly solvating
diluent such as cyclohexane, conditions might be found where other than a
simple ammonium salt exists, and such work is in progress.

Table 1. Comparison of ion-pair extraction constants for $HReO_4$ tracer out
          of $HClO_4$ solutions and diluent dielectric constants[9].

Solvent	K_1	ϵ
Cyclohexane	3×10^3	2.02
Triethylbenzene	2.4×10^4	2.26
Tetrachloroethylene	3.3×10^4	2.30
Trimethylbenzene	1.8×10^5	2.28
Benzene	3.7×10^6	2.28
Chlorobenzene	4.2×10^7	5.62
Anisole	1.2×10^8	4.33
o-Dichlorobenzene	1.5×10^8	9.93

Table 2. Dielectric constants of solutions [10].

Solute	Benzene	Cyclohexane
	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

FIGURE CAPTIONS

Fig. 1.   Total ammonium salt concentration, $[TLAHX]_o$, vs. $[TLA]_o\, a_{HX}$ for

chloroform diluent.   The composition of both phases was determined by

titration and from pH measurements [10].

Fig. 2.   Total ammonium bromide concentration, $[TLAHBr]_o$, vs. $[TLA]_o\, a_{HBr}$

for various diluents.   The composition of both phases has been determined

by titration and by use of radiobromide [10].

Fig. 3.   Plot of organic-phase trilaurylammonium perchlorate molarity, o,

and mean ion activity, $\diamondsuit$, in nitrobenzene vs. the product $[TLA]_o\, a_{HClO_4}$

[9].

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

nitrobenzene diluent.   The filled triangles indicate determinations with

radiobromide [10].

Fig. 5.   Total ammonium salt concentration, $[TLAHX]_o$, vs. $[TLA]_o\, a_{HX}$ for

benzene diluent [10].

Fig. 6.   Total ammonium salt concentration, $[TLAHX]_o$, vs. $[TLA]_o\, a_{HX}$ for

cyclohexane diluent.   The filled triangles indicate determinations with

radiobromide [10].

Fig. 7.   Ratio of organic-phase hydrogen ion concentration/initial amine

concentration = 0.1 M vs. aqueous hydrochloric acid activity for various

diluents [11].

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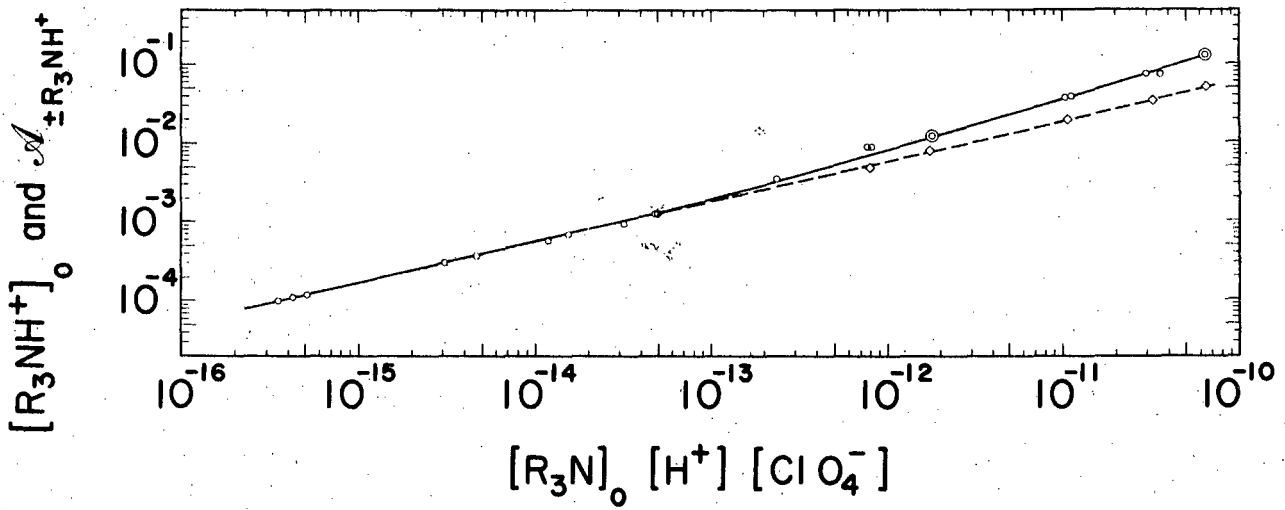
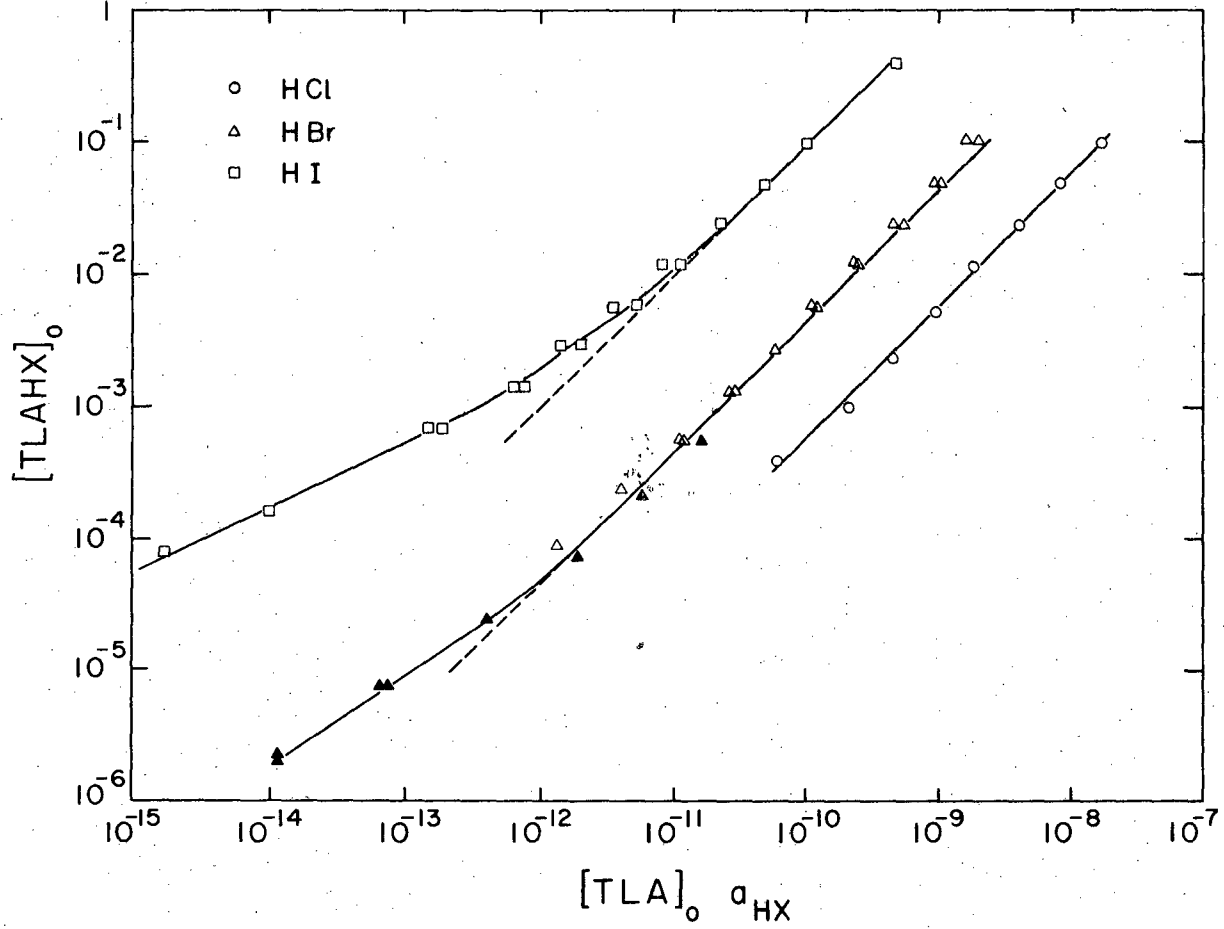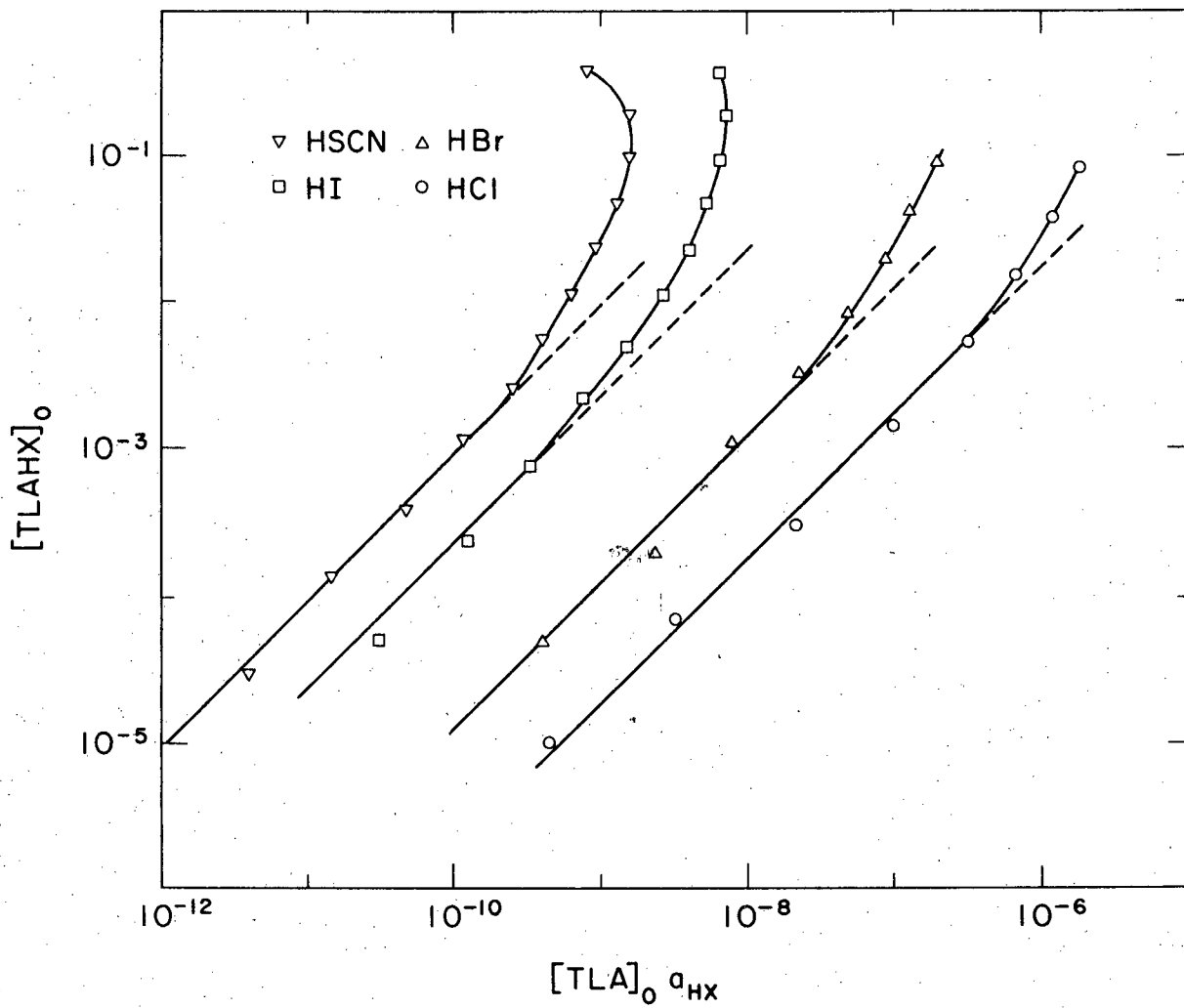[43] Bucher, J. and Diamond, R. M., unpublished work.

Fig. 1

MUB-6918

Fig. 2

Fig. 3

MUB-4280

Fig. 4

MUB-7129

Fig. 5

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Fig. 6

Fig. 7