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**Author**
Muller, Werner.

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# Ernest O. Lawrence Radiation Laboratory

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# AMINE HYDROHALIDE EXTRACTION STUDIES[*]

Werner Müller[†]

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Hydrohalides of tertiary amines can be used to extract metal ions from aqueous phases.[1] In order to gain a better understanding of the factors controlling the metal extraction, it is necessary to know the behavior of the extracting agent itself in organic solutions in equilibrium with aqueous phases.

The salts of high molecular weight amines, when dissolved in the common organic diluents, frequently exist as ion pairs.[2] Depending on the concentration of the amine salt and on the nature of the diluent, these ion pairs can undergo dissociation, or they can associate into higher aggregates.[3] The extent to which the amine salt is hydrated is determined by the anion, by the organic diluent and by the water activity of the aqueous phase.[4,5,6] The stability of the amine salt is limited by hydrolysis and, in presence of concentrated acidic aqueous phases, by the uptake of additional molecules of acid. .

In the following paper, the behavior of amine salt extractants is discussed in the case of a tertiary amine (trilaurylamine TLA = tri-n-dodecylamine) bound to hydrohalic or pseudohydrohalic acids: hydrofluoric,

hydrochloric, hydrobromic, hydroiodic and thiocyanic acid. The organic diluents
include cyclohexane, carbon tetrachloride, benzene, toluene, nitrobenzene and
chloroform. Conclusions drawn from this study will be applied to some aspects
of metal extraction.

The formation of the extracting agent by equilibrating an organic
solution (o) of the tertiary amine TLA with aqueous (a) hydrohalic acid HX can
be described by the equation I:

$$TLA_o + HX_a = TLAHX_o. \tag{I}$$

Information on the form in which the amine salt exists can be obtained by considering
application of the mass action law to this equilibrium I (Appendix). From
the slope $n$ in a log-log plot of the total amine salt concentration $[TLAHX]_o$
versus the product $[TLA]_o \, a_{HX} = [TLA]_o \, [H^+]_a \, [X^-]_a \, y^2_{\pm HX}$, a distinction can be
made among:

the existence of ion pairs ($n=1$),

their dissociation ($1/2 \leq n < 1$), or

their association into higher aggregates ($n > 1$).

Brackets [ ] designate molar concentration, $y_{\pm HX}$ is the stoichiometric molar
activity coefficient of the aqueous hydrohalic acid.

For a given hydrohalic acid (HBr), the influence of the amine salt
concentration on the equilibrium I and the role of the diluents can be seen in
Fig. 1, where the large range of concentrations covered is due to the use of
radiobromine, $^{82}$Br. A unique slope of one indicating the ion pair to exist
over the whole concentration range studied, is observed in the case of chloro-
form diluent. In nitrobenzene, at lower salt concentrations, $n$ becomes
smaller than unity, from which it can be concluded that the ion pairs

dissociate. For high amine salt concentrations in benzene—and to a larger

extent in carbon tetrachloride and cyclohexane—, the ion pairs are aggregated.

The absolute values of the equilibrium constant for the formation of an amine

salt according to equation I should only be compared when this salt exists in

the same form, i.e., as an ion pair. "Apparent" constants which are defined

for a given total salt concentration may differ from the absolute constants

for ion pair formation by several orders of magnitude, if diluents like carbon

tetrachloride or cyclohexane are used (Table I).

Table I. Comparison of absolute and apparent constants for the equilibrium
$$TLA_o + HBr_a = TLAHBr_o.$$

| Diluent | $K_{abs}$ (ion pair) $= \dfrac{[TLAH^+..Br^-]_o}{[TLA]_o\, a_{HBr}}$ | $K_{app}$ ([TLAHBr] $= 0.1$ M/$l$) $= \dfrac{[TLAHBr]_o}{[TLA]_o\, a_{HBr}}$ |
|---|---|---|
| Chloroform | $3.0 \times 10^7$ | $3.0 \times 10^7$ |
| Benzene | $1.0 \times 10^5$ | $3.6 \times 10^5$ |
| Cyclohexane | $1.5 \times 10^2$ | $1.0 \times 10^4$ |

For a given diluent (chloroform, Fig. 2; benzene, Fig. 3), the constants for

the ion pair formation from amine and aqueous hydrohalic acid increase as

a function of the anion in the order  chloride - bromide - iodide -

thiocyanate; the case of amine hydrofluoride will be discussed later.

The aggregation of the ion pairs, as indicated by the slopes in Figs. 2 and 3,

increases according to the same order of anions given above. Vapor pressure

measurements above amine and amine salt solutions in the same diluents indeed

show independently:

-the almost complete absence of association in chloroform (Fig. 4), and

-the increasing association in benzene from amine chloride to iodide

(Fig. 5).

It may be noted that here—as in some other experiments—the order iodide -

thiocyanate is reversed.

In the presence of aqueous phases, amine hydrohalides in organic

solution are hydrated. This hydration decreases for a given amine salt (e.g.,TLAHCl,

Fig. 6) depending on the diluent in the order cyclohexane, benzene or toluene,

carbon tetrachloride, chloroform. In the same diluent (benzene, Fig. 7) the

ratio water: amine salt decreases from chloride to iodide and thiocyanate. It

seems that for higher amine salt concentration—where aggregation occurs—more

water is bound by the amine salt than in the range where mainly ion pairs

exist.

The effect of the nature of the anion and the diluent on the constants

of equilibrium I, as well as the aggregation and hydration of the amine salt,

are believed to depend mainly on differences in hydration (in the aqueous phase)

and solvation (in the organic phase). In dilute aqueous solution, the hydro-

halic acids exist in form of hydrated ions. This hydration decreases from

hydrochloric to hydroiodic acid which favors the extractability into organic

phases in the same order.[7] The amine salt, which represents the species in

the organic phase after extraction of the mineral acid, is more solvated by

polar or polarizable diluents (chloroform, benzene) than by carbon tetra-

chloride or cyclohexane. This difference in the solvation of the amine salt

is considered to be the reason for the change of the equilibrium constants

(Eq. I) of a given amine hydrohalide in different diluents with low dielectric

constants. The amine salt solubility which reflects to some extent the solute-

solvent interaction, decreases from chloroform to cyclohexane and parallels

the solubility of water or of molecular hydrogen halides in the previously

mentioned diluents.[5]

The less solvated ion pairs try to increase their stability by electrostatic association to ion quadrupoles and even higher aggregates.[2] Vapor pressure measurements above concentrated organic solutions show the apparent molecular weight of a given amine salt to increase from chloroform to cyclohexane. On the other hand, in a given diluent, the interaction between the substituted ammonium cation and the anion decreases from hydrochloride to hydroiodide and thiocyanate. In the infrared absorption spectra, 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;[8] furthermore, the absorption bands narrow in the same sense because of decreasing hydrogen bonding. Again, the decreasing ion interaction favors the stabilization by electrostatic aggregation. Since the highest aggregates observed by vapor pressure measurements contain on the average only about four amine salt molecules, aggregation alone cannot explain the very high - and even negative - slopes in Figs. 1 and 3.

In presence of concentrated hydrohalic acid (HBr, HCl) or acidic halide solutions, organic phases of amine salts extract excess acid. Fig. 8 shows the composition of - initially - 0.1 M trilaurylamine solutions in different diluents after equilibration with hydrochloric acid of increasing concentration.[5] After a first step, in which the amine salt is formed, a plateau indicates the stability range of trilaurylamine monohydrochloride; the plateau ends when more acid is extracted into the organic phase. The formation of trilaurylammonium chloride in chloroform diluent begins at lower aqueous acid concentrations, the extraction of excess acid starts at higher concentrations than in benzene or cyclohexane. This difference in length and position of plateau for different diluents again is related to solvation: in chloroform, the extensive diluent - amine salt

interaction guarantees a large stability range of the extracting agent; in cyclohexane, the weak solvation of the amine salt by the diluent favors the extraction of and hence, the solvation by another acid molecule. The extraction of excess acid leads - in the aforementioned case - to amine dihydrochloride:

$$TLAHCl_o + HCl_a = TLA.2HCl_o \ . \tag{II}$$
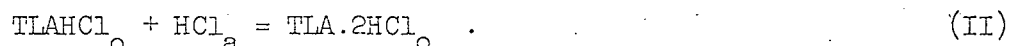
The dihydrochloride contains the $HCl_2^-$-ion, the existence of which is supported by physicochemical studies (viscosity, conductivity, freezing point, infrared absorption).[6]

The extraction of hydrofluoric acid - which is known to be associated by hydrogen bonding even in aqueous solution—leads to amine salts which contain more than one molecule HF per amine. Here (Fig. 9) no plateau indicating a stability range of a 1:1 complex between trilaurylamine and monomeric hydrofluoric acid is observed. Using radiofluorine, ^{18}F, however, it can be shown that such a 1:1 complex is formed at low acid-amine ratios: indeed, the amount of hydrofluoric acid extracted into a solution of 0.1 M trilaurylamine is proportional to the acid activity in the aqueous phase. The amine salt hydration which is initially proportional to the amount of extracted hydrofluoric acid attains a constant value when (in benzene) the acid/amine ratio is approximately two.

Some concluding comments may be devoted to the extraction of metals, the better understanding of which was among the aims of this study.

When amine salts were first used for the extraction of metals, it was hoped - because of the formal analogy between organic solutions of amine salts and solid anion exchangers - that by studying extraction equilibria, information on the nature of the metal complexes in aqueous phases could be obtained. The composition of the complex formed between the metal compound or ion and

the extracting agent can often be determined from the variation of the extraction coefficient $D$ of the metal as a function of the extractant concentration; $D$ is the ratio of the stoichiometric metal concentrations in the organic and the aqueous phase. If a metal salt $MeX_n$ is extracted from an aqueous phase (a) containing $X^-$ ions as a ligand by $m$ molecules of an amine salt extractant TLAHX in organic solution (o), the overall extraction equilibrium may be described by the equation:

$$MeX_{n_a} + m\ TLAHX_o = MeX_n \cdot mTLAHX_o$$
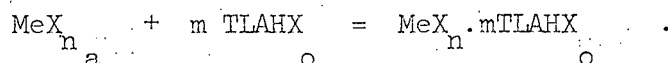
From the mass action law

$$K = \frac{[MeX_n \cdot mTLAHX]_o}{[MeX_n]_a [TLAHX]_o^m}$$

the simple relation

$$K' = \frac{D}{[TLAHX]_o^m}$$

can be derived under the following assumptions:

-the activity of $MeX_n$ in aqueous phase is proportional to the metal concentration in the aqueous solution of constant ligand concentration $[X^-]_a$,

-$MeX_n \cdot mTLAHX$ is the only complex formed, and its concentration can be neglected with respect to the total extractant concentration $[TLAHX]_o$,

-the ratio of the activities of the species in organic solution is proportional to the ratio of their concentrations.

Then, a plot of log $D$ versus log $[TLAHX]_o$ gives a slope $m$ which equals the ratio extractant: metal in the metal complex in the organic phase (slope analysis).

If trivalent metals are extracted by amine salts from halide phases, e.g.:

-ferric chloride from dilute hydrochloric acid[9,10] or

-americium chloride from concentrated lithium chloride solutions,[11,12,6]

a slope of 2 in a log-log plot of $D$ versus the amine salt concentration has been observed. This has been interpreted as indicating that a pentachlorometallate (III) ion $Me(III)Cl_5^{2-}$ exists in aqueous solution.

When macro or tracer amounts of ferric chloride are extracted by toluene solutions of trilaurylamine hydrochloride,[6,10] two different complexes can be distinguished by both loading experiments and slope analysis. A 2:1 complex is extracted from dilute, a 1:1 complex is extracted from concentrated chloride solutions. In both cases (1:1 and 2:1 complex), absorption spectra of the organic phases indicate the presence of tetrachloroferrate(III) ion. Therefore, it is assumed that the trilaurylammonium tetrachloroferrate:

$$TLAH^+ \quad FeCl_4^- \qquad \qquad (1:1 \text{ complex})$$

is able to form an ion quadrupole with a molecule of excess amine hydrochloride:

$$\begin{array}{l} TLAH^+ \quad FeCl_4^- \\ Cl^- \quad TLAH^+ \end{array} \qquad (2:1 \text{ complex}) \quad .$$
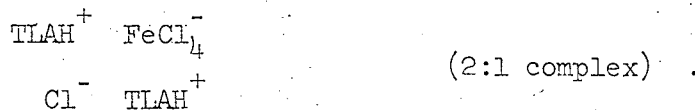
The diluent influence on iron (III) extraction from the same aqueous phase (1 M HCl) is seen in Fig. 10[(5)] where extraction coefficients $D$ of tracer iron are given as a function of trilaurylamine hydrochloride concentration. The extraction of a 2:1 complex is favored by decreasing amine salt—diluent interaction; solvation of the amine hydrochloride competes with metal extraction,

therefore the latter is highest in cyclohexane, but lowest in chloroform.  In

nitrobenzene, however, a 1:1 complex is formed which, as has been discussed

recently,[13] tends to dissociate because of the high dielectric constant of the

diluent.  These examples show that the composition and stability of a metal

complex after extraction by an amine salt into an organic phase depend on the

properties of the system amine salt - diluent and do not only reflect the

behavior of the metal ion in the aqueous phase.

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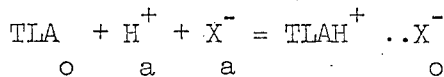
APPENDIX

$[TLAHX]_o$ = total amine hydrohalide concentration,

$[TLA]_o$ = total amine concentration, in M/$\ell$ organic phase;

$y_{\pm HX}$ = mean stoichiometric activity coefficient of the hydrohalic acid in aqueous phase,

$a_{HX} = [H^+]_a [X^-]_a \, y_{\pm HX}^2$

$K$ = equilibrium constant for the formation of the amine salt ion pair from amine and aqueous hydrohalic acid (equil. I).

## Ion Pair Formation

$$TLA_o + H^+_a + X^-_a = TLAH^+ .. X^-_o$$

$$K = \frac{[TLAH^+ .. X^-]_o}{[TLA]_o \, a_{HX}}$$

$$[TLAHX]_o = [TLAH^+ ... X^-]_o$$
$$= K[TLA]_o \, a_{HX}$$

## Ion Pair Dissociation
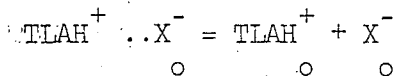
$$TLAH^+ .. X^-_o = TLAH^+_o + X^-_o$$

$$K_{Diss.} = \frac{[TLAH^+]_o [X^-]_o}{[TLAH^+ .. X^-]_o} = \frac{[TLAH^+]_o^2}{[TLAH^+ .. X^-]_o}$$

$$[TLAHX]_o = [TLAH^+ ... X^-]_o + [TLAH^+]_o$$
$$= K[TLA]_o \, a_{HX} + (K_{Diss} K[TLA]_o \, a_{HX})^{1/2}$$

## Ion Pair Association

$$p\ TLAH^+..X^-_o = (TLAH^+..X^-)_{p\ o}$$

$$K_{Assoc.} = \frac{[(TLAH^+..\ddot{X}^-)_p]_o}{[TLAH^+..X^-]^p_o}$$

$$[TLAHX]_o = [TLAH^+..X^-]_o + p[(TLAH^+..X^-)p]_o$$

$$= K[TLA]_o\ a_{HX} + p\ K_{Assoc.}(K[TLA]_o\ a_{HX})^p$$

Figure Captions

Fig. 1. Total amine salt concentration $[TLAHBr]_o$ versus $[TLA]_o \, a_{HBr}$ for various

diluents. The composition of both phases determined by titration and by

use of radiobromine. Acid activity calculated from Ref. 14.

Fig. 2. Total amine salt concentration $[TLAHX]_o$ versus $[TLA]_o \, a_{HX}$ for chloro-

form diluent. The composition of both phases determined by titration and

from $p_H$ - measurements. Acid activities calculated from Ref. 14, 15,

assuming equal activity coefficients for HI and HSCN.

Fig. 3. Total amine salt concentration $[TLAHX]_o$ versus $[TLA]_o \, a_{HX}$ for benzene

diluent.

Fig. 4. Vapor pressure measurements of amine and amine salt solutions in chloro-

form at $25^\circ C$. The ordinate is proportional to the vapor pressure differences

between the water saturated solutions and the water saturated diluent as

determined with a Vapor Pressure Osmometer(301-A, Mechrolab Inc., Mountain

View, Calif.).

Fig. 5. Vapor pressure measurements of amine and amine salt solutions in

benzene at $25^\circ C$.

Fig. 6. Water content of water saturated trilaurylammonium chloride solutions

in various diluents. Results corrected for solubility of water in the

diluent. In part Ref. 5,6.

Fig. 7. Water content of water saturated amine salt solutions in cyclohexane.

Results corrected for solubility of water in cyclohexane.

Fig. 8. Hydrogen ion/amine ratio of -initially-C = 0.1 M trilaurylamine solutions

in various diluents in equilibrium with hydrochloric acid. From Ref. 5.

Fig. 9. Hydrogen ion and water concentration of -initially- 0.1 M trilaurylamine

solution in benzene in equilibrium with aqueous hydrofluoric acid. Composi-

tion of both phases determined by titration and by use of radiofluorine. Acid

activity calculated from Ref. 16.

Fig. 10.  Extraction coefficients  D  of ferric chloride (tracer $^{59}$Fe) as a

function of the total amine hydrochloride concentration $[TLAHCl]_o$ in

various diluents.  Extraction from 1.0 M hydrochloric acid.  Ref. 5, 10.
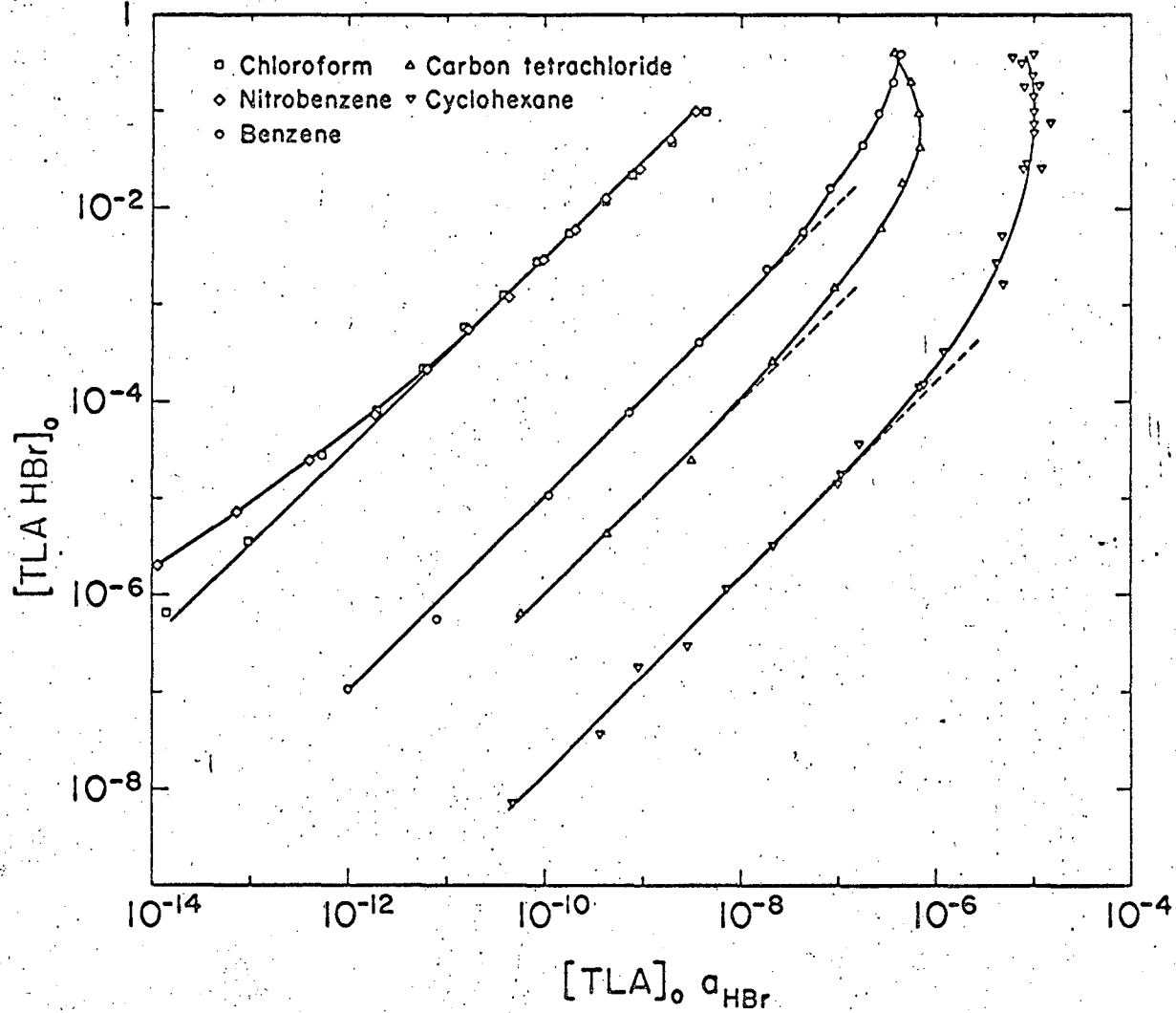
Fig. 1

Fig. 2

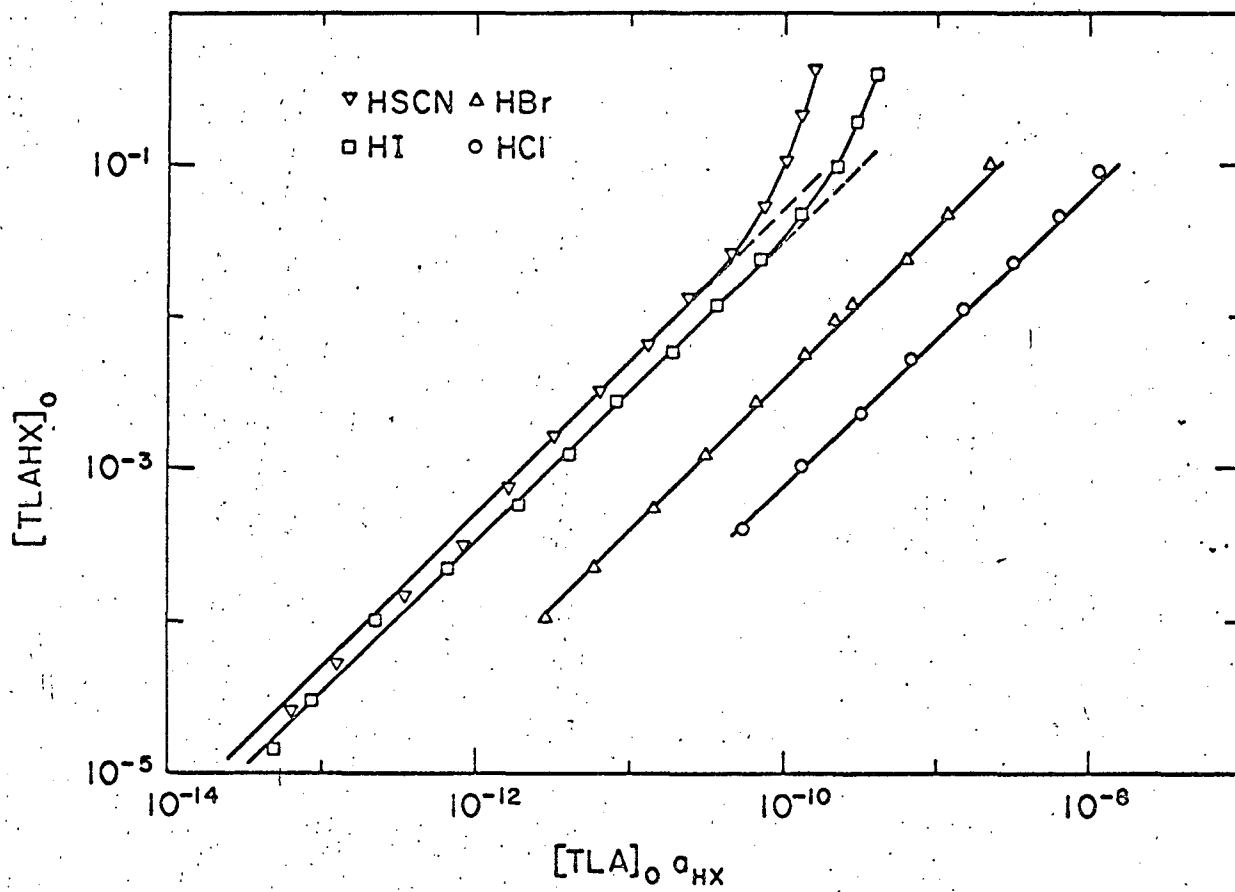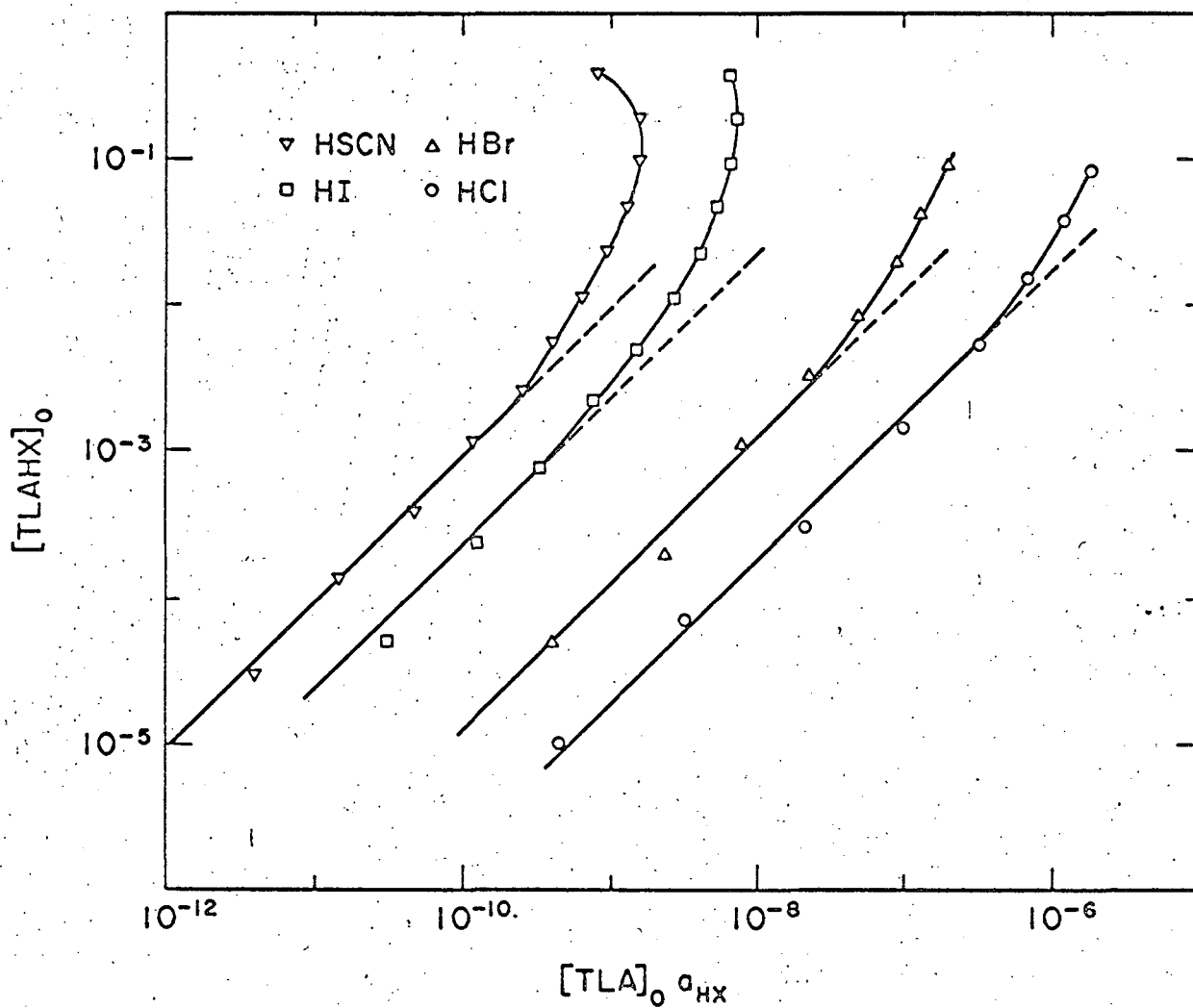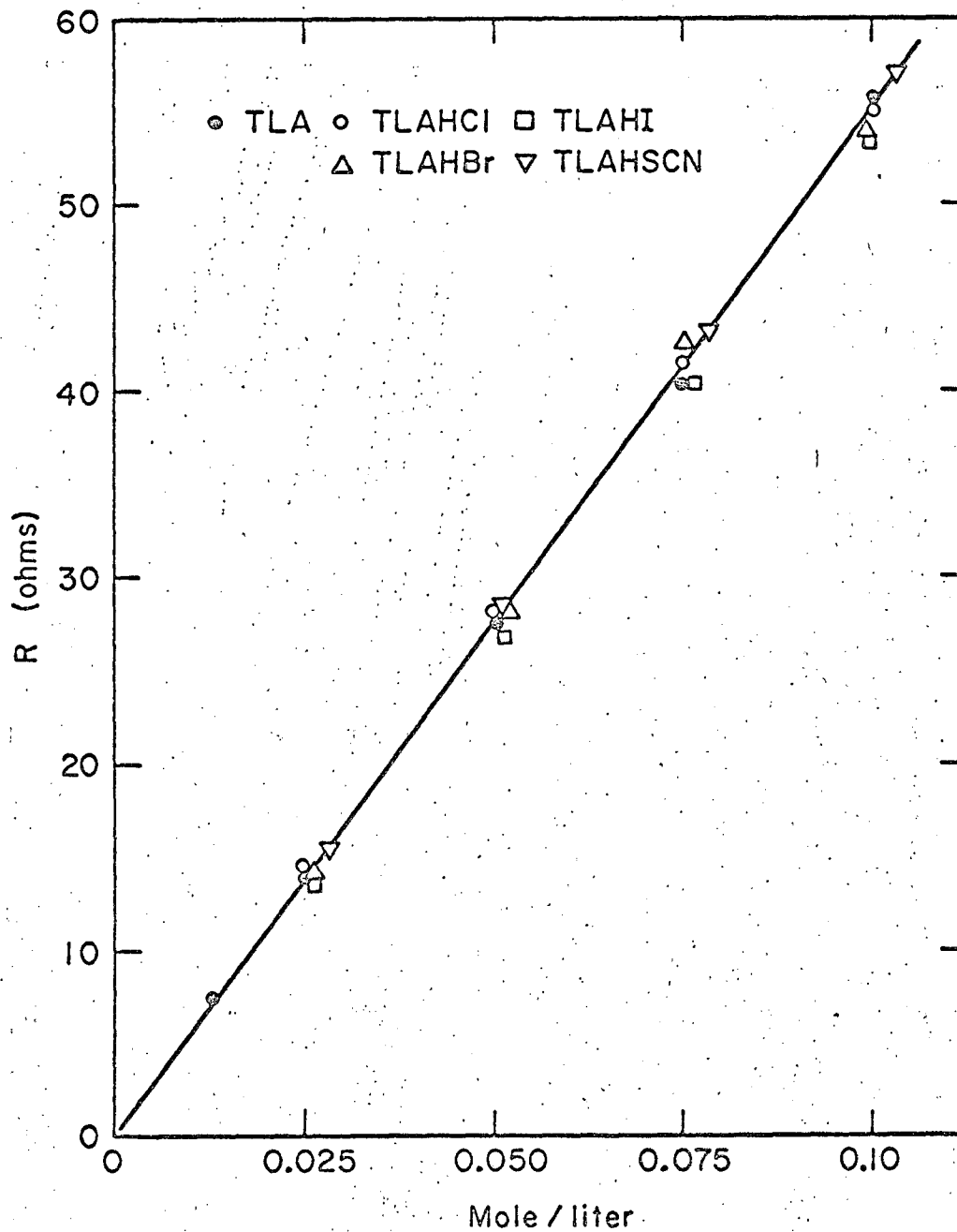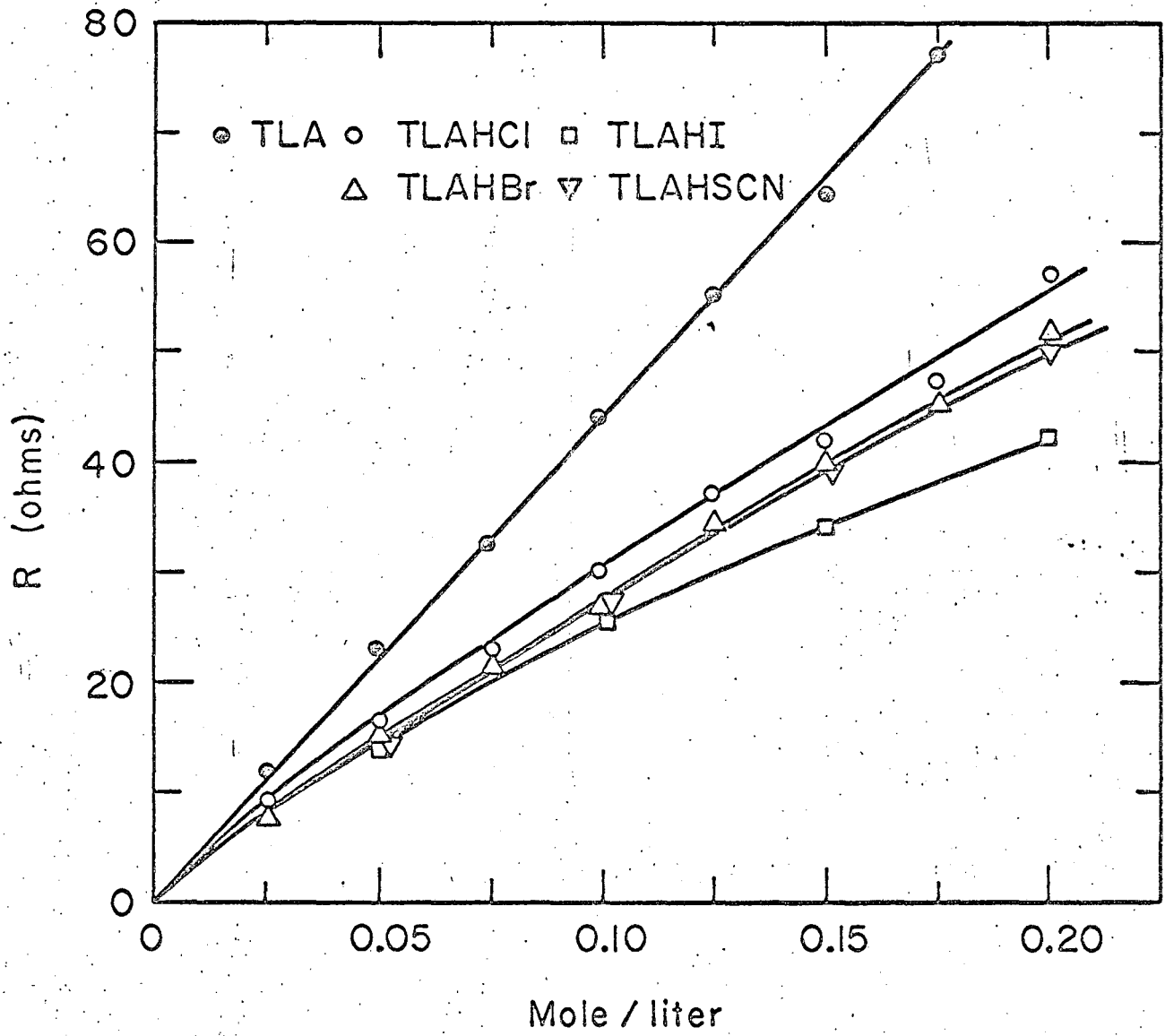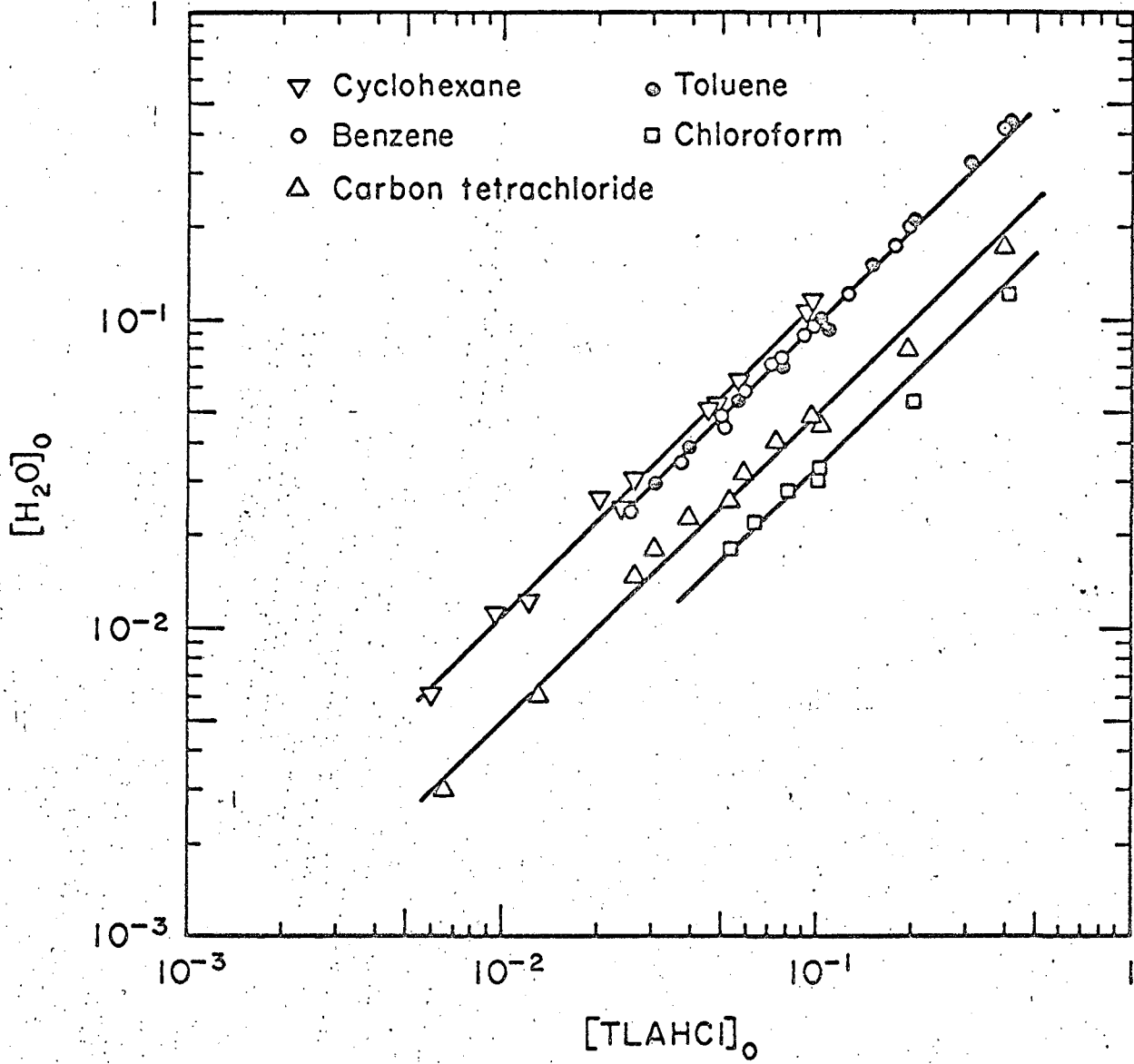Fig. 3

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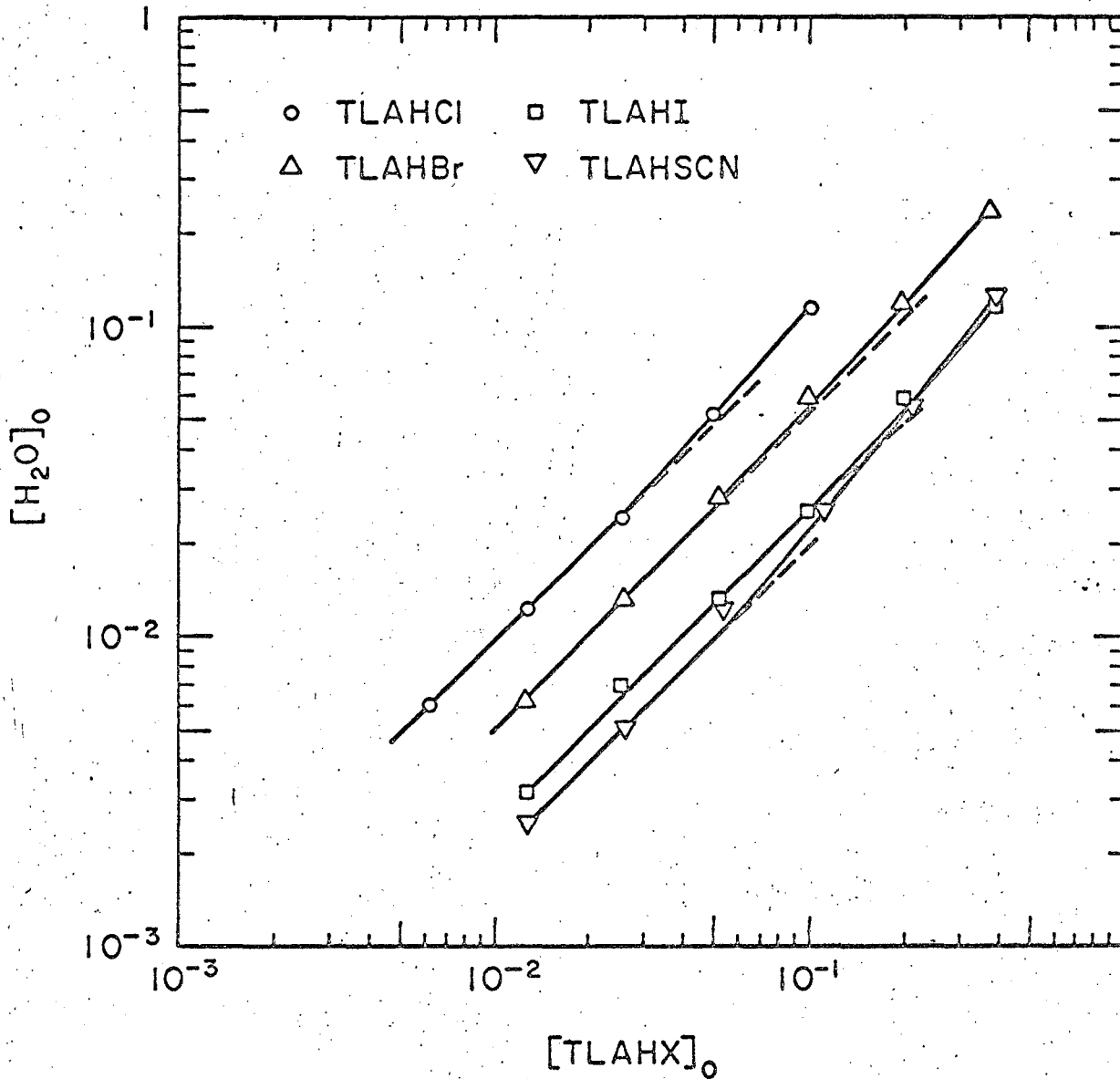Fig. 4

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Fig. 5

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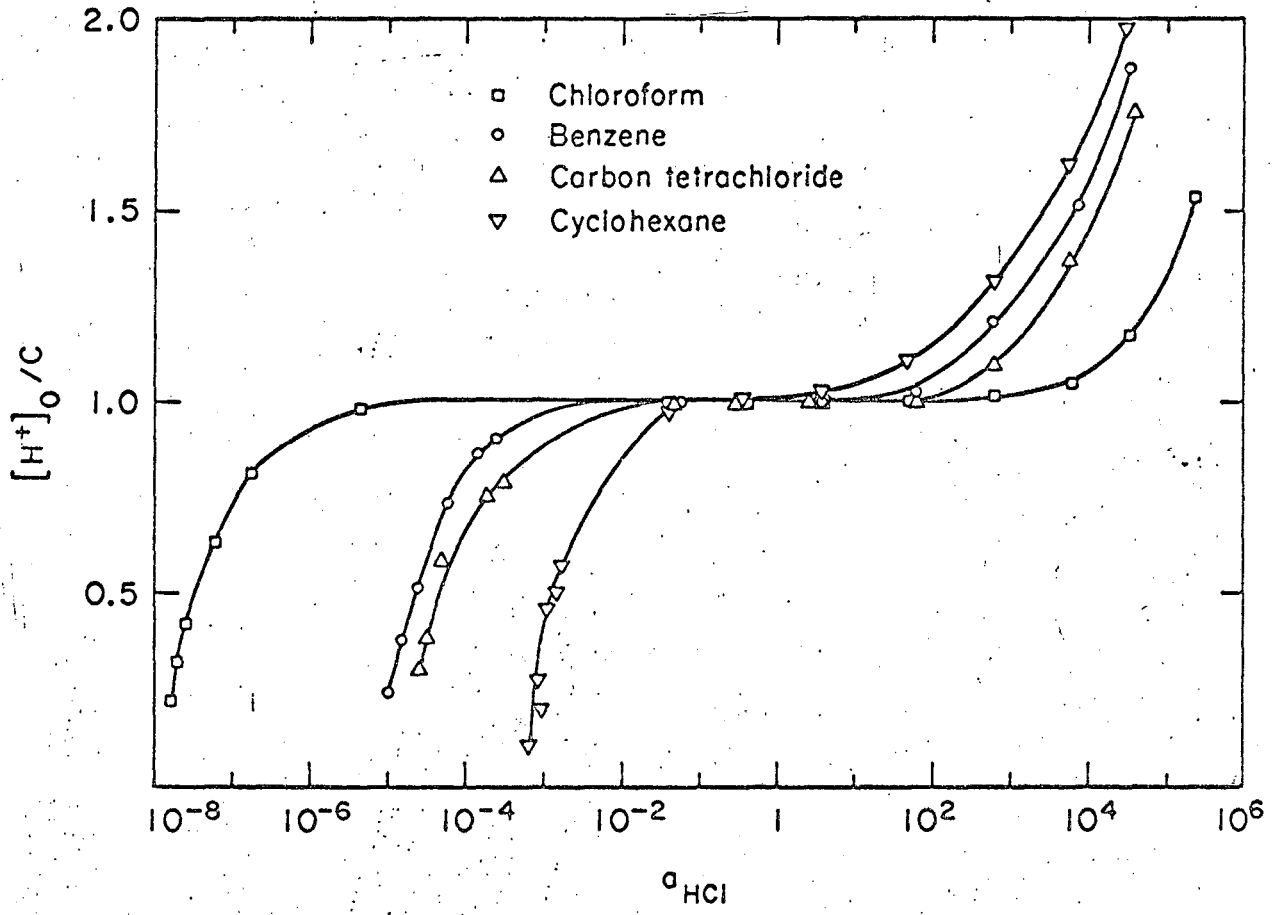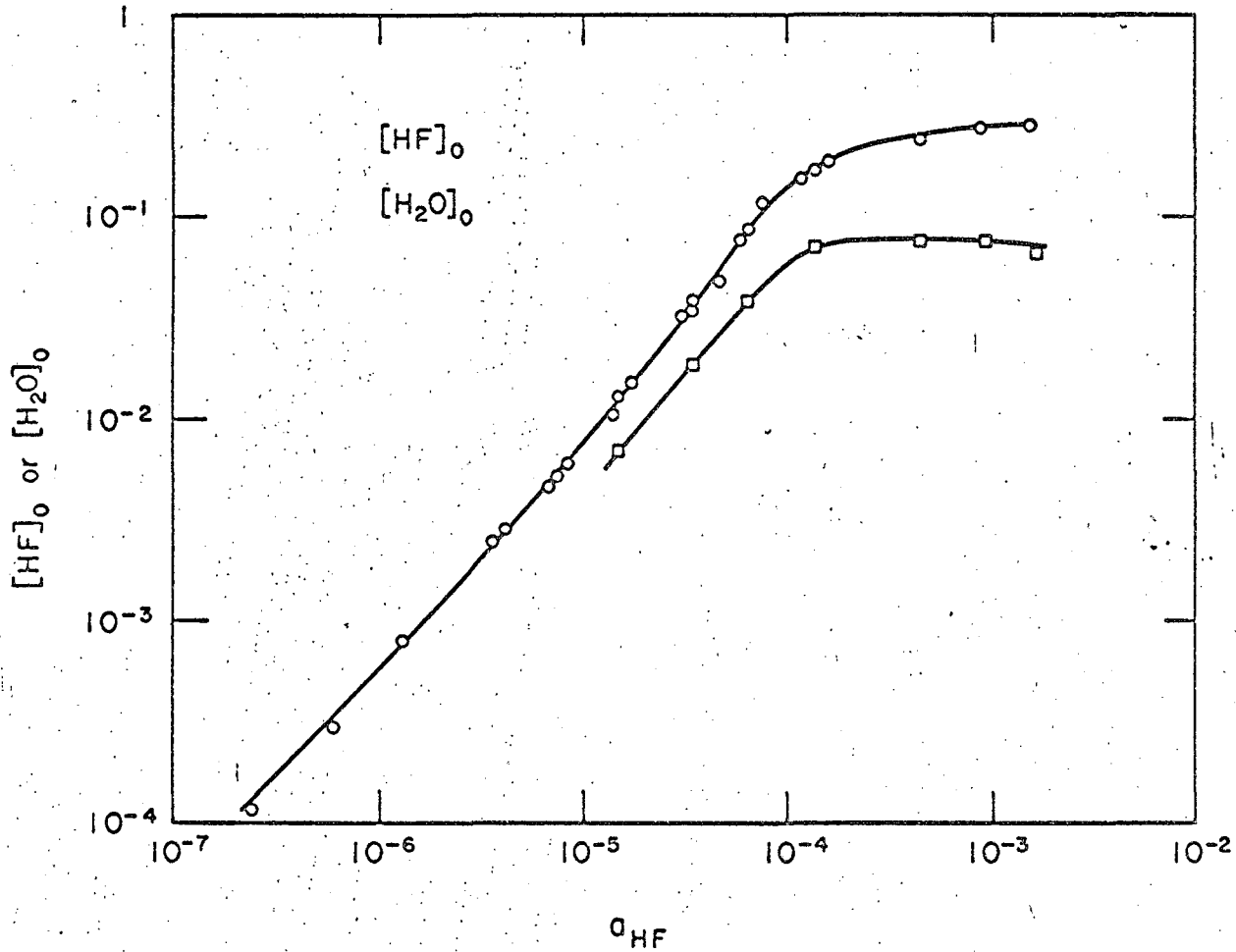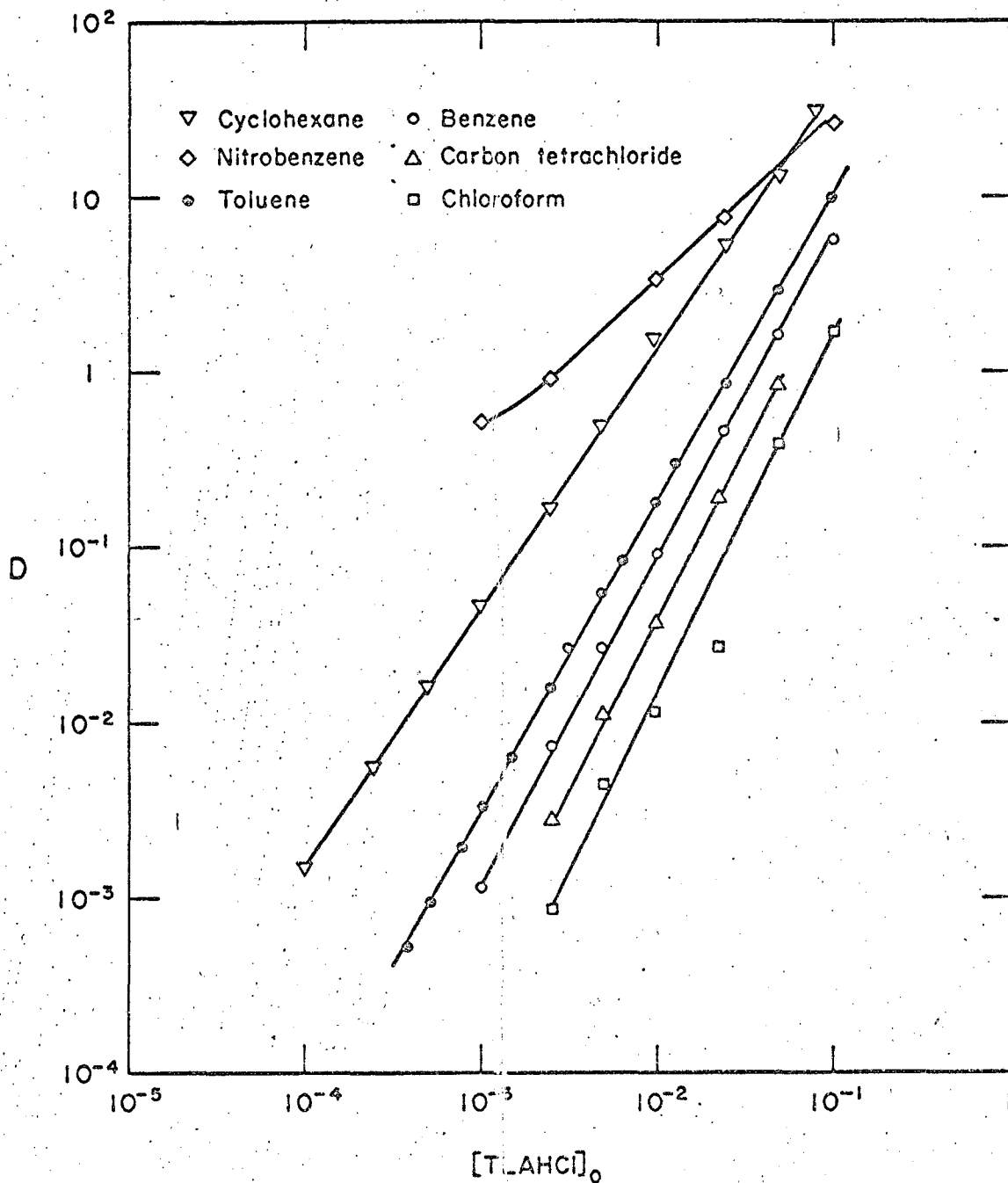Fig. 6                                    MUB-6922

Fig. 7

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Fig. 8

MUB-6923

Fig. 9          MUB-6926

Fig. 10

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