Submitted to Journal of Physical Chemistry

UCRL-19599
Preprint

RECEIVED
LAWRENCE
RADIATION LABORATORY

JUN 23 1970

LIBRARY AND
DOCUMENTS SECTION

EXTRACTION OF HBr, HCl AND HNO_3 BY TRIOCTYLPHOSPHINE OXIDE IN NITROBENZENE AND IN 1,2-DICHLOROETHANE

J. J. Bucher, E. R. Held, J. A. Labinger,
B. A. Sudbury, and R. M. Diamond

May 1970

AEC Contract No. W-7405-eng-48

TWO-WEEK LOAN COPY

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

UCRL-19599

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

DISCLAIMER

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

EXTRACTION OF HBr, HCl AND HNO_3 BY TRIOCTYLPHOSPHINE OXIDE IN NITROBENZENE AND IN 1,2-DICHLOROETHANE[1]

J. J. Bucher, E. R. Held,[2] J. A. Labinger,[3] B. A. Sudbury[2] and R. M. Diamond

Lawrence Radiation Laboratory
University of California
Berkeley, California 94720

May 1970

Abstract

The extraction of HBr, HCl and HNO_3 into solutions of trioctylphosphine oxide (TOPO) in either nitrobenzene or 1,2-dichloroethane has been studied. When the organic-phase stoichiometric ratio $TOPO/H^+$ was > 2, the extracting species was a dissociated two-TOPO acid complex for HBr and HCl. Below the same stoichiometric limit and below an aqueous HNO_3 activity of 10^{-3}, the same two-TOPO acid complex was found for HNO_3; above aqueous activities of 10^{-3}, increasing amounts of "extra" HNO_3 extracts. The organic-phase cation complex was considered to be the same as the anhydrous one found previously in the TOPO extraction of $HReO_4$ and $HClO_4$ in the same two diluents. Consequently the coextracted water is assumed to be associated with the anions. The resulting organic-phase "hydration" numbers are: 1.9 for Br^- and 3 for Cl^- in both diluents; and ~ 2 for NO_3^- in nitrobenzene. The order of extractability was HNO_3 > HBr > HCl.

In the first part of this study of mineral acid extraction by tri-n-octylphosphine oxide (TOPO), it was shown that $HReO_4$ or $HClO_4$ was extracted into dilute TOPO solutions in nitrobenzene or in 1,2-dichloroethane as a dissociated and anhydrous species.[4] The cationic portion of the acid complex consisted of two TOPO molecules solvating a bare proton, e.g., $2TOPO \cdot H^+$. It was of interest to extend this study of acid extraction by TOPO to other acids. If they involved this same cation, it would be possible to determine the hydration of the anion in these organic media, as any coextracted water can then be attributed to the dissociated anion. If, on the other hand, acids with progressively more basic anions are used, for example the HBr, HCl, and HNO_3 employed in the present study, there is a possibility that the nature of the extracted species may change from a pair of dissociated ions to an associated molecular adduct, such as the 1:1 complex, TOPO·HX.

Experimental

Reagents.——The TOPO used was obtained from Carlisle Chemical Corp., Reading, Ohio. After washing the raw TOPO with mild base and water, it was recrystallized four or five times from warm pentane. Solutions of HCl were prepared from 37% Baker reagent grade HCl, and the HNO_3 solutions from 71% Baker reagent grade HNO_3. Solutions of HBr were made from 48% Baker and Adamson reagent grade HBr after the following purification. The HBr was saturated with H_2S gas to reduce any Br_2 to HBr and then distilled. The constant-boiling fraction (48% HBr) was collected. This stock solution and all other HBr dilutions were kept in amber-glass bottles. Standardization of these solutions was done with sodium hydroxide to the bromothymol blue end-point. Tracer solutions of $^{82}Br^-$ were prepared by irradiating a few milligrams of LiBr with neutrons in the Vallecitos Test Reactor and dissolving the product in distilled water treated with H_2S. Tracer solutions of

$^{38}Cl^-$ were prepared by irradiating a few milligrams of NH_4Cl with neutrons in the Mark III Triga Berkeley Research Reactor, and then dissolving the salt in distilled water. The NH_4Cl used in the irradiation was made from gaseous NH_3 and HCl, as the commercial reagents were too high in sodium content. Eastman White label nitrobenzene and "spectro grade" Matheson, Coleman and Bell 1,2-dichloroethane were used. Matheson, Coleman and Bell stabilized and premixed single-solution Fischer reagent was used for the water titrations.

Procedures.—Standardized solutions of either HBr or HCl containing radioactive $^{82}Br^-$ or $^{38}Cl^-$ were shaken for not less than one hour for HBr and one-half hour for HCl with various TOPO solutions. These shaking times were determined to be sufficient to reach equilibrium. After centrifugation, aliquots of both the organic and aqueous phases were taken for γ-counting in a well-type Na(Tl)I scintillation counter. Knowing the original concentration of acid and the total number of counts of tracer added, the measured counting rates yield the equilibrium concentrations of HBr or HCl in each phase. Correction of the $^{38}Cl^-$ tracer data to a consistent time base was made to compensate for the short half-life (37.1 minutes) of this tracer. Where sufficient acid extracted, acid-base titrations were also used to determine the equilibrium acid content of each phase. Acid-base titrations were exclusively used for determination of HNO_3 extractions because of the lack of a suitable tracer for this acid. The amount of water co-extracted with HBr, HNO_3 and HCl was analyzed for by the Karl Fischer method, using a dead-stop end-point. All experimental work was done at room temperature, 23° ± 2°C.

Results and Discussion

The experimental results are shown in Figs. 1 - 10. Raw data are usually indicated by circles connected by solid lines; experimental data corrected, as described below, are usually indicated by square symbols connected by dashed lines.

TOPO-H_2O.—The extraction of water by TOPO in the two diluents has already been presented and discussed in an earlier paper.[4] Essentially 1.3 and 1.0 moles of H_2O extract per mole of TOPO in nitrobenzene and in 1,2-dichloroethane, respectively, at the temperature used (23 ± 2°C) and in the concentration range studied.

TOPO-HX-H_2O.—Since the dielectric constants of both nitrobenzene (ε = 34.8 at 25°C)[5] and 1,2-dichloroethane (ε = 10.4 at 25°C)[5] are relatively high, only the expression for HX extraction by TOPO into dissociated species will be considered,

$$H^+ + X^- + xH_2O + nTOPO\ (org) = H^+\cdot nTOPO\cdot wH_2O\ (org) + X^-\cdot(x-w)\ H_2O\ (org) \quad . \quad (1)$$

The corresponding equilibrium constant is,

$$\mathcal{K}_n^d = \frac{[H^+\cdot nTOPO\cdot wH_2O]_0[X^-\cdot(x-w)H_2O]_0 y_\pm^2}{[TOPO]_0^n\ y_{TOPO}^n (H_2O)^x\ (H^+X^-)} = K_n^d\ \frac{y_\pm^2}{y_{TOPO}^n} \quad , \qquad (2)$$

where parenthesis signify activity, brackets denote molar concentrations, y is a molar activity coefficient, and K_n^d is a mixed concentration quotient. Equation (2) implies that a log-log plot of the organic-phase acid concentration,

$[H^+]_0$, vs. the half-power of the aqueous-phase acid activity should yield a straight line with a slope of unity for a constant value of equilibrium TOPO concentration. Such plots are shown in Figs. 1 - 3 for 0.20 and 0.10 M TOPO and HBr in nitrobenzene (Fig. 1); for 0.25, 0.10 and 0.020 M TOPO and HCl in 1,2-dichloroethane (lines 2, 3 and 4 in Fig. 2) and 0.50 M TOPO and HCl in nitrobenzene (line 1, Fig. 2); and for 0.50, 0.283, 0.116, 0.050 and 0.010 M TOPO and HNO_3 in nitrobenzene (Fig. 3). (Molar activity coefficients used to calculate the aqueous HBr, HCl and HNO_3 activities were taken from a compilation by Gazith.[6]) It can be seen that the initial slope of the curve for each TOPO concentration in Figs. 1 and 2 is one, but may depart from unity in some instances at higher organic-phase concentrations. The square points are corrected both for the TOPO used-up in forming the extraction complex and for the organic-phase activity coefficients. Correction of the organic-phase acid concentrations from the equilibrium TOPO concentrations to a constant (initial) TOPO value is by means of the expression:

$$[H^+]_0' y_\pm' = [H^+]_0 y_\pm \frac{[TOPO]'}{[TOPO]} \quad , \tag{3}$$

where the primed quantity refers to the initial concentration and the first power dependence on the TOPO concentration will be justified later. Activity coefficients in the organic phase were calculated from the Mayer-Poirier expression.[7] For nitrobenzene, a distance of closest approach, a, of 6 Å was used. For 1,2-dichloroethane, the calculated activity coefficients were used for acid concentrations up to 10^{-3} M. For organic-phase concentrations much beyond 10^{-3} M, the calculated activity coefficients appeared to become too small. Consequently, we have applied a set of activity coefficients based upon the data for TOPO-$HReO_4$-1,2-dichloroethane from a previous paper.[4] That is, we

have taken as coefficients the values necessary to bring the $HReO_4$ data onto a smooth straight line of proper slope determined by the points below 10^{-3} M. These empirical activity coefficients were, indeed, larger and yielded straight lines of unit slope with the present extraction systems also. Some justification for this procedure, besides the fact that it appears to work, is obtained from the paper of Inami and Ramsey.[8] These workers demonstrated clearly that the mole ratio of gauche (polar form) to trans (non-polar form) 1,2-dichloroethane is significantly greater when salt solutions are introduced than the value in pure 1,2-dichloroethane. This result suggests the effective dielectric constant near ions is probably somewhat higher than indicated by the measured value for the pure diluent. Since the Mayer-Poirier calculation is quite sensitive to the dielectric constant value used, especially for lower values such as that of 1,2-dichloroethane, a change in it of a few units can drastically change the calculated activities. The empirical activity coefficients would indicate an effective dielectric constant of about 17-21 operating on the ions.

From the straight dashed lines of unit slope that can be drawn through the corrected points (and which are extensions of the lines of unit slope given by the data at lower concentrations where corrections are negligible) it is concluded from Figs. 1 and 2 that the extracting species with both HBr and HCl in these TOPO-diluent systems is dissociated. A dashed line of initial slope unity is drawn for most sets of data in Fig. 3, TOPO-HNO_3-nitrobenzene, and it can be seen that these lines do indeed connect the corrected data, but only if data below an aqueous HNO_3 activity of $\sim 10^{-3}$ are considered. Beyond an aqueous activity of $\sim 10^{-3}$, the considerably steeper slopes indicated by the corrected points might be thought to indicate ion pairing. Yet the deviations in slope

apparently depend upon the aqueous nitric acid activity and not upon the organic-phase concentrations. This is certainly contrary to the situation expected for ion pairing, which clearly increases with increasing organic-phase ion concentration. More likely the deviations result from the neglect of the well-documented[9] ease with which "excess" HNO_3 can add to already extracted nitrate. As a first step, this corresponds to the extraction of the binitrate ion, $H(NO_3)_2^-$ or $NO_3^- \cdot HNO_3$, but still higher anionic complexes have been suggested, e.g., $NO_3^- \cdot 2HNO_3$.[9] Since the data have been corrected for used-up TOPO on the premise that two TOPO molecules are involved per acid molecule extracted, the amount of equilibrium TOPO calculated is too low if significant amounts of $NO_3^- \cdot HNO_3$ are extracted. This leads to an overcorrection via Eq. (3) for the organic-phase acid concentration and hence to corrected curves with slopes greater than one. However, it is concluded that the extracting species, at the various TOPO concentrations used, for an aqueous HNO_3 activity $< 10^{-3}$ (little excess acid extracts) is dissociated. It is probable that the extracted species for aqueous HNO_3 activity $> 10^{-3}$ is also dissociated; for if the $2TOPO \cdot H^+ NO_3^-$ species is dissociated, that cationic species with the larger anion, $NO_3^- \cdot HNO_3$, is even more likely to be so. However, without knowing explicitly the amounts of the various possible anionic species present in the organic phase at each point, slope analysis of the region above an aqueous HNO_3 activity $> 10^{-3}$ in Fig. 3 does not give much information.

Having determined that the extracting acid complex is dissociated in each of the acid-TOPO-diluent systems studied (with the described limitation on the aqueous activity for HNO_3), it remains to determine the value of n, the number of TOPO molecules complexed per acid. From Eq. (2) the slopes of log-log plots of extracted acid vs. TOPO concentration at a constant aqueous acid

activity (a_{HX}) should yield directly the value of n/2. Figure 4 is such a plot for aqueous solutions of 0.47 (line 1), 0.085 (line 2) and 0.0043 M HBr (line 3) with nitrobenzene as the diluent. Similarly, Fig. 5 is for 0.10 and 1.0 M HCl and TOPO in 1,2-dichloroethane; and Fig. 6 shows acid extraction for 0.127 and 0.0349 M HNO_3 and nitrobenzene. As before, the square points indicate corrections for organic-phase activity coefficients and for equilibrium aqueous acid concentrations when different from the initial values. The slopes of the dashed lines through the points not needing correction and the corrected points are unity indicating n = 2; two TOPO molecules are involved in the extracted species for TOPO concentrations up to $\sim$ 1.0 M for HBr-TOPO-nitrobenzene, (Fig. 4), and up to $\sim$ 0.5 M for HCl-TOPO-1,2-dichloroethane, (Fig. 5). As before, the TOPO-HNO_3-nitrobenzene system (Fig. 6) is less simple in behavior. With data obtained at an aqueous acid concentration (0.0349 M) low enough to yield little excess extracted HNO_3, curve 3, the dashed line through the corrected points has the expected slope of unity, and again it is concluded two TOPO molecules are involved in the extracted species. The set of data shown by curve 1 corresponds to an initial HNO_3 concentration of 0.127 M, and at this higher aqueous activity most of the extracted nitrate is probably converted to binitrate. The initial TOPO concentrations are therefore corrected to equilibrium concentrations assuming the organic-phase acid complex is all binitrate (i.e.; one TOPO molecule per extracted nitric acid is used up in the complex), and the organic-phase activity coefficients used were for organic-phase concentrations of half of the indicated stoichiometric acidity. This correction of the data is shown by the dashed line 2 in Fig. 6. The reasons for the downward deviation of data at high TOPO concentrations are not clear to us. It should, however,

be noted the spacing between the data of curve 3 and the uncorrected data of curve 1 is already too great by a factor of 1.5 if only a NO_3^- complex is assumed to be extracted, and this is consistent with the proposal that excess nitric acid is being extracted. With either nitrate or binitrate anions, however, the slopes in Fig. 6 indicate that only a 2TOPO cation is involved, at least below 0.1 M TOPO.

To evaluate K_n^d, a log-log plot (Fig. 7) of the square-root of the numerator in Eq. (2) vs. the square-root of the denominator (the square-roots were taken to halve the number of decades used) is employed. This plot combines previous data from Figs. 1, 2, 4 and 5, and data later used in the water stoichiometry determinations, for TOPO-HBr in both nitrobenzene and 1,2-dichloroethane and for TOPO-HCl in 1,2-dichloroethane. The excellent fits to straight lines of unit slope indicate these three systems can indeed be described by a single dissociated, two-TOPO organic-phase species. Values for these systems and for TOPO-HNO_3-nitrobenzene for aqueous HNO_3 activity $< 10^{-3}$ are presented in Table I.

Table I. Equilibrium quotients for extraction of HBr, HCl and HNO_3.

Diluent	Acid	K_2^d
Nitrobenzene	$HReO_4$[a]	$1._2 \times 10^{+3}$
	HBr	$1._1 \times 10^{-1}$
	HNO_3	$1._5$
1,2-dichloroethane	$HReO_4$[a]	$9._6$
	HBr	$4._4 \times 10^{-3}$
	HCl	$2._5 \times 10^{-4}$

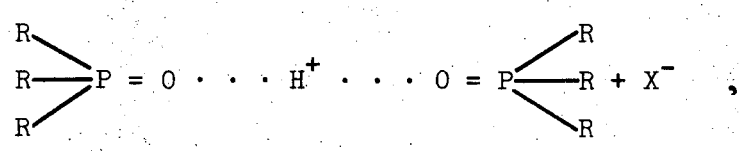
[a]From Ref. 4.

For 0.30 M TOPO in nitrobenzene and in 1,2-dichloroethane the amount of water, less the diluent water, coextracted by the organic-phase HBr complex as the acid concentration increases is shown in Fig. 8. In both diluent systems the total amount of water decreases as $[H^+]_0$ increases. The amount of water extracted by the equilibrium amount of uncomplexed TOPO must be subtracted; this concentration of non-acid-bound TOPO is calculated as $[TOPO]_{total} - 2[H^+]_0$. After correction of the extracted water for the amount of water bound by this uncomplexed TOPO, curve 3 results for both diluent systems. The slope suggests an average of 1.9 molecules of H_2O are coextracted by HBr. Similar data are presented for HCl extracted by 0.25 M TOPO in 1,2-dichloroethane (Fig. 9); for both HCl and HNO_3 extracted by 0.5 M TOPO in nitrobenzene and for 0.116 M TOPO-nitrobenzene and HNO_3 (Fig. 10). The initial slope for the corrected data in Fig. 9 is about 3 and becomes somewhat less as $[H^+]_0$ increases (curve 3). Curve 2 illustrates an attempt to further correct the data by taking into account the significant change of water activity resulting from the aqueous acid concentrations necessary to cover the range of $[H^+]_0$ considered. That is, the amount of water extracted is corrected by a factor, in this case the water activity to the third power, and the resulting curve has a slope close to 3 (curve 2).

The data in Fig. 10 fortunately do not need correction for water activity changes and yield directly a slope of three for HCl-nitrobenzene (curve 1'), the initial slope of two for 0.5 M TOPO-HNO_3-nitrobenzene (curve 2'), and a slope approximately zero for 0.116 M TOPO-HNO_3-nitrobenzene (curve 3). Line 2' is established assuming the principal species is the nitrate complex, since $a_{HNO_3} < 10^{-3}$; curve 3' results from the assumption the principal species present is the binitrate complex ($a_{HNO_3} > 10^{-3}$), as suggested from the aqueous acid variation data in Fig. 3.

Conclusions

At all organic-phase concentrations in nitrobenzene observed in this study (up to 10^{-1}M) and at values of $[H^+]_0$ up to $\sim 10^{-1}$ M in 1,2-dichloroethane for each of the various acid-diluent combinations, the extracted acid species is dissociated. The experimentally determined value of two for the number of TOPO molecules coordinated to the proton suggests the dissociated extraction complex is the same as found previously for $HReO_4$ or $HClO_4$ extraction,[4]



where X^- may be Br^-, Cl^- or, if the aqueous HNO_3 activity is less than $\sim 10^{-3}$, NO_3^-; beyond this aqueous activity increasing amounts of $NO_3^- \cdot HNO_3$ are suggested to occur in the organic phase. We do not know if the cation is symmetric or asymmetric about the proton.

Since this $2TOPO \cdot H^+$ cation was found to be anhydrous when $HReO_4$ or $HClO_4$ was extracted, the coextracted water found in each diluent-acid system in this study is thought most likely to be associated with the anion. Thus Br^- would have 1.9 molecules of water in either nitrobenzene or 1,2-dichloroethane, and Cl^- would have 3. Nitrate ion has $\sim$ 2 waters associated with it (line 2', Fig. 10), while $NO_3^- \cdot HNO_3$, probably the significant species in the data of line 3', Fig. 10, appears to be anhydrous; both of these last assignments have more uncertainty than is the case with Cl^- or Br^-, due to the probable presence of a small amount of the other (nitrate) species.

What do these hydration numbers mean? The numbers are small enough to certainly represent first-shell solvation of the anions. And they probably are a lower limit to the aqueous-phase coordination numbers for two reasons. One is that in water the water molecules bound to the anion will be stabilized by hydrogen-bonding to water molecules farther out in the bulk medium. The other is that we do not know whether the value found in this work for an ion represents the average for a number of species or not; that is, does the value 3 for Cl^- mean that essentially all extracted Cl^- ions have 3 water molecules, or that there is a mixture of 2- and 4- coordinated species giving an average number of three, or a mixture of 1-, 2-, 3-, 4- coordinated species, etc.? But it is interesting that for Cl^- and Br^- where data in both solvents are available, the same number is obtained. For chloride this appears to be true even when compared with an ion-paired species in CCl_4. A study[10] of HCl extraction by tributylphosphine oxide in CCl_4 gives for the extracted species the proportions 2.1:1.08:3.2 for TBPO:HCl:H_2O. In addition, the authors claim that infra-red evidence suggests that the proton is not hydrated to a hydronium ion.

A few other studies of strong acids by TOPO or the related compound tributylphosphine oxide (TBPO) have been reported in the literature besides the already cited work with HCl. Direct comparison with the present work is not usually possible. For example, the extraction of HNO_3 by TBPO in the low dielectric constant solvent benzene[11] or by TOPO in cyclohexane[12] suggests that only the molecular nitric acid complex is formed, TOPO·HNO_3. Only inconclusive evidence that nitric acid may be extracted in an ionized form is given in a study of methylenebis (di-n-hexylphosphine oxide) in o-dichlorobenzene (a relatively high dielectric solvent, $\varepsilon = 9.9$ at 25°C)[13] and in CCl_4[14] where possibly

a coordination number greater than one is observed. We believe it likely that only in high-dielectric-constant diluents do conditions exist which will allow the moderately basic nitrate ion to free itself from the proton and form an ionized species with a TOPO cation, rather than an adduct of molecular HNO_3 with TOPO.

The order of extractability, as reflected by the extraction quotients in Table I, is reasonable. Of the ions studies, Cl^- (as illustrated by the above organic-phase hydration numbers) needs solvation the most and so is the most highly hydrated; consequently it is the least easily transferred into the water-poor organic phase. Bromide ion is somewhat larger, needs solvation less, and so is more easily transferred from water into the organic phase. Nitrate is still larger, and from its size alone should extract still better, but it is also a significantly stronger base than Br^- and this property may necessitate more hydration than would be expected for a monatomic anion of comparable size. These two effects almost compensate; the extraction of NO_3^- is only an order of magnitude better than that of Br^-. In contrast, the extraction of ReO_4^-, a still larger anion but also a weakly basic one, is about four orders of magnitude larger than that of Br^-.

Footnotes and References

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Undergraduate summer visitor, 1968.

(3) Undergraduate summer visitor, 1967.

(4) J. J. Bucher, T. J. Conocchioli and R. M. Diamond, to be published, this journal (1970); Lawrence Radiation Laboratory Report UCRL-19556, March (1970).

(5) A. A. Maryott and E. R. Smith, Table of Dielectric Constants of Pure Liquids, NBS Circular 514, 1951.

(6) M. Gazith, Compiled and Calculated Molal and Molar Activity Coefficients of Various Electrolytes, Israel Atomic Energy Commission Report, IA-1004 (Oct. 1964).

(7) J. C. Poirier, J. Chem. Phys. 21, 965 (1953).

(8) Y. H. Inami and J. B. Ramsey, J. Chem. Phys. 31, 1297 (1959).

(9) Y. Marcus and A. S. Kertes, Ion Exchange and Solvent Extraction of Metal Complexes, (Wiley-Interscience, New York, 1969), p. 673 and references therein.

(10) G. P. Nikitina and M. F. Pushlenkov, Radiokhimiya 5, 445 (1963).

(11) J. Goffart, L'Extraction Liquide-Liquide des Lanthanides et des Actinides par les Oxydes D'Alkylphosphine et les Bis-(Di-alkylphosphinyl)-Alcanes, Thesis, University of Liége, 1968; J. Goffart and G. Duyckaerts, Anal. Chim. Acta. 39, 57 (1967).

(12) J. C. White and W. J. Ross, Nucl. Sci. Ser., NAS-NS 3102 (1961).

(13) J. E. Mrochek, J. W. O'Laughlin, H. Sakurai and C. V. Banks, J. Inorg. Nucl. Chem. 25, 955 (1963).

(14) J. W. O'Laughlin, D. F. Jensen, J. W. Ferguson, J. J. Richard and C. V. Banks, Anal. Chem. 40, 1931 (1968).

Figure Captions

Fig. 1. Variation of organic-phase acid content with the half-power of the aqueous HBr activity for 0.20 (line 1) and 0.010 (line 2) TOPO in nitrobenzene; ● - denotes uncorrected data and □ gives data corrected for complexed TOPO and for activity coefficients of the organic-phase acid. The dashed line and line 2 are drawn with unit slopes.

Fig. 2. Variation of organic-phase acid content with the half-power of the aqueous HCl activity for 0.50 M (line 1) TOPO in nitrobenzene; and for 0.25, (line 2), 0.10 (line 3) and 0.20 M (line 4) TOPO in 1,2-dichloroethane. ●, denotes uncorrected data; □, gives data corrected for complexed TOPO and for activity coefficients of the organic-phase acid. Dashed lines are drawn with unit slope.

Fig. 3. Variation of organic-phase acid content with the half-power of the aqueous HNO_3 activity for 0.50 (line 1), 0.28_3 (line 2), 0.11_6 (line 3), 0.050 (line 4) and 0.010 M (line 5) TOPO in nitrobenzene. ●, denotes uncorrected data; □, denotes data corrected for complexed TOPO (see text) and for activity coefficients of the organic phase. Large-dash lines are drawn with slope unity.

Fig. 4. Variation of organic-phase acid content with TOPO concentration in nitrobenzene for aqueous HBr concentrations of 0.482 (line 1), 0.0852 (line 2) and 0.00427 M (line 3) HBr. ●, denotes uncorrected data; □ is data corrected for used-up HBr and for organic-phase activity coefficients. Dashed lines are drawn with unit slope.

Fig. 5. Variation of organic-phase acid content with TOPO concentration in 1,2-dichloroethane for aqueous HCl concentrations of 1.0 (line 1) and

0.10 M (line 2) HCl. ●, denotes uncorrected data; □ is data corrected for used-up HCl and for organic-phase activity coefficients. Dashed lines are drawn with unit slope.

Fig. 6. Variation of organic-phase acid content with TOPO concentration in nitrobenzene for aqueous HNO_3 concentrations of 0.127 (line 1) and 0.0349 M (line 3) HNO_3. ●, denotes uncorrected data; □, is data corrected for used-up HNO_3, activity coefficients and estimated equilibrium TOPO concentrations (see text). Dashed lines are drawn with slope unity.

Fig. 7. Variation of square-root of the organic-phase acid activity vs. the product $\{[TOPO]_0^2 (HX)\}^{1/2}$. Line 1 is for TOPO-HBr-nitrobenzene; line 2 is for TOPO-HBr-dichloroethane; and line 3 is for TOPO-HCl-1,2-dichloroethane. Lines are drawn with unit slope.

Fig. 8. Water content vs. HBr organic-phase concentration (as the aqueous HBr concentration increases) for a total TOPO concentration of 0.30 M in nitrobenzene and 1,2-dichloroethane. Lines 1 and 2 are the total organic-phase water less diluent water for nitrobenzene and 1,2-dichloroethane respectively. Line 3 is the total organic-phase water less both the diluent water and water bound to TOPO for both diluents; ▲, 1,2-dichloroethane; □, nitrobenzene.

Fig. 9. Water content vs. HCl organic-phase concentration (as the aqueous HCl concentration increases) for a total TOPO concentration of 0.25 M in 1,2-dichloroethane. Line 1 is the total organic-phase water less diluent water; line 3 is the total organic-phase water less both diluent water and water bound to TOPO; and line 2 (▲) is a third power correction for decreased water activity.

Fig. 10. Water content vs. HCl and HNO_3 concentration in the organic phase (as the aqueous HCl and HNO_3 concentration increases) for a total TOPO concentration of 0.50 M and 0.11_6 M TOPO in nitrobenzene. Lines 1, 2 and 3 are the total organic-phase water less diluent water for 0.5 M TOPO, HCl, 0.5 M TOPO, HNO_3 and 0.11_6 M TOPO, HNO_3, respectively. Lines 1', 2' and 3' are the total organic-phase water less both the diluent water and the water bound to TOPO for the above TOPO-acid combinations respectively.

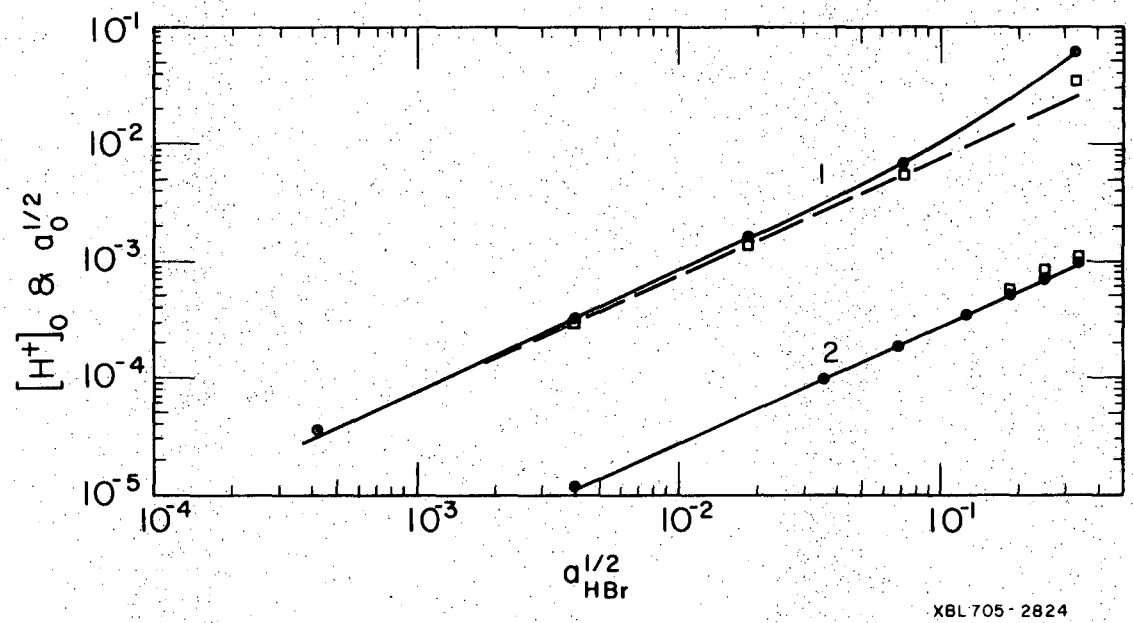

10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
$[H^+]_o$ & $a_o^{1/2}$
1
2
10^{-4}
10^{-3}
10^{-2}
10^{-1}
$a_{HBr}^{1/2}$
XBL 705-2824

Fig. 1

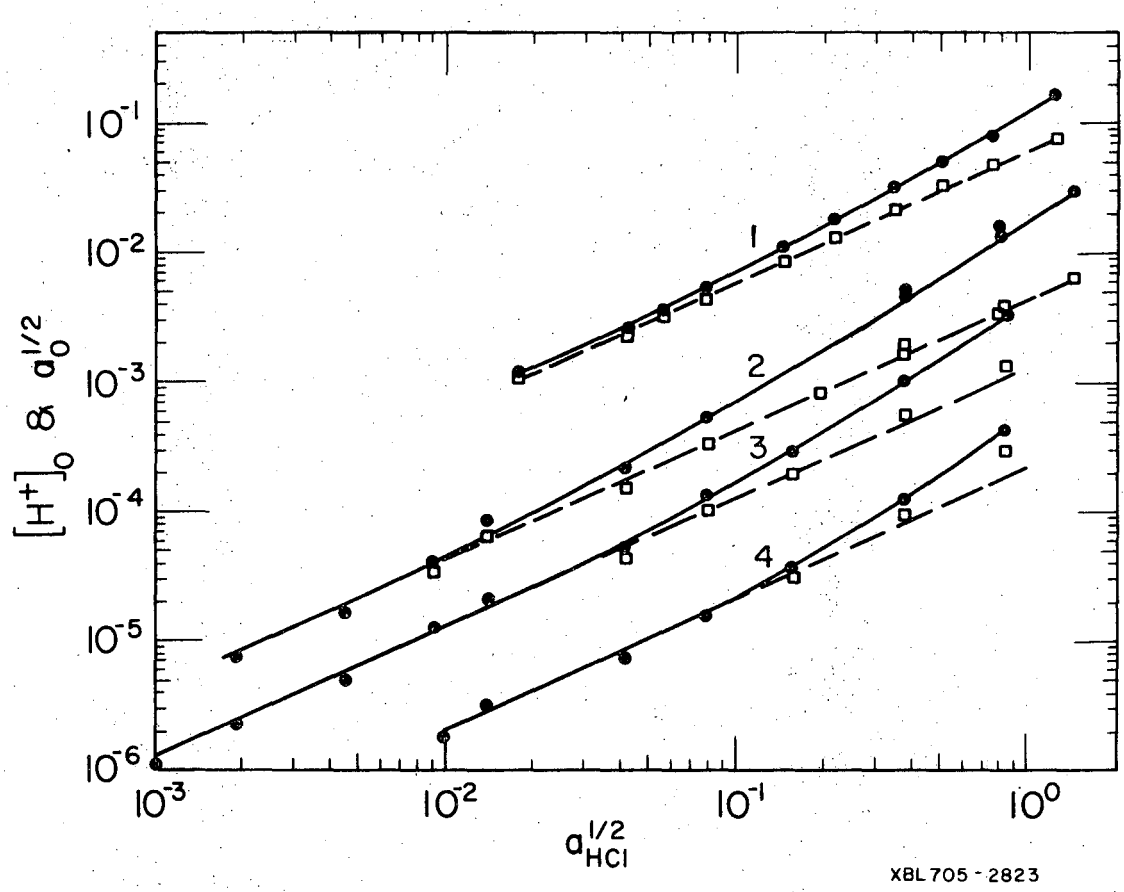

10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
$[H^+]_0$ & $a_0^{1/2}$
1
2
3
4
10^{-3}
10^{-2}
10^{-1}
10^{0}
$a_{HCl}^{1/2}$
XBL 705 - 2823

Fig. 2

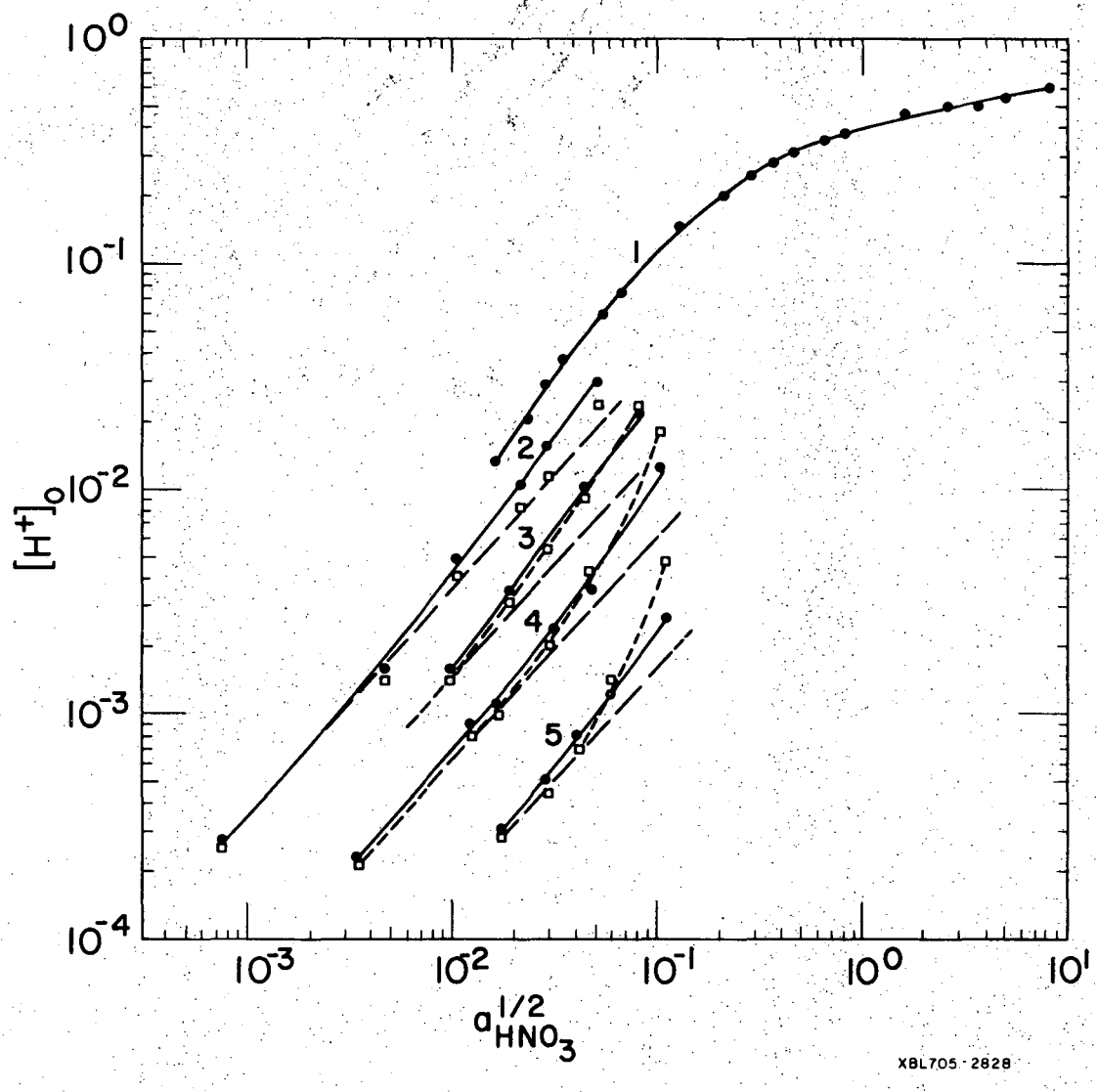

10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
$[H^+]_o$
1
2
3
4
5
10^{-3}
10^{-2}
10^{-1}
10^0
10^1
$a^{1/2}_{HNO_3}$
XBL705-2828

Fig. 3

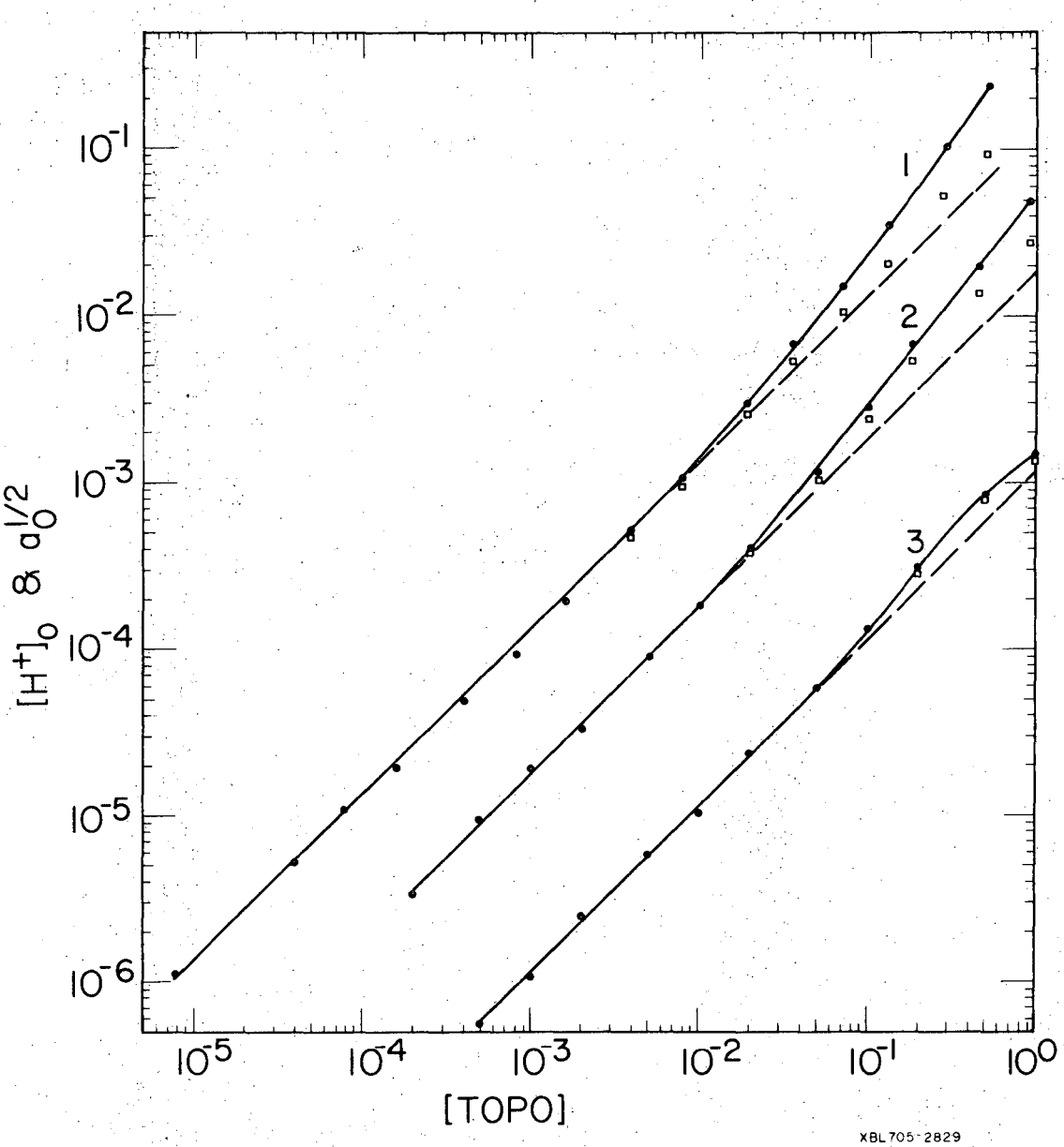

10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
$[H^+]_o$ & $a_o^{1/2}$
1
2
3
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}
[TOPO]
XBL705-2829

Fig. 4

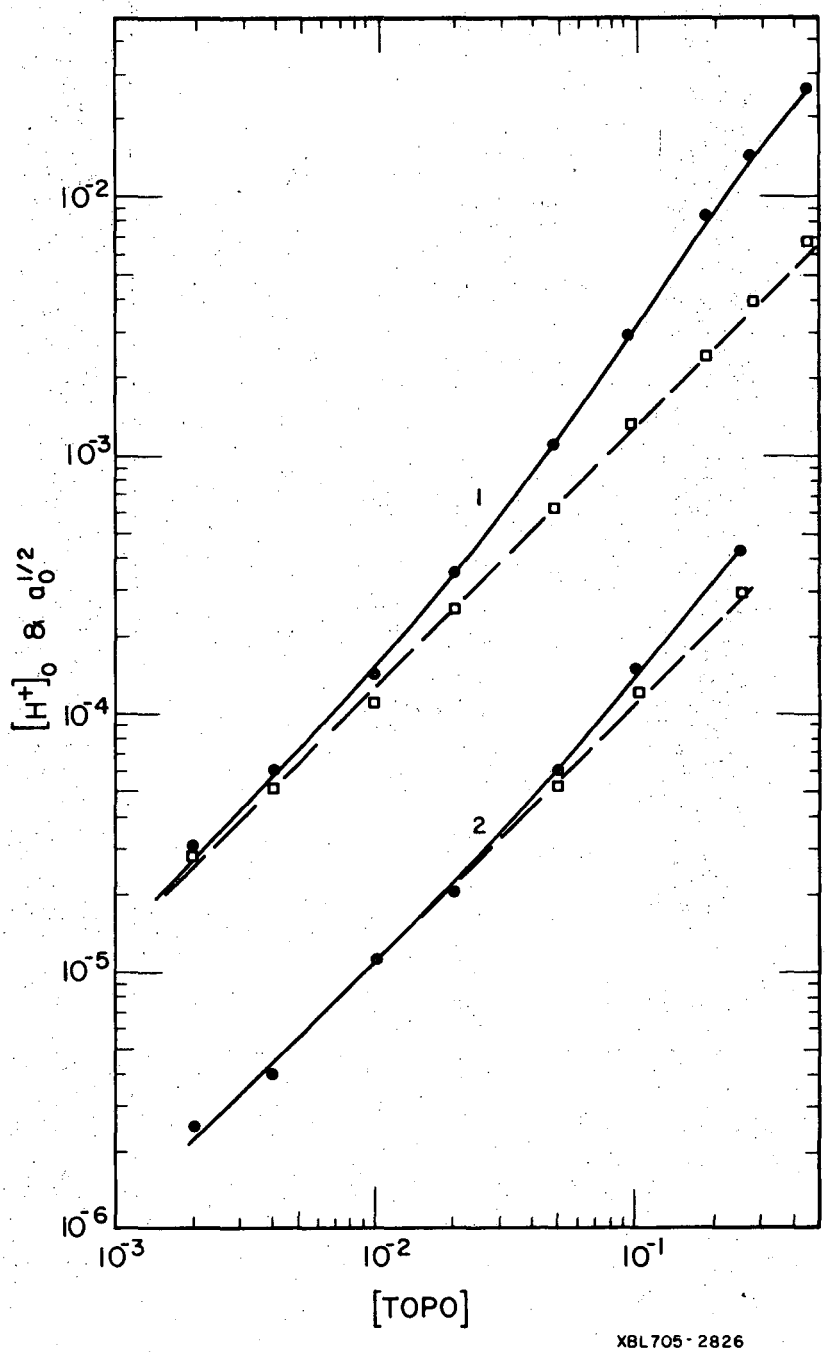


Fig. 5

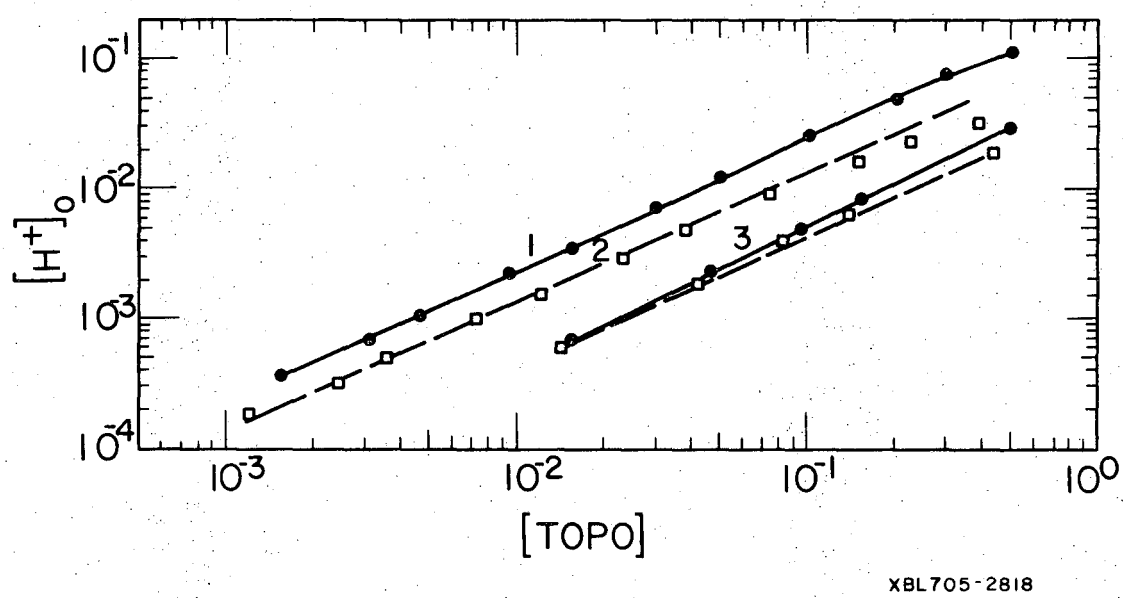


Fig. 6

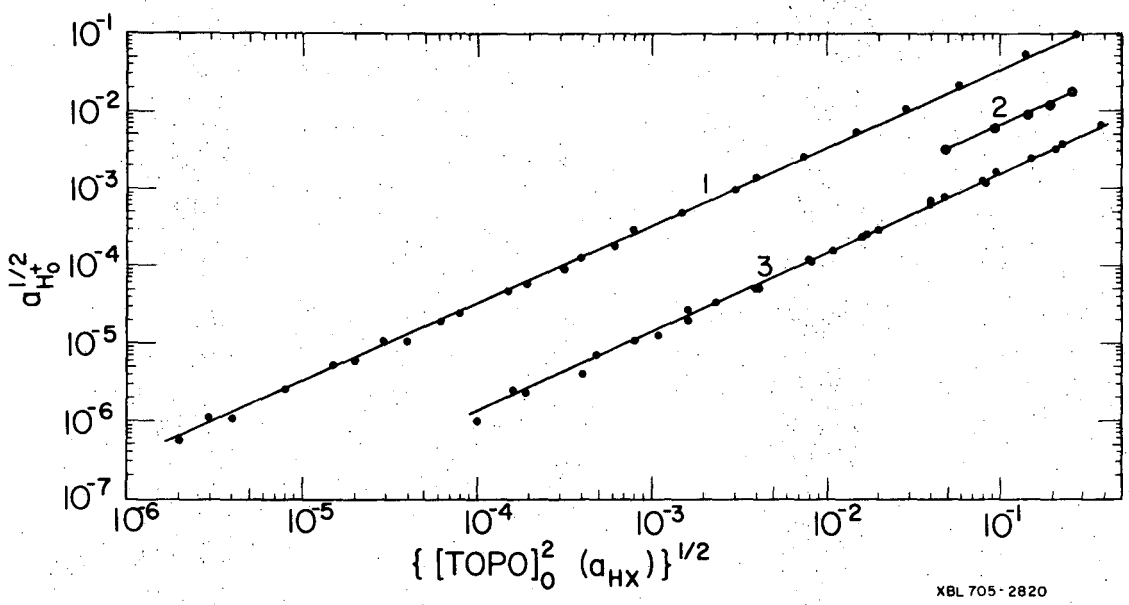

10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
$a_{H_o^+}^{1/2}$
1
2
3
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
$\{[TOPO]_o^2 \ (a_{HX})\}^{1/2}$
XBL 705-2820

Fig. 7

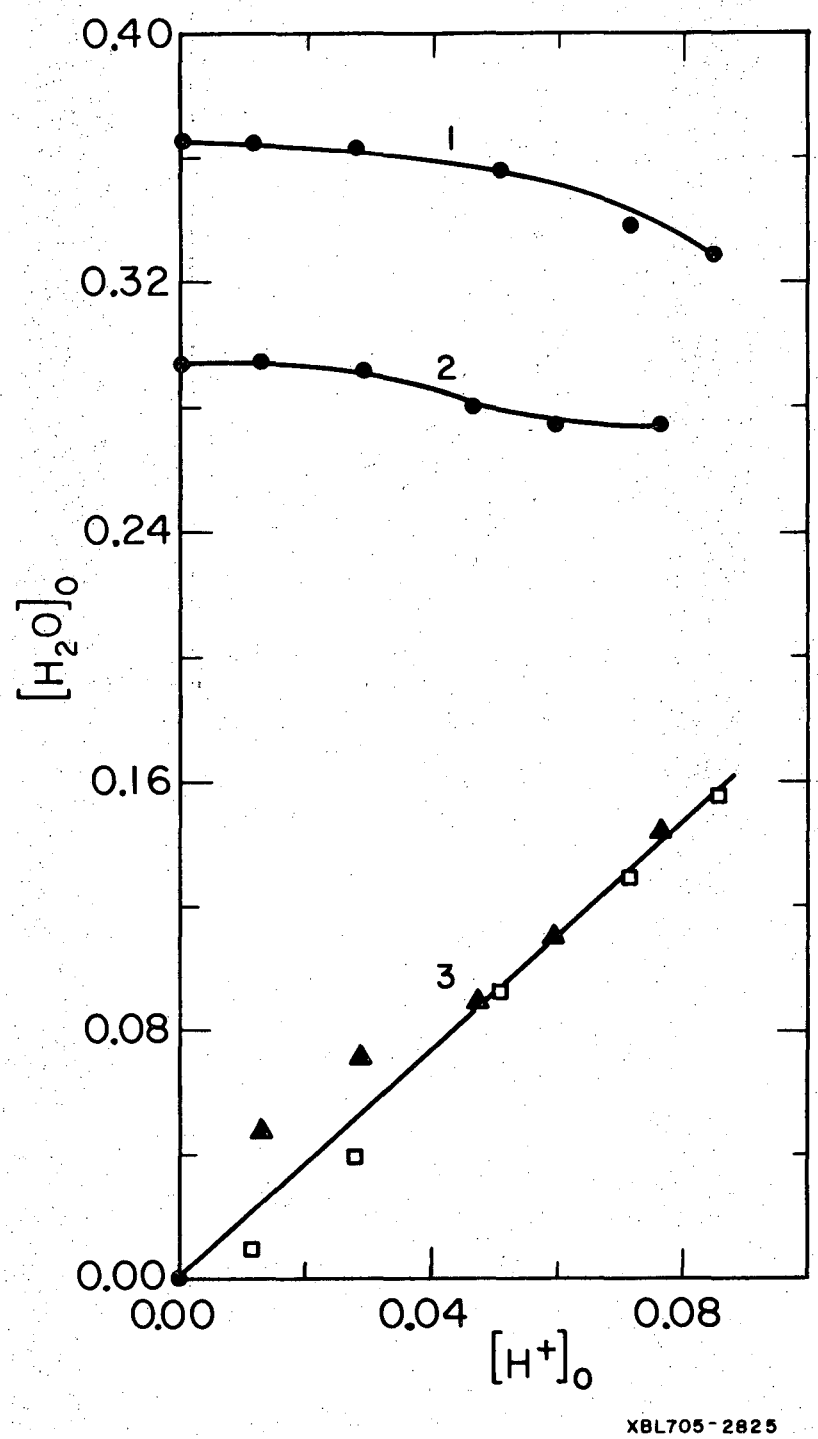


Fig. 8

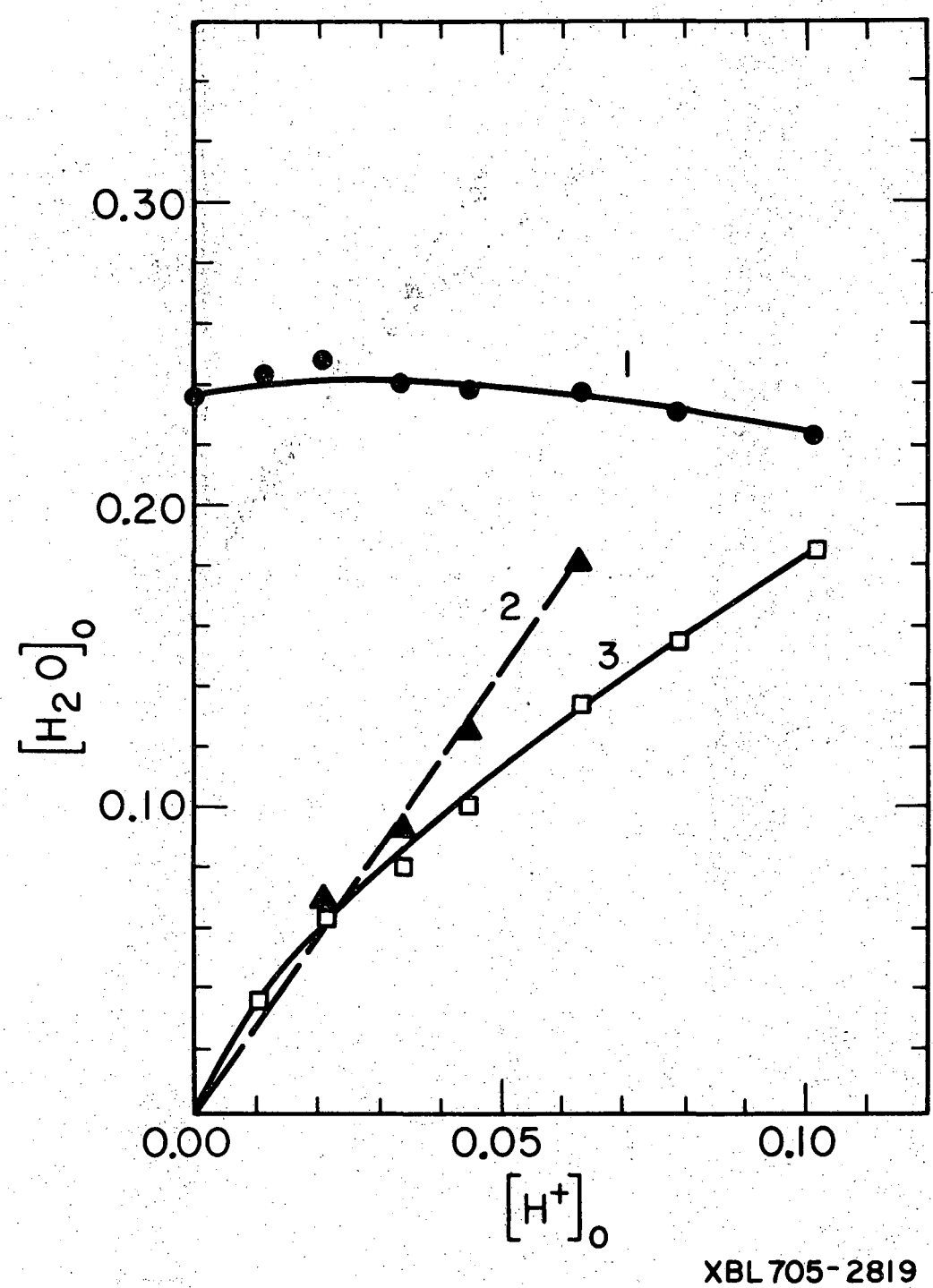


Fig. 9

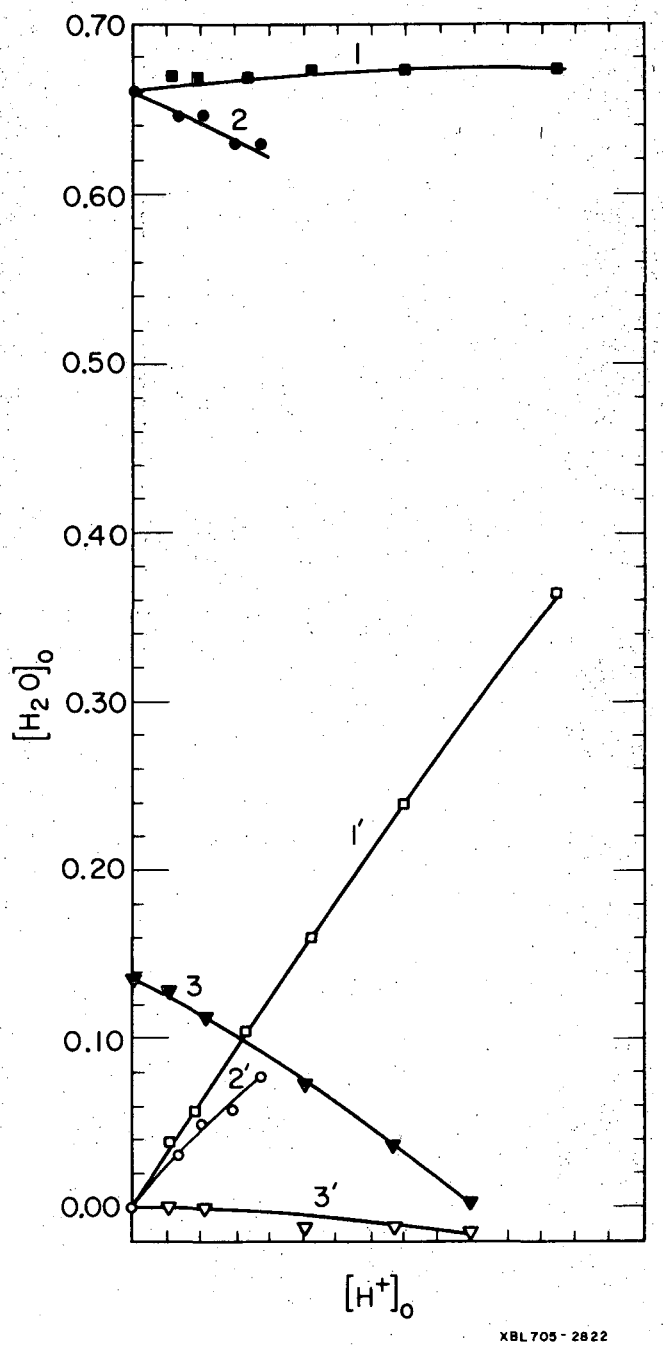


Fig. 10

LEGAL NOTICE

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

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

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

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

TECHNICAL INFORMATION DIVISION
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720