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EXTRACTION OF $HReO_4$, HNO_3, HBr AND HCl BY TRIOCTYLPHOSPHINE OXIDE IN NITROBENZENE AND IN 1,2-DICHLOROETHANE, AND HYDRATION OF THE ANIONS*

J. J. Bucher, T. J. Conocchioli†, E. R. Held††,
J. A. Labinger‡, B. A. Sudbury‡‡, and R. M. Diamond

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

February 1974

ABSTRACT

The extraction of $HReO_4$, HNO_3, HBr and HCl into solutions of trioctylphosphine oxide (TOPO) in either nitrobenzene or 1,2-dichloroethane has been studied. In both diluent systems when the stoichiometric ratio $TOPO/H^+$ was > 2, the extracting species was a two-TOPO acid complex, which was dissociated at lower organic-phase concentrations. The cation portion of the acid complex was found to be anhydrous. Consequently, the coextracted water is assumed to be associated with the anions. The resulting organic-phase "hydration" numbers are: 0.4 for ClO_4^- (ReO_4^-), 1.9 for Br^- and 3 for Cl^- in both diluents. The order of extractability was $HReO_4$ > HNO_3 > HBr > HCl, as expected.

INTRODUCTION

In two previous studies dealing with the extraction of $HReO_4$, $HClO_4$, and $HAuCl_4$ by dilute solutions of trioctylphosphine oxide (TOPO) in benzene, $CHCl_3$ [1]; CCl_4 and aliphatic hydrocarbons [2], the organic-phase acid cation was established to be a two-TOPO solvated proton, $2TOPO \cdot H^+$. This was either ion paired with the accompanying anion or still further aggregated in these low-dielectric diluents. The amount of coextracted water was always less than the amount of acid extracted (especially for the $HAuCl_4$ complexes). Clearly the TOPO was extracting a bare unhydrated proton, somewhat similar to the situation with the even more basic trialkylamine extractants. Comparison of the infra-red spectra [2] for these TOPO complexes with those of the less basic extractant tributyl phosphate (TBP), an extractant which does fit the hydronium ion-core model, revealed a totally different absorption pattern. Those peaks which we think are characteristic of a hydronium-ion-based acid complex (the spectra for TBP being representative) were absent in the TOPO spectra, while a new peak at much longer wavelength appeared. This result confirmed that the cationic portion of the TOPO-acid complex is very different from the hydronium-ion-based core of many TBP systems.

It was thus of interest to extend this study of acid extraction by TOPO to other acids, for if we can demonstrate that the same anhydrous cation is involved, then a determination of the coextracted water would indicate the amount of water bound to the anion. This would be particularly true if a diluent is used that allows dissociation of the cation-anion pair. So in addition to a study of $HReO_4$ or $HClO_4$ extraction by dilute TOPO solutions, acids with progressively more basic anions, namely HBr, HCl, and HNO_3, have been examined.

It is expected that the greater aqueous anion hydration for these latter acids will be reflected in decreased extraction into the organic-phase and increased amounts of co-extracted water. To prevent any aggregation beyond ion pairs and, in fact, to reduce the amount of ion pairing itself, 1,2-dichloroethane (ε = 10.4 [3] at 25°C) and nitrobenzene (ε = 34.8 [3] at 25°C) were used as diluents.

EXPERIMENTAL

A. 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 and HNO_3 were prepared from 37% Baker reagent grade HCl and from 71% Baker reagent grade HNO_3. The $HClO_4$ solutions were prepared by dilution from G. F. Smith reagent grade $HClO_4$, 70-72%, while $HReO_4$ solutions were made by dissolving Re_2O_7 (Varlacoid Chemical Company, 99.5% purity) in distilled water. 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 all these stock acid 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. The $^{186}ReO_4^-$ tracer was prepared by irradiating $KReO_4$ in the Vallecitos Test Reactor at a flux greater than 10^{14} neutrons/cm^2-sec for six days. A saturated

stock solution (∿ 0.04 M) was obtained by dissolving the irradiated $KReO_4$ sample in a minimum amount of water. 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 "spectra 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.

B. Procedures

Standardized solutions of HBr, $HReO_4$, or HCl containing radioactive $^{82}Br^-$, $^{186}ReO_4^-$, or $^{38}Cl^-$ tracers, respectively, were shaken for not less than one hour for the HBr and $HReO_4$ solutions and for only one-half hour for the HCl solutions with various TOPO-diluent 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, $HReO_4$, 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 sometimes 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 coextracted with HBr, HNO_3 and HCl was analyzed for by the Karl Fischer method, using a dead-stop end-point [4]. For 1,2-dichloroethane the concentration of bound water in the organic phase was also measured by means of tritiated water counted in a room-temperature liquid-scintillation counter. All experimental work was done at room temperature, 23° ± 2°C.

RESULTS AND DISCUSSION

The extraction of HX by TOPO solutions may be expressed:

$$H^+ + X^- + xH_2O + nTOPO(org) = \begin{cases} H^+\cdot nTOPO\cdot wH_2O\ldots X^-\cdot(x-w)H_2O(org) & (1a) \\ H^+\cdot nTOPO\cdot wH_2O(org) + X^-\cdot(x-w)H_2O(org) & (1b) \end{cases}$$

where Equation (1a) indicates the extracted species are ion paired and Equation (1b) indicates they are dissociated. The corresponding equilibrium constants are:

$$K_n^a = \frac{(H^+\cdot nTOPO\cdot wH_2O\ldots X^-\cdot(x-w)H_2O)_0}{(TOPO)_0^n(H_2O)^x(H^+X^-)} = K_n^a \frac{y_{HX}}{y_{TOPO}^n} \qquad (2a)$$

$$K_n^d = \frac{(H^+\cdot nTOPO\cdot wH_2O)_0\ (X^-\cdot(x-w)H_2O)_0}{(TOPO)_0^n(H_2O)^x(H^+X^-)} = K_n^d \frac{y_\pm^2}{y_{TOPO}^n} \qquad (2b)$$

where parentheses signify activity, brackets denote molar concentrations, y is a molar activity coefficient, and $K_n^{a,d}$ is a mixed concentration quotient. Equation (2) implies that a log-log plot of the organic-phase acid concentration, $[HX]_0$, vs. the denominator should yield a straight line with a slope of unity for the ion-paired case (a) and a slope of one-half for the dissociated system (b), if the proper choice is made for n, the number of TOPO molecules coordinated in the complex,

and if the water activity doesn't change significantly. Figure 1 shows such plots for the extraction of $HReO_4$, HBr and HCl by TOPO in nitrobenzene, and Fig. 2 gives the results for the same acids by TOPO in 1,2-dichloroethane. Experimentally, the value of n has been found to be 2 in each instance by observing the dependence of the extraction on the TOPO concentration alone. The square-root of the denominator for Equation (2) has been employed in order to halve the number of decades required. This change doubles the value of the expected slopes as outlined above. For each of the TOPO-acid systems (except for TOPO-HBr-1,2-dichloroethane), shown in Figs. 1 and 2, a line of slope unity can be placed through the points representing the lower organic-phase concentrations. This indicates that Equation (2b) describes the extraction process in these regions; the acid complex is dissociated. The extension of this line of unit slope is shown as a dashed line, and falls below the experimental points at higher organic-phase acid concentration. This is expected, since $y_{\pm}$ is no longer close to unity. An attempt to estimate where the experimental values would be if only Debye-Hückel type activity coefficients were responsible for the observed deviations is shown by the dash-dot curve. This is generated by dividing the slope unity line with activity coefficients calculated by using a Debye-Hückel expression with $\mathring{a} = 6$. Clearly, the more concentrated organic-phase experimental points do not fall on this estimated curve for complete dissociation, but deviate upward. At the highest concentrations studied the plot of raw data approaches a line of slope two, and suggests that ion association is occurring. This happens with HCl, HBr, and even $HReO_4$ in dichloroethane systems, and with HCl and HBr in the concentration ranges studied in nitrobenzene.

The TOPO-$HReO_4$-nitrobenzene system gives the least indication of association; this is as expected, due to the large size and hence low charge density of ReO_4^-.

The curves for each TOPO-HX-diluent system in Figs. 1 and 2 are the result of combining sets of data obtained by determining the organic-phase acid concentration at either a fixed TOPO concentration and varying aqueous acid activity or at a fixed aqueous acid activity and varying TOPO concentration. Examples of these individual types of distribution studies can be seen in Figs. 2 and 4 in Ref. 1 . The range of TOPO concentrations in this work was from 0.00010M up to 0.25 - 1.00M. Activity coefficients used for the calculation of the aqueous acid activities were taken from the compilation of Gazith [5]. They were calculated as: $A_{HX} = (HX) = [C]^2 y_{\pm}^2$.

Values for the dissociated (Equation (2b)) and associated (Equation (2a)) equilibrium quotients for most of the acid-TOPO-diluent systems are listed in Table I. An entry for the associated HNO_3-nitrobenzene-TOPO system is missing. Data were taken, but not included for the following reasons. When the nitric acid complex associates, it is not clear that only an associated 2:1 TOPO:acid complex occurs (as is found with the other stronger acids), where the nitric acid is still ionized, but ion paired. Another possibility that is typical in lower dielectric diluents, involves the association of the nitric acid to form a 1:1 molecular complex [6-10], TOPO·HNO_3. Furthermore, it is well known that additional nitric acid molecules may add to form binitrate, and even higher anionic nitric acid solvates [11], and this may occur at rather dilute organic-phase acid concentrations. Preliminary analysis of the more concentrated HNO_3 data indicated that the latter two possibilities were both occurring. These complications made this system too difficult to unravel in the more concentrated organic-phase solutions from extraction data alone. It was felt, however, to be sufficiently

TABLE I. EQUILIBRIUM QUOTIENTS FOR EXTRACTION OF $HReO_4$, HBr, HCl and HNO_3.

Diluent	Acid	K_2^d	K_2^a	$K_{association}$
Nitrobenzene	$HReO_4$	9×10^2	--	--
	HNO_3	2	--	--
	HBr	1×10^{-1}	7	7×10^1
	HCl	3×10^{-3}	1	3×10^2
1,2-dichloroethane	$HReO_4$	9	4×10^3	4×10^2
	HBr	--	5	--
	HCl	1×10^{-4}	4×10^{-1}	3×10^3

interesting to demonstrate that if a low enough organic-phase acid concentration is maintained ($< \sim 10^{-2}$M), and extraction is examined in a high dielectric-constant diluent, nitric acid no longer behaves as a weak acid, but is dissociated [12], and yields the same $2TOPO \cdot H^+$ cation as with stronger acids.

The order of acid extraction is as expected: $HReO_4(HClO_4) > HNO_3 > HBr > HCl$ in both diluents, and mirrors the increasing importance of anion hydration in the aqueous phase, i.e., $Cl^- > Br^- > NO_3^- > ReO_4^-(ClO_4^-)$, which hinders the extraction. The tabulated equilibrium quotients also show that it is easier to transfer the same charged species into a higher dielectric medium (nitrobenzene) than into a lower dielectric medium (DCE), particularly for the dissociated complex. This is as would be expected from simple considerations of the Born charging expression and the energy of ion pairing [13].

In order to make an estimate of the amount of water coextracted with the acid complex, it is first necessary to determine the considerable amounts of water extracted by TOPO alone. The equilibrium for this distribution of water into an organic-phase solution of TOPO can be written:

$$nTOPO(org) + mH_2O = mH_2O \cdot nTOPO(org) \quad . \tag{3}$$

The corresponding equilibrium constant is

$$K_{H_2O} = \frac{(mH_2O \cdot nTOPO)_0}{(H_2O)^m (TOPO)_0^n} = \frac{[mH_2O \cdot nTOPO] y_{H_2O}}{(H_2O)^m [TOPO]^n y_{TOPO}^n} = K_{H_2O} \frac{y_{H_2O}}{y_{TOPO}^n} \tag{4}$$

With the assumption that y_{H_2O}/y_{TOPO}^n is a constant in the dilute solutions used, Equation (4) suggests that a log-log plot of organic-phase water concentration vs. equilibrium TOPO concentration should generate a line of slope n,

where n is the number of TOPO molecules coordinated in each extracted water complex. In Fig. 3 the organic-phase water concentration, $[H_2O]_0$, is plotted against the initial (not equilibrium) TOPO concentration. The amount of water extracted by the diluent alone, calculated as the product of the molar solubility in the diluent and the volume fraction of diluent in the organic medium, has been subtracted to obtain the points plotted. The water solubility found in this study of nitrobenzene was 0.163 M [14].
For 1,2-dichloroethane a value of 0.125 M was determined [15]. The slope of one found in Fig. 3 for each diluent-TOPO system

indicates that one TOPO molecule is involved in each TOPO-water complex. The observed stoichiometry of one water per TOPO molecule in 1,2-dichloroethane might suggest that a monohydrate is formed [16]; however, in nitrobenzene the 1.2:1 ratio of water to TOPO clearly indicates that an additional higher-water complex is also extracted. In a later paper dealing in more detail with water extraction by TOPO in these two (and other) diluents, it will be shown that at least a mono- and a dihydrate are extracted in both the nitrobenzene and 1,2-dichloroethane systems. The stoichiometric ratio of one water to one TOPO in 1,2-dichloroethane is simply an accident of room temperature (like the 1:1 stoichiometry of water in pure TBP [17] at room temperature) and not an indication of the TOPO-water complex structure [18,19]. The amount of free TOPO, uncomplexed by water, in each system is small, and in this paper no distinction is made between unhydrated and hydrated TOPO. Thus, the symbol [TOPO] denotes the TOPO concentration not complexed by acid.

For 0.10 M TOPO in nitrobenzene and in 1,2-dichloroethane the amount of water, less the diluent water, coextracted by the organic-phase perchloric acid complex as the acid concentration increases is shown in Fig. 4. In both diluent systems the total amount of water decreases as $[H^+]_0$ increases. From this total, the amount of water extracted by the equilibrium uncomplexed TOPO must be subtracted; and this non-acid-bound TOPO concentration is calculated as $[TOPO]_{total} - 2[H^+]_0$. After correction, curve 3 results. This line indicates that about 0.4 molecule of water co-extracts with each $HClO_4$ acid complex in either nitrobenzene or DCE. Assuming the cation portion of this TOPO-acid complex is similar to the $HAuCl_4$, $HClO_4$ and $HReO_4$ complexes previously studied (and i.r. spectra do indicate this), namely an anhydrous $2TOPO \cdot H^+$ species, the 0.4 water molecule must be associated with the organic-phase anion. This value is in excellent agreement with the finding from a more direct study [20] where the organic-phase hydration of tetra-alkylammonium perchlorate salts was found to average $\sim$ 0.4 molecules of water per salt molecule. In the TOPO-DCE system, at the acid concentrations examined, the acid complex is mostly ion paired; while in the TOPO-nitrobenzene system the complex is probably partly dissociated.

In Fig. 5, the amount of water co-extracted by the HBr complex is shown for 0.30 M TOPO in nitrobenzene and in DCE. Curve 3 in this figure is the resultant after correction for the water extracted by both the TOPO uncomplexed by acid (determined as in the previous paragraph) and the diluent. The single slope suggests an average of 1.9 molecules of water are co-extracted by the bromide anion in both diluent systems. Similar data are presented in Fig. 6 for the HCl acid complex extracted by 0.25 M TOPO in 1,2-dichloroethane and by 0.50 M TOPO in nitrobenzene. For the HCl-nitrobenzene system the

resultant curve (line 3) has a slope of three, which is also the value for the initial slope of the corrected data for HCl-1,2-dichloroethane. In the latter system , however, the slope becomes somewhat less than three as $[H^+]_0$ increases (line 4). This results, we believe, from neglecting the significant change of water activity resulting from the rather high aqueous acid concentrations necessary to reach the upper range of $[H^+]_0$ considered. If the amounts of water extracted by the TOPO and by the TOPO-acid complex are corrected for the water activity to the appropriate power (approximately first and third, respectively), the resulting corrected curve has a slope close to three for HCl-1,2-dichloroethane also. It is clear from Figs. 1 and 2 that for both the HBr and HCl, within the range of $[H^+]_0$ used in these water determinations, the acid complexes are predominantly ion paired.

Again, the average values of 1.9 and 3 found for bromide and chloride ion hydration in these organic diluents are in very good agreement with the values of 1.8 and 3.3 obtained in tetra-alkylammonium salt-nitrobenzene systems [21]. It is gratifying that the values of anion hydration found in the present study (on fairly complex systems) should be so similiar to the values from the simpler, more direct systems previously studied. Further, the organic-phase hydration numbers are remarkably similiar to the values found by Bockris and Saluja [22] in aqueous solutions by compressibility and ionic vibration methods. It is not obvious that they should be, as the environment of the coordinated water molecules is quite different in the two cases. Discussion of what the individual values mean has already been given elsewhere [21], but we would repeat one of the conclusions: these anion values should be considered only lower

limits to the first-shell coordination numbers as they represent average values for distributions that may well range from 0 (unhydrated anions) to 4 or even 6 water molecules (the first-shell coordination number).

CONCLUSIONS

All of the acids examined, $HReO_4$, HNO_3, HBr, and HCl, extract as $2TOPO \cdot H^+X^-$ salts in nitrobenzene and in dichloroethane. (The i.r. spectra indicate the similarity to TOPO-acid complexes studied in other diluents, and the difference from the hydronium-ion core found with the TBP complexes.) Even the HNO_3 product is based on the $2TOPO \cdot H^+$ cation, in contrast to its behavior in low-dielectric-constant solvents.

The extraction quotients show that the larger, less basic, anions extract better, $ReO_4^- > Br^- > Cl^-$, due to their lower aqueous hydration, and that this effect is less pronounced for the ion-pair case, as some of the lost hydration energy is compensated for in the ion pairing. Also, extraction is better into the higher-dielectric-constant nitrobenzene than into dichloroethane, since there are no specially strong diluent-acid complex (chemical) interactions.

Finally, knowing that the acidic cation is anhydrous allows determination of the hydration of the anion in these diluents (but not as well as with tetraalkylammonium salts). This anion hydration is not directly related to the first-shell coordination number, but is probably an average of the distribution over coordination numbers ranging from 0 to the maximum first-shell number.

FOOTNOTES AND REFERENCES

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†Present address: Linwood College, St. Louis, Missouri.

††,‡,‡‡Summer Visitors, Undergraduate Research Participation Program, 1967 and 1968.

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FIGURE CAPTIONS

Fig. 1. Variation of the organic-phase acid concentration and the square-root of the organic-phase acid activity vs. the product $\{[TOPO]^2(HX)\}^{1/2}$ with nitrobenzene as the diluent. Line 1 is for the TOPO-$HReO_4$-nitrobenzene system; line 2 is the TOPO-HNO_3 system; line 3 is the TOPO-HBr system and line 4 is the TOPO-HCl-nitrobenzene system. Dashed lines indicate an extension of the unit slope (dissociated) line; the dashed-dot curves indicate where the raw extraction curve would lie if the line of unit slope is corrected for Debye-Hückel type activity coefficients; the long-short-short dashed lines indicate the ion-pair (association) contribution.

Fig. 2. Variation of the organic-phase acid concentration and the square-root of the organic-phase acid activity vs. the product $\{[TOPO]^2(HX)\}^{1/2}$ with 1,2-dichloroethane as the diluent. Line 1 is for the TOPO-$HReO_4$ system; line 2 is for TOPO-HBr, and line 3 is for the TOPO-HCl system. Dashed lines indicate an extension of the unit slope (dissociated) line; the dashed-dot curves indicate where the raw extraction curve would lie if the line of unit slope is corrected for Debye-Hückel type activity coefficients; the long-short-short dashed lines indicate the ion-paired (association) contribution.

Fig. 3. Variation of water content of the organic phase with initial TOPO concentration in nitrobenzene and in 1,2-dichloroethane. ($[H_2O]_0$ = total H_2O minus H_2O dissolved by the diluent.) □, is for the TOPO-nitrobenzene system; ○, is for the TOPO-1,2-dichloroethane system and is the average of measurements using both the Karl Fischer method and tritiated water as a tracer. Lines are drawn initially with unit slope, and this slope is continued with dashed lines.

Fig. 4. Water content vs. $HClO_4$ concentration in the organic phase (as the aqueous $HClO_4$ concentration increases) for a total TOPO concentration of 0.10 M in nitrobenzene and in 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 the water bound to TOPO for 1,2-dichloroethane (Δ) and nitrobenzene (□), and has a slope of 0.4.

Fig. 5. 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 in 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: Δ, 1,2-dichloroethane; □ , nitrobenzene. The average slope of line 3 is 1.9.

Fig. 6. Water content vs. HCl organic-phase concentration (as the aqueous HCl concentration increases) for a total TOPO concentration of 0.50 M in nitrobenzene (line 1) and of 0.25 M in 1,2-dichloroethane (line 2). Line 4 is the total organic-phase water less both diluent water and water bound to TOPO in the DCE system. Line 3 is the total organic-phase water less both diluent water and water bound to TOPO in nitrobenzene (Δ) and the result of a third power correction for decreased water activity in the TOPO-DCE system (∇). The dashed line is drawn with a slope equal to three.

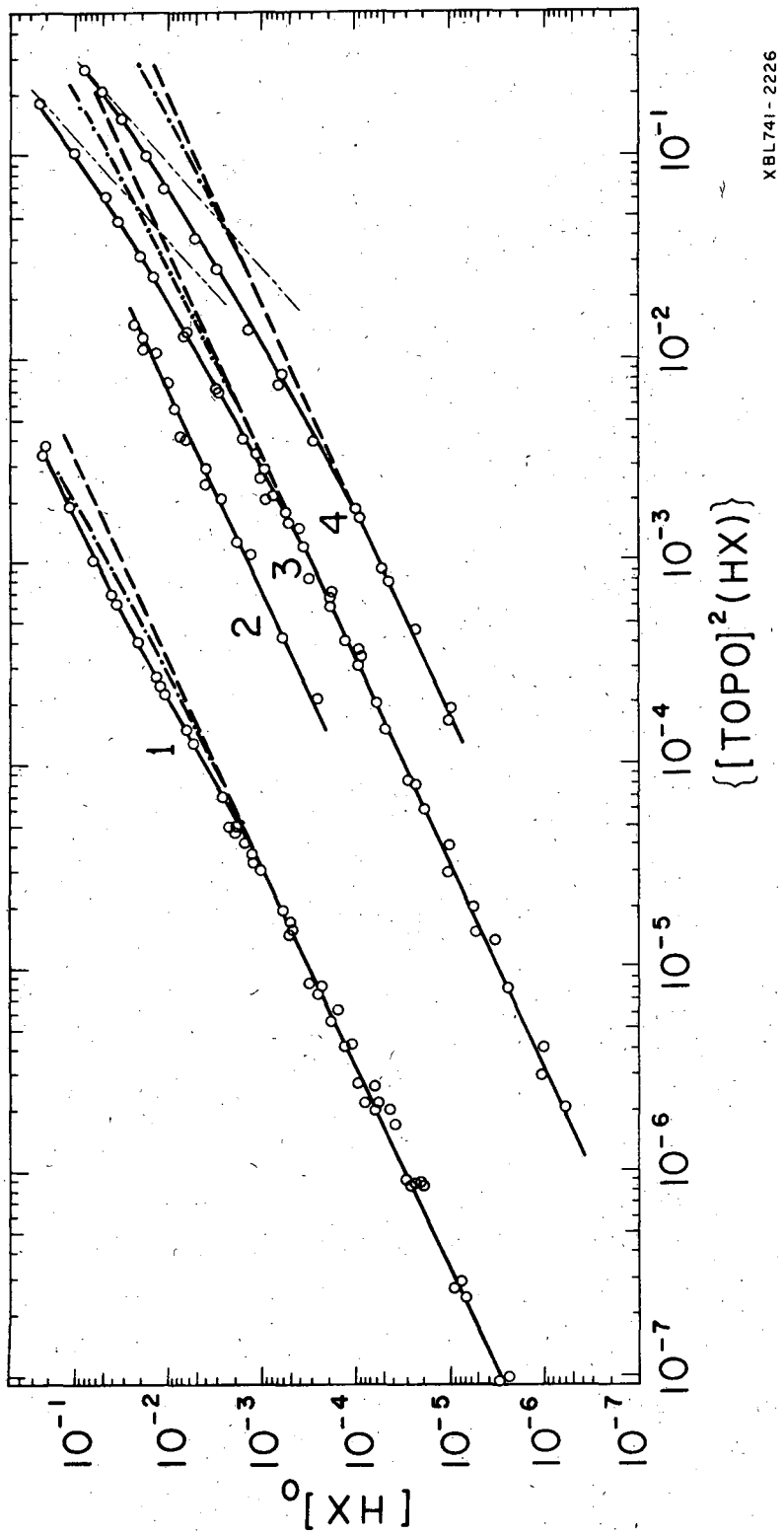

Fig. 1

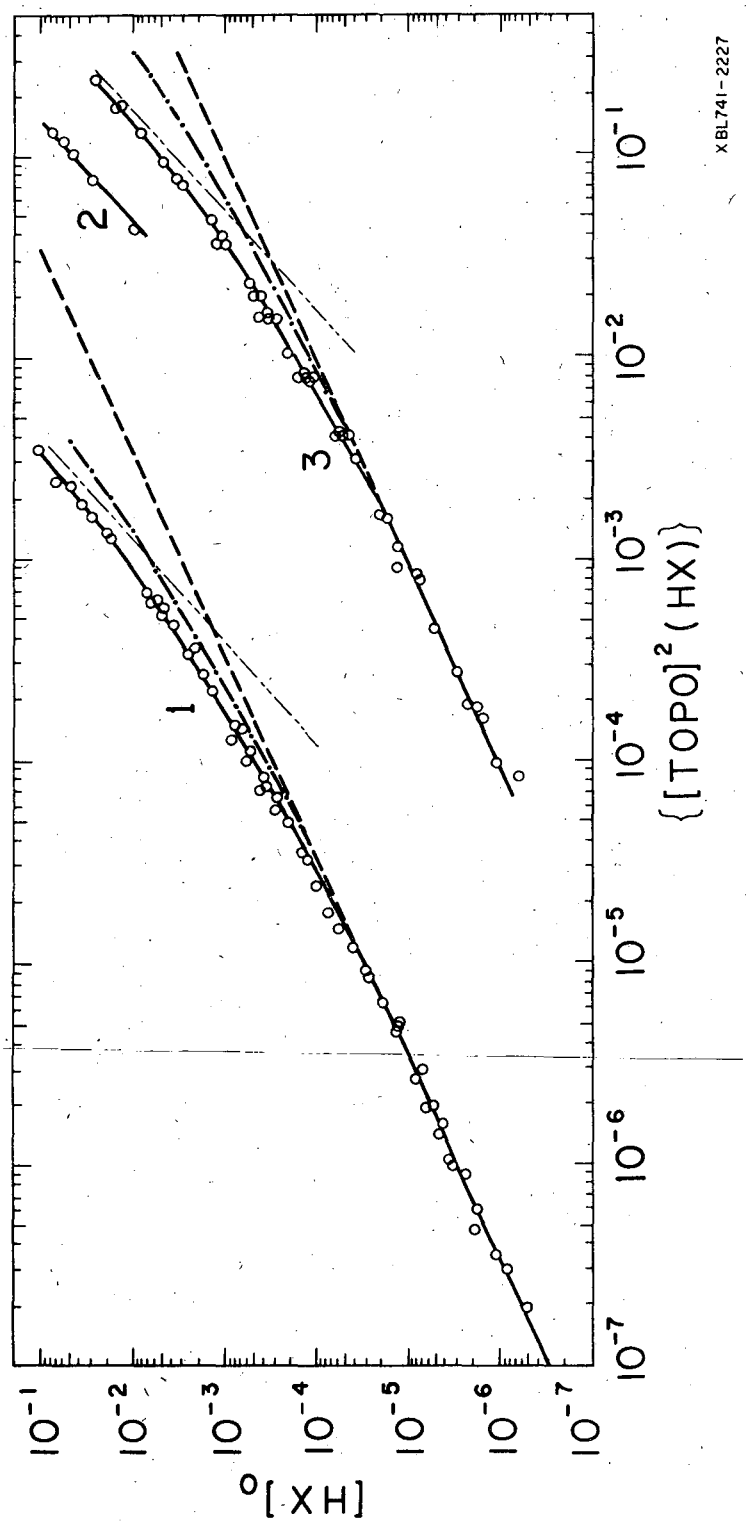

Fig. 2

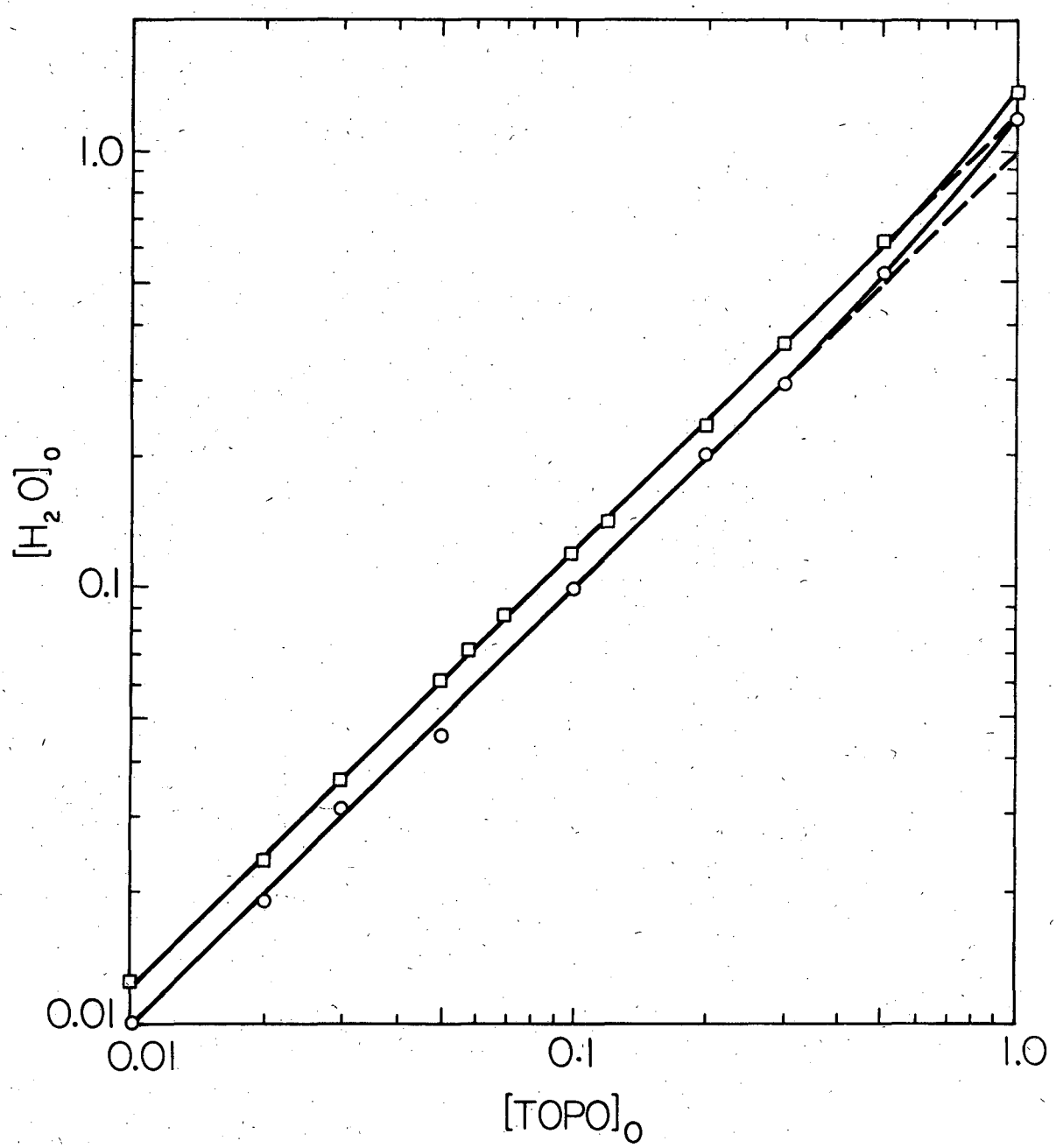

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Fig. 3

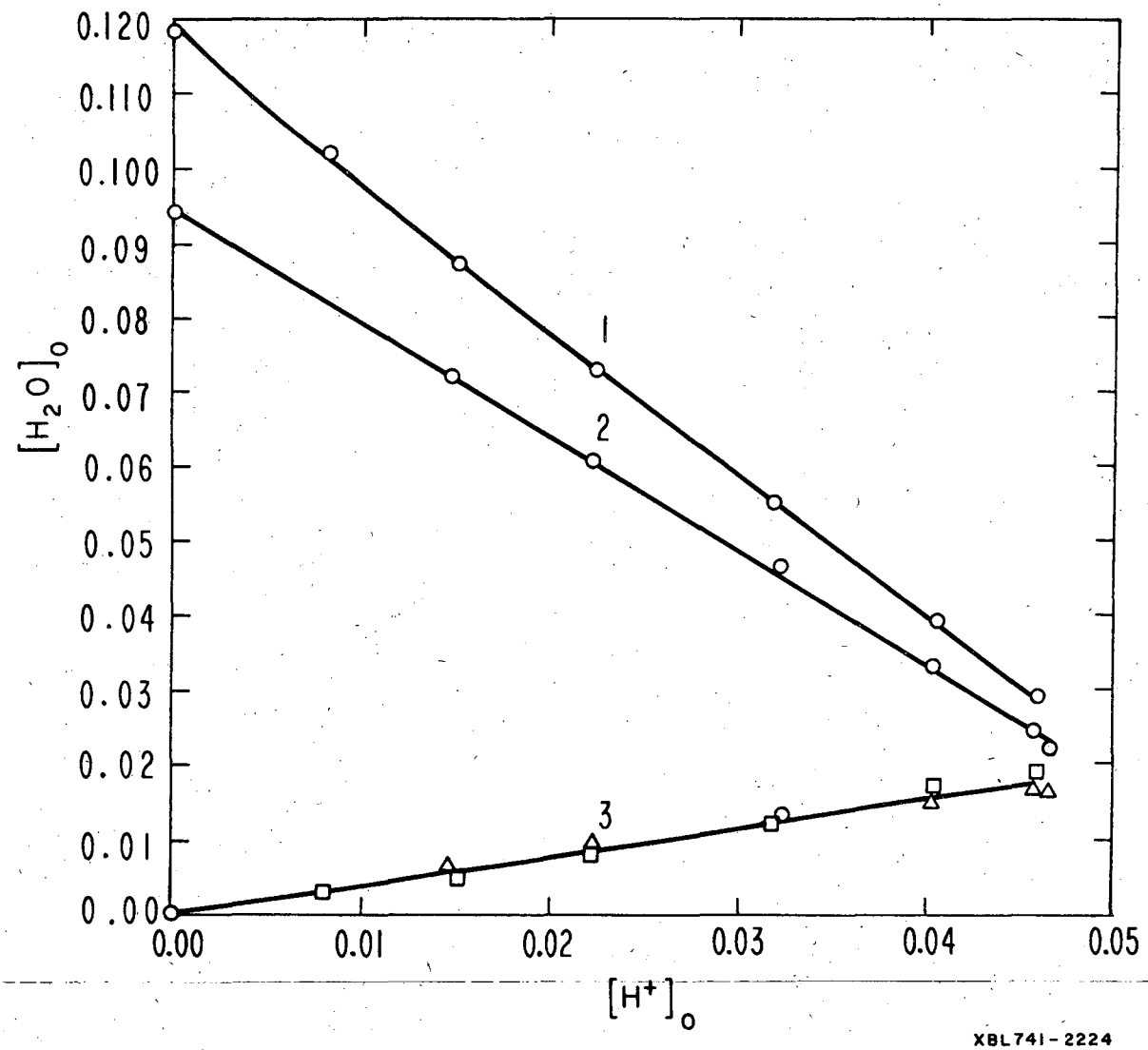
0.120
0.110
0.100
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
$[H_2O]_o$
1
2
3
0.00
0.01
0.02
0.03
0.04
0.05
$[H^+]_o$
XBL741-2224

Fig. 4

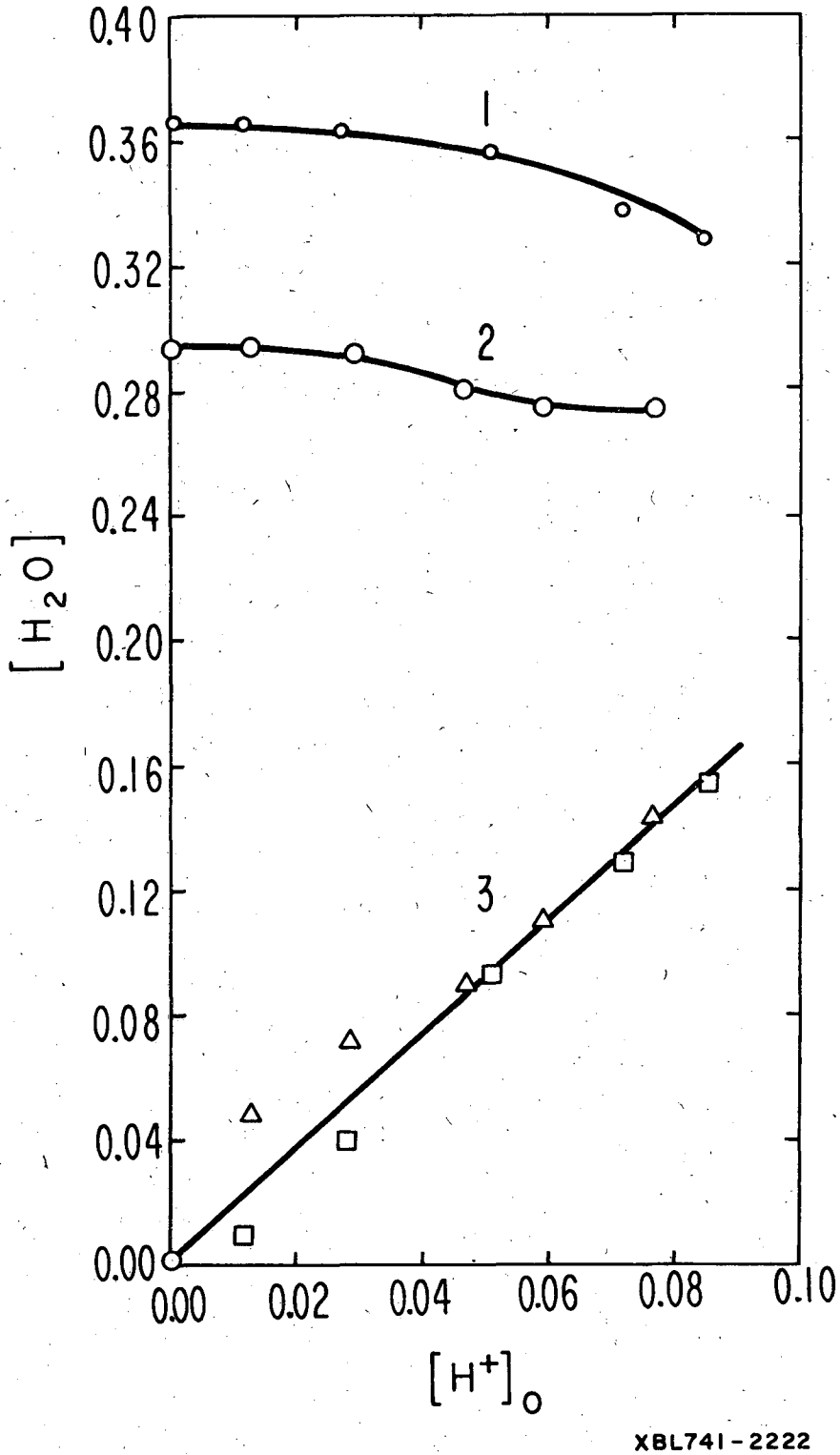
0.40
0.36
0.32
0.28
0.24
0.20
0.16
0.12
0.08
0.04
0.00
[H2O]
1
2
3
0.00
0.02
0.04
0.06
0.08
0.10
[H+]o
XBL741-2222

Fig. 5

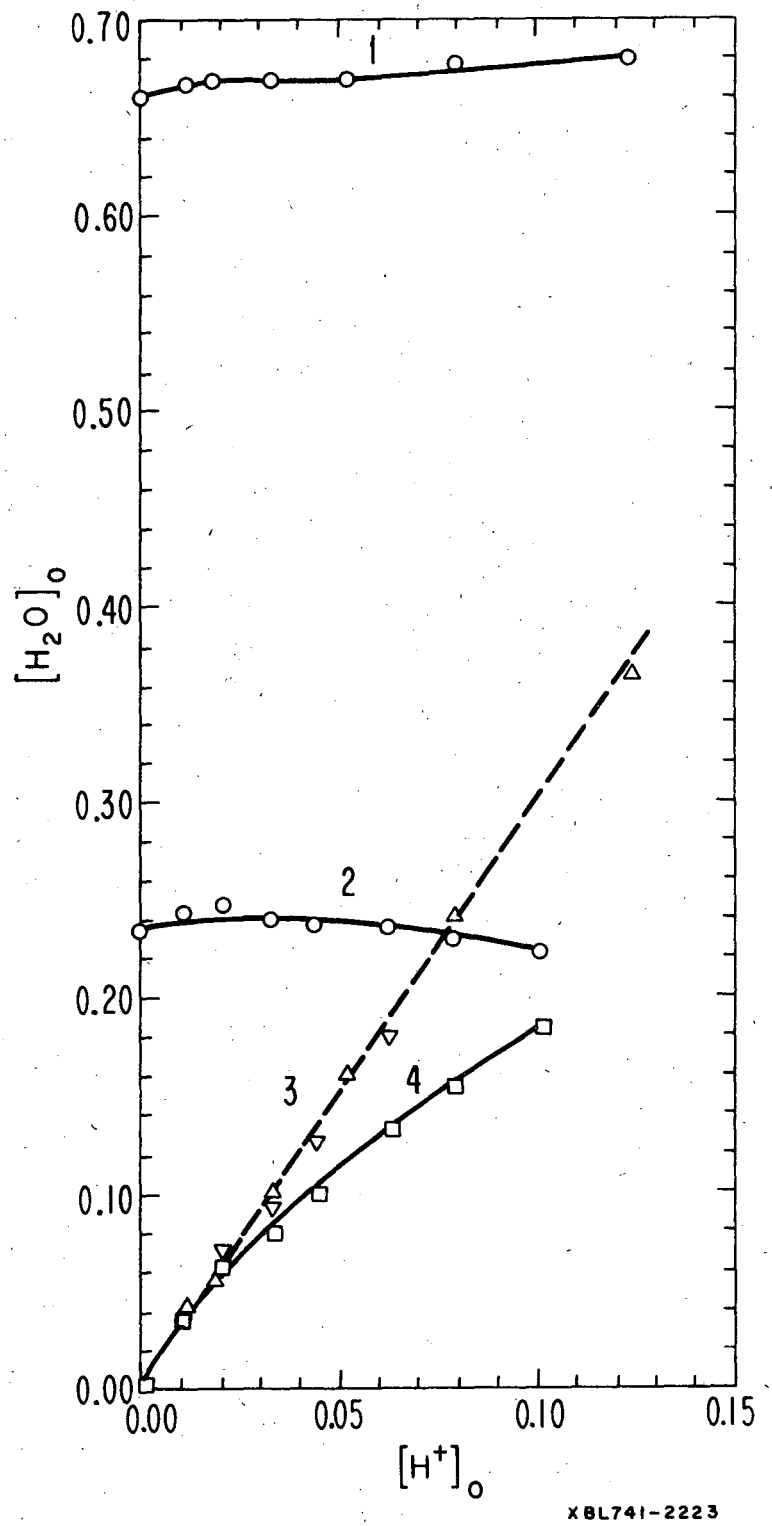
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
$[H_2O]_o$
0.00
0.05
0.10
0.15
$[H^+]_o$
1
2
3
4
XBL741-2223

Fig. 6

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