Submitted to Journal of
Inorganic and Nuclear Chemistry

LBL-2342
Preprint c. 2

ANION AND DILUENT STABILIZATION OF TRIBUTYL PHOSPHATE AND TRIS-ETHYLHEXYL PHOSPHATE COMPLEXES IN THE EXTRACTION OF $HAuCl_4$, $HReO_4$, HI, AND HBr

J. J. Bucher, R. Zuehl, and R. M. Diamond

RECEIVED
LAWRENCE
RADIATION LABORATORY

MAR 5 1974

LIBRARY AND
DOCUMENTS SECTION

December 1973

Prepared for the U.S. Atomic Energy Commission
under Contract 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

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY

LBL-2342
c.2

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.

ANION AND DILUENT STABILIZATION OF TRIBUTYL PHOSPHATE AND TRIS-ETHYLHEXYL PHOSPHATE COMPLEXES IN THE EXTRACTION OF $HAuCl_4$, $HReO_4$, HI, and HBr*

J. J. Bucher, R. Zuehl†, and R. M. Diamond

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

December 1973

ABSTRACT

The extraction of $HAuCl_4$, $HReO_4$, HI, and HBr by dilute solutions ($\leqslant$ 0.4M) of tributyl phosphate and tris-ethylhexyl phosphate in isooctane, CCl_4, benzene and 1,2-dichloroethane was examined. From acid distribution data and i.r. spectra of the organic phases, it was concluded that the extraction of strong acids fit the hydronium-ion-core model. It was demonstrated that, in addition to the influence of the diluent, the acid anion also played a role in determining the ratio of the step-wise complexes, with the more basic anions (I^-,Br^-) favoring lower trialkyl phosphate solvation numbers. Differences between TBP and TEHP in solvating the (hydrated) hydronium cation also were demonstrated.

INTRODUCTION

In a previous study [1,2] of $HReO_4$ and $HClO_4$ extraction by dilute solutions of tributyl phosphate (TBP) in various diluents, step-wise complexing to yield a 2TBP·acid and a 3TBP·acid species was found. This behavior, within the range of TBP concentrations employed, was particularly evident in isooctane and in CCl_4. In each system the TBP and additional waters were thought to be bonded to the three positive sites of the H_3O^+ ion.

In a high dielectric constant diluent, 1,2-dichloroethane , which permitted dissociation of the extracted ions, only a 3TBP·acid complex was observed [1]. In this case the hydronium (or more likely, the partially hydrated hydronium) cation loses its direct contact with the anion, and so must obtain its solvation more completely from the TBP, thus favoring the higher 3:1 species.

In this work, the extraction of a stronger acid, $HAuCl_4$, and of two weaker acids, HBr and HI, by TBP in some of the previously studied diluents is presented. It is expected that for the $HAuCl_4$-TBP-diluent systems a greater range of 3TBP·acid complex should be realized, since the anion, $AuCl_4^-$, is even less basic than ReO_4^- or ClO_4^-, and so solvates even more poorly the acidic cation. Conversely, with the somewhat more basic anions, I^- and Br^-, it is expected, if anion interaction is a contributing factor to the stability of the 2TBP·acid species, that a greater range of 2:1 complex would be realized. With HI and HBr, extraction into the TBP-CCl_4 system is of prime interest, since the $HReO_4$-TBP-CCl_4 system already has demonstrated that both 2:1 and 3:1 TBP complexes can be obtained in a convenient range of TBP concentrations. Additionally, the TBP-HBr-CCl_4 and the TBP-$HReO_4$-isooctane systems were re-examined, since the conclusions of earlier work [1,3] appear to be in disagreement with the present

expectations. Finally, some examples of extraction by tris-2-ethylhexyl phosphate (TEHP) in several diluents are also presented. This extractant, with larger branched alkyl groupings, may show the effect of steric hindrance, another means whereby the acid cation extractant number can be influenced.

EXPERIMENTAL

Reagents

The TBP was Matheson, Coleman, and Bell (M.C.B.), reagent grade, and was purified by washing with sodium carbonate and water. The washed TBP was dried over Linde 5A molecular sieves and stored in an amber bottle. All dilutions of TBP in the various solvents were made on a volume-percent basis using volumetric glassware. The TEHP was obtained from Union Carbide Corp. as the commercial plasticizer, Flexol TOF. After a preliminary vacuum distillation, the TEHP was treated in the same manner as TBP. A stock solution of $HAuCl_4$ was made by dissolving Englehard Industries gold chloride in water and filtering. Determination of the stock solution was done by electrodeposition onto platinum-iridium gauze electrodes from a basic gold cyanide-hydroxylamine solution. Dilutions from this gold stock were made with 0.010M HCl to prevent hydrolysis. Reagent grade 57% hydroiodic acid (Merck) and 48% hydrobromic acid (Baker and Adamson) were further purified by saturation with H_2S gas and subsequent distillation. The stock solution and dilutions were stored in amber-glass bottles.

Gold tracer, $^{198,199}Au$, was prepared by irradiating gold foil (> 99.9% purity) with neutrons for 6 days at a flux greater than 10^{14} neutrons/cm^2-sec in the Vallecitos Test Reactor. After dissolving the gold foil in aqua regia, the solution was taken to near dryness and then 6M HCl was added. This solution

was also taken to near dryness and the gold tracer was finally prepared by adding 0.10M HCl. Bromide tracer, ^{82}Br, was also made by neutron irradiation of a few mg of LiBr under the same conditions as for gold. After bombardment, the LiBr was dissolved in H_2S-saturated water to reduce the appreciable amounts of free bromine. The free sulfur was removed by filtering. Iodide tracer, Na ^{131}I in 0.1M NaOH solution, was obtained from New England Nuclear Corp. and was used as received.

Benzene, 1,2-dichloroethane, and CCl_4 were all J. T. Baker reagent grade; the isooctane was a "spectro grade" reagent from M.C.B. The Karl Fischer reagent used in the water determinations was M.C.B. stabilized and premixed single-solution. The methanol used in the Karl Fischer analysis blank was Baker and Adamson, "Special anhydrous" reagent ($\leqslant$ 0.005% H_2O).

Procedures

The procedures used to obtain the distribution and water data in this study were similar to those already outlined in earlier studies [1,2]. An additional precaution was taken when obtaining the HI data. For these studies H_2S gas was introduced over the organic solutions in successive treatments, until the organic phase was approximately saturated ($\sim$ 0.3M H_2S).

RESULTS AND DISCUSSION

Extractant-H_2O

The equilibrium for the distribution of water into a solution of an extractant in an organic diluent is assumed to be maintained independently of any other extraction equilibria, and can be written:

$$n(RO)_3PO\ (org.) + mH_2O = mH_2O \cdot n(RO)_3PO\ (org.) \qquad (1)$$

with a corresponding equilibrium constant:

$$K_{H_2O} = \frac{(mH_2O \cdot n(RO)_3PO)_o}{(H_2O)^m((RO)_3PO)_o^n} = \frac{[mH_2O \cdot n(RO)_3PO]_o y_{H_2O}}{(H_2O)^m[(RO)_3PO]_o^n y^n_{(RO)_3PO}} \qquad (2)$$

where parentheses signify activities, brackets denote molar concentrations, and y is a molar activity coefficient. With the assumption that in these dilute solutions, the ratio $y_{H_2O}/y^n_{(RO)_3PO}$ is a constant, Equation (2) suggests that a log-log plot of the organic-phase water concentration (corrected for water uptake of the diluent), $[H_2O]_o$, vs. the equilibrium extractant concentration, $[(RO)_3PO]_o$, should generate a line of slope n, where n is the number of extractant molecules bound to each extracted water complex. In Fig. 1, $[H_2O]_o$ is plotted vs. the initial TEHP concentration in isooctane. A line of slope one can be drawn through the points. This suggests that a water complex containing only one TEHP molecule occurs at these (and lower) TEHP concentrations. This behavior is quite similar to that already found for many TBP-diluent systems [1,2,4-8]. Also included in this figure is the previously determined water data for the TBP-isooctane system [1]. Up to an extractant concentration of ~ 0.07M, both TBP and TEHP extract almost exactly the same amounts of water and in the same manner. However, beyond this concentration, the TBP system begins to show evidence of increased water extraction, while the TEHP-isooctane system appears to remain regular. Some preliminary evidence from vapor-phase osmometric studies [9] indicates that the activity-coefficient changes for TBP, as compared to TEHP at the same molar concentrations, are more severe. Whether this increased water extraction for TBP is only an activity-coefficient effect or is the result

of an additional species being formed, or both, is an interesting but unanswerable question from these data. It is clear, however, that TEHP-isooctane is more ideal. With both extractants, the majority of the molecules are unhydrated. The K_{H_2O} for the 1:1 TEHP:H_2O complex is 0.14 $(mol/l.)^{-1}$, using the equilibrium (not the initial) concentration of TEHP to evaluate the constant [10].

TBP- or TEHP-HX

The extraction of HX by solutions of TBP or TEHP in a diluent may be expressed as

$$H^+ + X^- + xH_2O + n(RO)_3PO\ (org.) = H^+\cdot n(RO)_3PO\cdot xH_2O\ \ldots\ X^-\ (org.) \qquad (3)$$

$$= H^+\cdot n(RO)_3PO\cdot xH_2O\ (org.) + X^-\ (org.) \qquad (3')$$

if the possibility of water on the anion is ignored.

The corresponding equilibrium constants are

$$K_n^a = \frac{[H^+\cdot n(RO)_3PO\cdot xH_2O\ \ldots\ X^-]y_{HX}}{[(RO)_3PO]_o^n\, y^n_{(RO)_3PO}\ (H_2O)^x\ (HX)} = K_n^a\,\frac{y_{HX}}{y^n_{(RO)_3PO}} \qquad (4)$$

$$K_n^d = \frac{[H^+\cdot n(RO)_3PO\cdot xH_2O]_o[X^-]_o\, y_\pm^2}{[(RO)_3PO]_o^n\, y^n_{(RO)_3PO}\ (H_2O)^x\ (HX)} = K_n^d\,\frac{y_\pm^2}{y^n_{(RO)_3PO}} \qquad (4')$$

Equations (3) and (4) describe the extraction of HX in low-dielectric-constant media where the extracted species are ion paired, while Equations (3') and (4') describe the extraction of species which are dissociated.

Since it has previously been demonstrated that the TBP-$HReO_4$ and TBP-$HClO_4$ species were ion paired in isooctane [1], CCl_4 [1], and benzene [2], and were mostly dissociated in 1,2-dichloroethane [1] if the organic-phase acid complex was less than 10^{-3}M, it is mainly of interest in this study to determine the value of n, the TBP or TEHP coordination number. As indicated by Equations (4) and (4'), the slopes of log-log plots of extracted acid $(HX)_o$ vs. extractant concentration at constant a_{HX} yield directly the value of n if the complex is associated, or n/2 if the complex is dissociated. Such plots are shown in Figs. 2 and 3, for TBP-CCl_4, and in Figs. 4 and 5 for TBP-benzene and TBP-isooctane systems, respectively.

Part II of Fig. 2 illustrates the step-wise complexing for TBP-$HReO_4$-CCl_4, with the dashed lines indicating resolution of the raw data into components having slopes two (n = 2) and three (n = 3). Curve f in this figure indicates similar results are obtained with "trace distribution" experiments ($[HReO_4] < 10^{-4}$M out of 3M HCl) as when macro amounts of $HReO_4$ acid are used, curves d and e. In part I of this same figure, lines a, b, and c show the extraction of $HAuCl_4$ by TBP-CCl_4, and a line of slope three (n = 3) holds even down to TBP concentrations where the $HReO_4$ system shows a slope of 2. In Fig. 3,

part I, only lines with slope two are observed for TBP-HI-CCl_4. Similarly, for the HBr data shown in part II, only curves with a slope of two (n = 2) are found in the range of TBP concentration studied [11].

The TBP-acid-benzene systems are shown in Fig. 4. Lines b and c are for HI and $HReO_4$, respectively, and are drawn with slopes two (n = 2). Curve a is for $HAuCl_4$, and can be resolved into components with n = 2 and n = 3. More similar to the TBP-CCl_4 systems, the TBP-isooctane systems are shown in Fig. 5. Extraction of $HAuCl_4$ by TBP-isooctane is shown in lines a, b, and c, and a line of slope three (n = 3) is drawn with each set of data. For TBP-$HReO_4$ (curves d and e) the extraction data can be resolved into components with slopes of two and three. It should be noted, the 3TBP-$HReO_4$ complex is observed as a major species to lower TBP concentration than in TBP-$HReO_4$-CCl_4 [12]. The HI system (not shown) was also examined. At the higher TBP concentrations, an n = 3 component was indicated. However, since the extraction of HI was lower than that for $HReO_4$, and the third-power TBP dependence quickly lowered the organic-phase acid concentration to the blank extraction value for HI alone, an insufficient range of TBP concentration was realized to test the extraction pattern of HI against the other HX-isooctane systems.

In previous work [1,2] where only the TBP-$HReO_4$,-$HClO_4$ systems were examined, although in several diluents, it was concluded that the differences in TBP coordination number observed resulted from the differing abilities of the diluents to solvate TBP and the extracted cationic complex. Benzene molecules can help stabilize the extracted (partially hydrated) hydronium cation via their π electrons, and so for $HReO_4$ only two molecules of TBP need be coordinated, along with the associated (ion-paired) ReO_4^- anion. Measurements

of TBP activities [8,13-17] in both benzene and CCl_4 indicate the interaction of TBP with either diluent is quite similar in magnitude and may even slightly favor CCl_4. However, the ability of CCl_4 to furnish (basic) solvation for the cationic complex is less than that of benzene, and as a consequence, a third TBP is coordinated in the $HReO_4$-$HClO_4$ systems at a TBP activity which still yields only a two-TBP species in benzene. Isooctane is poorer than either of the above diluents in solvating either TBP (as indicated by activity studies [8,14,18]) or, more importantly, the extracted acid complex, as indicated by the still greater range of three TBP:acid species observed in this solvent. Thus, while it was clear from the previous studies how the diluents affected TBP extraction and the nature of the extracted species, it was not clear how large a role was played by the associated anion. With the present sets of data, where the TBP-diluent is held constant and the anion is varied, an answer to this question can now be obtained.

But first it is worth noting that basically the same hydronium-ion core is involved in all these TBP-cationic complexes whether they be 2:1 or 3:1 [19]. The infrared spectra for the complexes found in TBP-CCl_4 for $HAuCl_4$ (3:1), $HReO_4$ (mostly 3:1, some 2:1), and HBr (2:1) are shown in Fig. 12. The similarity of these spectra indicate to us, that even though the TBP coordination number has changed, the acid complex in each case is of the same type. These spectra show, principally, the bands of the (hydrated) hydronium ion [20], which makes up the cationic core of the extracted acid complex.

For TBP-$HReO_4$-benzene only a two TBP:acid complex is found, at least up to TBP concentrations where the assumption of a constant activity-coefficient ratio might be expected to hold. However, for the TBP-$HAuCl_4$-benzene system,

where presumably the same degree of diluent stabilization is present, an additional step of complexing is observed, both the 2:1 and 3:1 species are found. We believe this occurs because the less basic $AuCl_4^-$ anion is less effective than ReO_4^- in furnishing some of the solvation needs of the hydronium cation. Thus, a third TBP may displace the $AuCl_4^-$ from the vicinity of one of the H_3O^+ protons at higher TBP concentrations, although the anion remains bound to the cation electrostatically as a somewhat more distant ion pair.

With the somewhat poorer diluent CCl_4, only a 3:1 complex is found with $HAuCl_4$. But the more basic ReO_4^- anion also yields a 2:1 complex at lower TBP concentrations, where the anion can displace an extractant molecule from the H_3O^+ cation. With the still more basic I^- and Br^- anions (anions of somewhat weaker acids), additional stabilization is obtained in the resulting close ion pair, so the anion more readily displaces a TBP, and only a 2:1 TBP:acid complex is produced in the available concentration range of TBP.

As noted before, in comparison to the above diluents, isooctane is the poorest solvent, and so it is expected that the range of 3:1 TBP:acid complex in isooctane would be greater than in benzene or CCl_4. This is observed for all the anions studied.

Another aspect explored in this paper is the effect of the size of the alkyl groups of the extractant on the degree of step-wise complexing. The results of substituting TEHP for TBP in the $HAuCl_4$-, $HReO_4$-, HBr-isooctane and $HReO_4$-CCl_4 and $HReO_4$-benzene systems are shown in Figs. 6 and 7. Immediately evident is the favoring of the 2:1 extractant:acid complex with TEHP-isooctane, as compared, on a molar basis, with TBP-isooctane. It is only with the most weakly basic anion $AuCl_4^-$ that any three TEHP complex is observed. All of the associated

$HReO_4$-diluents systems show little evidence for 3:1 TEHP:acid complexes. Thus, it appears that the larger ethylhexyl groups on TEHP sterically hinder the formation of the 3:1 complex compared to the behavior of the smaller TBP molecules. But that the anion also plays an important role in producing the 2:1 TEHP:acid complex is shown by the results in the dichloroethane systems, Fig. 8. Here only dissociated 3:1 complexes are observed; all the lines in the figure are drawn with a slope of 3/2. That is, by dissociating the complex in dichloroethane, i.e., by simply removing the anion from the proximity of the cation, only the formation of a 3:1 complex can be observed. Special notice should be taken of the TBP-HBr-DCE system. In none of the other diluents is there any indication of a 3:1 HBr complex. Yet by dissociating the Br^- in dichloroethane, by not allowing it to solvate the cation, a 3:1 extractant:acid complex results. We believe this to be a strong indication of the importance of anion-cation interaction in governing the extractant coordination number in these cationic complexes.

It is from the equilibrium quotients, Table 1, that further interesting differences between TBP and TEHP and between diluents become evident. In calculating the quotients (see Equations (4 and 4')), molarities were used for both $(RO)_3PO$ and acid complex concentrations, activities as calculated from the Gazith tabulation [21] were employed for the aqueous acid concentrations, an average value of x = 3 was taken for the exponent of the water activity, and equilibrium extractant concentrations, i.e.; non-hydrated TBP or TEHP concentrations (adjusted with a first power correction for water activity changes) were used. For those instances where the equilibrium quotient was calculated from distribution of a tracer acid out of a macro solution of HCl, the aqueous activity coefficients were estimated in the following way. For the mean activity coefficient of

hydrogen ion, the value for HCl at that particular concentration was taken, and for the anion, X^-, the mean activity coefficient for HX corresponding to that same concentration was used.

Some difficulties arise in evaluating these quotients, especially for the 3:1 complexes when they don't predominate over a large range of TBP or TEHP concentrations. As stated before, a constant value for the ratio of the organic-phase (acid complex and extractant) activity coefficients is assumed. From several of the figures, it can be estimated that this assumption breaks down at a TBP concentration of about 0.2M in the CCl_4 and 0.1M in the benzene systems, and at a somewhat lower concentration than 0.1M in the isooctane systems. For instance, in Fig. 5, line c, for $HAuCl_4$ and TBP in isooctane, the data clearly have departed from a slope three line at 0.1M TBP. Yet, it seems unreasonable to suppose that another higher complex than $H_3O^+ \cdot (TBP)_3 \cdot AuCl_4^-$ is extracting. Instead, we believe the deviation is a breakdown in the assumption that the activity-coefficient ratio is constant. As a result of this uncertainty in the organic-phase activity coefficients at higher concentrations, we have used only those data anchored safely at lower (more ideal) TBP or TEHP concentration in evaluating the tabulated equilibrium quotients. For example, in Fig. 4, line c, in the $HReO_4$-TBP-benzene system, no attempt is made to fit a 3:1 complex to that upper portion of the curve which is deviating from the indicated line of slope two at a TBP concentration greater than 0.1M.

The order of extractability of the acids observed for either the 2:1 or 3:1 complexes, for TBP or TEHP, and for any of the diluents studied, is the same, and is the order expected from their aqueous hydration energies. $HAuCl_4$, the strongest acid, due to its very weak anion hydration requirements, is better

extracted than $HReO_4$. So too, $HReO_4$ extracts better than the yet weaker acid HI, and HI extracts better than HBr, which has the most highly hydrated anion. This order should be most readily noticeable with the 3:1 complexes, as they involve the more coordinatively saturated cations with the anions less tightly ion paired. The scanty amount of data on K_3^a does seem to indicate this.

Comparison of the 2:1 quotients, K_2^a, shows that the values in CCl_4 tend to be lower than those in isooctane or in benzene. This is probably due to the interaction of CCl_4 with the TBP itself, reducing the effective concentration of the TBP and hence the acid extraction. The same thing happens with benzene also, but benzene can also interact via its π-electrons with the cationic complex and so compensates for the otherwise unfavorable diluent-extractant interaction. In addition, benzene may show a special dispersion-force interaction with the large electron cloud on the $AuCl_4^-$ anion, yielding an unusually large value of K_2^a relative to ReO_4^- and the other anions. However, with small anions the ion pair formed with the cationic complex is probably tighter so that the influence of the diluent is reduced, and then the values of K_2^a for, say Br^-, might be expected to be more similar in the different diluents than with the larger anions. There may even be a weak interaction [23] between CCl_4 and the halides, I^- and Br^-, which enhances their extraction relative to $AuCl_4^-$ and ReO_4^-.

Finally, comparison of the 2:1 equilibrium quotients for TBP and TEHP in the same diluent and for the same acid indicates TEHP is about a factor of two poorer in extraction than TBP. This suggests that the larger branched alkyl tails on the TEHP molecules lead to some mutual steric hindrance [22] and hence a decrease in extraction. If steric interference is occurring for the 2:1 complexes, it should be even more evident with the 3:1 TEHP species. Thus,

this (expected) steric hindrance prolongs the range of 2:1 complex, so that 3:1 species only appear at higher TEHP concentrations than with TBP. A difficulty is that these higher TEHP concentrations are, however, in the concentration range where a detailed knowledge of the organic-phase activity coefficients is necessary for slope analysis.

The amount of water associated with the 3:1 TBP:$HAuCl_4$ complex in CCl_4 is shown in Fig. 9. The slope of the resultant curve in this figure indicates that between 2.5 and 3 water molecules are extracted with the ion-paired 3TBP complex. Similar data for the 2:1 TEHP:$HClO_4$ complex in isooctane are shown in Fig. 10, and the resultant curve has an initial slope of ~ 2.5. Water extraction with the 2:1 TBP:HBr complex in CCl_4 is shown in Fig. 11, and the curve has a nearly constant slope of 2, even though the water activity changes from 0.75 to < 0.5 over the $[H^+]_o$ range considered. In a previous determination of associated water for $HClO_4$-TBP-isooctane [1], 4-5 water molecules were found to be coordinated, but this was for a 3:1 acid complex. Other studies indicated ~ 2.5 water molecules coordinated to the 3:1 acid complex for TBP-$HClO_4$-CCl_4 [24]; while a value of ~ 3 was found for a 2:1 complex in the TBP-$HClO_4$-benzene system [2,25].

All of the above-mentioned systems have sufficient coextracted water to allow the formation of a hydronium-ion core, and enough additional water to allow bridges between H_3O^+ and some of the coordinated extractant molecules and/or hydration of the accompanying anions. The addition of a bridging water between H_3O^+ and the extractant molecule may result in a more open structure for the extraction complex and could thus reduce somewhat the crowding of the alkyl tails on TBP or TEHP with the 3:1 species.

SUMMARY AND CONCLUSION

In the present study, it is shown that the nature of the anion can significantly affect the extractant-cation ratio. The largest, least-basic anion will be able to interact least with the hydronium-based cation, favoring the saturated 3:1 complex. The smallest, most-basic anion can most readily displace a TBP or TEHP molecule from the cationic complex and so favor the 2:1 species. Thus, slope analyses of the $HAuCl_4$ extraction systems indicate that mainly the 3:1 species is extracted into isooctane or CCl_4 by either TBP or TEHP, while only the 2:1 complex is observed with HBr in these diluents. For $HReO_4$ extraction, intermediate behavior is found, namely a mixture of 3:1 and 2:1 species. The order of observing the coordinatively saturated 3:1 complex follows the acid strength, $HAuCl_4$ > $HReO_4$ > HI > HBr, exactly as expected.

It is also shown that the nature of the diluent influences the composition of the extracted species. The more inert the diluent, the less solvation it can provide the extracted ions, and the more the ions must depend upon each other and upon the extractant. So with any anion, the best (ion-pair) diluent with which to observe the 3:1 complex is isooctane. Benzene provides the best solvation of the cationic complex (through its π-electrons) and so favors the 2:1 species (this predominates even for $HAuCl_4$). Carbon tetrachloride falls in between these two extremes. Use of the higher-dielectric-constant solvent, dichloroethane, allows for dissociation of the anion and cation so that all specific solvation of the cationic complex must come from the extractant. This strongly favors the 3:1 species with the acids we have used; for HBr this is the only solvent system in which the saturated 3:1 complex is observed at all.

A comparison of the data for the 2:1 complexes shows, at least for the larger anions, that CCl_4 has poorer extraction than either isooctane or benzene.

This is probably due to the interaction of CCl_4 with the TBP (or TEHP) itself, reducing its effective concentration. This occurs also with benzene, but in that case is compensated for by the interaction of benzene with the cation of the extracted complex. Finally, it was shown that use of the much bulkier extractant, tris-ethylhexyl phosphate, rather than TBP, tended to favor the 2:1 complex because of steric hindrance, and in the 2:1 complex decreased acid extraction by about a factor of ~ 2. Not enough data are available, but it would be expected, if steric hindrance is really occurring, that the 3:1 complexes would suffer even a larger reduction.

In spite of the number of ways in which it has been found possible to affect the composition of the extracted acid complex, infrared spectra on many of the 3:1 and 2:1 species observed with the different acids in the different diluents indicate that they all are based on the same fundamental cationic unit, a hydronium-ion core. Water uptake data always show at least one water molecule extracted. These spectra are very different from those [26] observed with the 2:1 anhydrous cationic species produced with these same acids and diluents, but with the much more basic trioctylphosphine oxide as the extractant.

FOOTNOTES AND REFERENCES

*Work performed under the auspices of the U. S. Atomic Energy Commission.

†Summer Visitor, Undergraduate Research Participation Program, 1969.

[1] J. J. Bucher and R. M. Diamond, J. Phys. Chem. 73, 675 (1969).

[2] J. J. Bucher and R. M. Diamond, J. Phys. Chem. 73, 1494 (1969).

[3] D. C. Whitney and R. M. Diamond, J. Phys. Chem. 67, 2583 (1963).

[4] S. Nishimura, C. H. Ke, and N. C. Li, J. Am. Chem. Soc. 90, 2 (1968).

[5] A. M. Rozen, L. P. Khorkhornia, G. D. Agashkina, E. G. Teterin, A. N. Mal'tseva, and E. V. Voronetskaya, Radiokhimiya 12, 345 (1970).

[6] Yu. G. Frolov and V. V. Sergievskii, Radiokhimiya 13, 760 (1971).

[7] E. Brauer and E. Hogfeldt, J. Inorg. Nucl. Chem. 23, 115 (1961).

[8] A. M. Rozen, "Physical Chemistry of Solvent Extraction", in "Solvent Extraction Chemistry", D. Dyrssen, J. Liljenzin, and J. Rydberg, ed., North-Holland Publishing Co., Amsterdam, 1967, pp. 227-230.

[9] J. J. Bucher, R. B. Garrett, and R. M. Diamond, to be published.

[10] This value compares favorably with the value of 0.14 found for TBP in kerosene by E. Brauer and E. Hogfeldt, Ref. 7.

[11] This result is at variance with the conclusions of an earlier study, Ref. 3. The reason for this disagreement is likely the limitations of the acid-base titration methods employed in the earlier study. See also the studies of V. I. Levin and M. D. Kozlova, Radiokhimiya 8, 533 (1966), and A. S. Kertes and V. Kertes, J. Appl. Chem. 10, 287 (1960). Both studies indicate a lower-than-three TBP solvation number.

[12] The resolution of these present curves is different from that done in an earlier work (Ref. 1); the reason is not clear, although the previous study was a measurement of ReO_4^- tracer out of macro $HClO_4$, rather than out of macro $HReO_4$ as in the present case.

[13] W. F. Johnson and R. L. Dillon, Physical Properties of TBP-Diluent Solutions, HW-29086 (September 1, 1953).

[14] A. M. Rozen, L. P. Khorkhornia, V. G. Yuskin, and N. M. Novikova, Dokl. Akad. Nauk SSSR 153, 1387 (1963).

[15] V. A. Mikhailov, S. K. Kharchencko, and L. I. Ponomarwa, Russ. J. Phys. Chem. 41, 426 (1967).

[16] D. Dyrssen and Dj. Petković, J. Inorg. Nucl. Chem. 27, 1381 (1965).

[17] J. J. Van Aartsen and A. E. Korvezee, Rec. Trav. Chim. Pays-Bas 83, 752 (1964).

[18] M. F. Pushlenkov, E. V. Komarov, and O. N. Shuvalov, Radiokyimiya 4, 543 (1963).

[19] Z. A. Grankina, L. K. Chuchalin, B. I. Peshchevitskii, I. A. Kuzin, and S. P. Khranenko, Russ. J. Phys. Chem. 43, 1371 (1969). See also for comparison: J. J. Bucher and R. M. Diamond, J. Inorg. Nucl. Chem. 34, 3545 (1972).

[20] L. W. Schroeder, J. Chem. Phys. 52, 1972 (1970).

[21] M. Gazith, Compiled and Calculated Molar and Molal Activity Coefficients of Various Electrolytes, Israel Atomic Energy Commission Report, IA-1004, October 1964.

[22] But see T. H. Siddall, J. Inorg. Nucl. Chem. 13, 151 (1960), who found little indication of steric hindrance in forming two solvate·uranyl nitrate compounds with TEHP or TBP.

[23] This interaction may be of the type studied spectroscopically by P. C. Dwivedi and C. N. R. Rao, Spectrochimica Acta 26A, 1535 (1970); and M. J. Blandmer, T. E. Gough, and M. C. R. Symons, Trans. Faraday Soc. 62, 286; 301 (1966).

[24] D. C. Whitney and R. M. Diamond, J. Phys. Chem. 67, 209 (1963).

[25] S. Siekierski and R. Gwóźdź, Nukleonika, 5, #4 (1960, Warsaw).

[26] J. J. Bucher and R. M. Diamond, J. Inorg. Nucl. Chem. 34, 3546 (1972).

Table 1. Concentration quotients for extraction of HX by TBP and TEHP

Solvent	Extractant	Acid	K_2^a	K_3^a
isooctane	TBP	$HAuCl_4$[a]	$\leqslant 2 \times 10^{-1}$	3×10^{2}
	TEHP	$HAuCl_4$[a]	2×10^{-1}	6×10^{1}
	TBP	$HReO_4$[a]	2×10^{-2}	5×10^{-1}
	TEHP	$HReO_4$[a]	1×10^{-2}	
		$HClO_4$		
	TEHP	HI[a]	9×10^{-4}	
	TEHP	HBr	9×10^{-5}	
CCl_4	TBP	$HAuCl_4$[a]	$\leqslant 8 \times 10^{-2}$	2×10^{1}
	TBP	$HReO_4$[b]	3×10^{-3}	3×10^{-2}
	TEHP	$HReO_4$[b]	2×10^{-3}	
	TBP	HI[c]	1×10^{-3}	
	TEHP	HI[a]	4×10^{-4}	
	TBP	HBr	2×10^{-4}	
benzene	TBP	$HAuCl_4$[a]	1×10^{1}	1.5×10^{2}
	TBP	$HReO_4$	1×10^{-2}	$\leqslant 3 \times 10^{-2}$
	TEHP	$HReO_4$	5×10^{-3}	
	TBP	HI[a]	2×10^{-3}	
	TEHP	HI[a]	8×10^{-4}	
			K_2^d	K_3^d
dichloroethane	TBP	$HReO_4$[d]		9×10^{-5}
	TEHP	$HReO_4$[d]		4×10^{-5}
	TBP	HBr[d]		5×10^{-7}

(continued)

Table 1 (continued)

a) Trace amounts of HX in macro amount of HCl.

b) Combination of macro amounts of $HReO_4$ and trace $HReO_4$ distribution out of HCl.

c) Combination of macro amounts of HI and trace HI out of HCl.

d) Quotients are not corrected to equilibrium TBP or TEHP concentrations.

FIGURE CAPTIONS

Fig. 1. Variation in water content of the organic phase with initial TBP or TEHP concentration in isooctane, ■-TBP (curve 1), and ●-TEHP (line 2). Lines are drawn with unit slope except for the upper portion of TBP (curve 1).

Fig. 2. Variation in acid content of the organic phase with TBP concentration in CCl_4 for 0.50M $HAuCl_4$, 1.0M HCl (line a), 0.001M $HAuCl_4$, 1.0M HCl (line b), 0.001M $HAuCl_4$, 0.1M HCl (line c), 2.91M $HReO_4$ (curve d), 1.60M $HReO_4$ (curve e), and 8×10^{-5}M $HReO_4$, 3.0M HCl (curve f). Lines a, b, and c are drawn with slope three, while curves d, e, and f are resolved into dashed n = 3 lines (▼) and n = 2 lines.

Fig. 3. Variation in acid content of the organic phase with TBP concentration in CCl_4 for 3.65M HI (line a), trace amount of HI, 6.0M HCl (line b), 6.4M HBr (line c), 5.0M HBr (line d), 3.89M HBr (line e), 3.2M HBr (line f), and 0.92M HBr (line g). All lines are drawn with slope two. In part II the symbol 0 indicates data using radioactive Br^- tracer, ■ indicates data using acid-base titration techniques.

Fig. 4. Variation in acid content of the organic phase with TBP concentration in benzene for 0.012M $HAuCl_4$, 3.0M HCl (curve a), 0.1M HI, 6.0M HCl (line b), and 3.21M $HReO_4$ (line c). For curve a the dashed lines indicate resolution into n = 3 (▲) and n = 2 components. For lines b and c, the dashed lines indicate the extension of slope two lines.

Fig. 5. Variation in acid content of the organic phase with TBP concentration in isooctane for 0.50M $HAuCl_4$, 1.0M HCl (line a), 0.010M $HAuCl_4$, 1.0M HCl (line b), 0.0010M $HAuCl_4$, 0.10M HCl (line c), trace amounts of $HReO_4$ ($< 10^{-4}$M) out of 3.0M HCl (curve d) and out of 1.0M HCl (curve e). Lines a, b, and c are drawn with slope three and the dashed portion of line c is an extension of this slope. Curves d and e are resolved into n = 2 and n = 3 components as indicated by the dashed lines.

Fig. 6. Variation in acid content of the organic phase with TEHP concentration in isooctane for trace amounts of $HAuCl_4$, 6.0M HCl (curve a), trace amounts of HI, 3.0M HCl (line b), 4.90M HBr (line c), 4.0M $HClO_4$ (line d), 2.0M $HClO_4$ (line f), trace amounts of $HReO_4$, 3.0M HCl (line e), and trace $HReO_4$, 1.0M HCl (line g). All lines are drawn with slope two except curve a, where the n = 2 (▼) and n = 3 components are indicated by dashed lines.

Fig. 7. Variation in acid content of the organic phase with TEHP concentration in benzene for 3.2M $HReO_4$ (line a) and in CCl_4 for 2.96M $HReO_4$ (line b) and trace amounts of $HReO_4$, 3.0M HCl (line c). All lines are drawn with a slope two.

Fig. 8. Variation in acid content of the organic phase with TEHP concentration in 1,2-dichloroethane for 0.30M $HReO_4$ (curve 1) and with TBP in 1,2-dichloroethane for 0.10M $HReO_4$ (curve 2), 0.01M $HReO_4$ (curve 4), and 1.0M HBr (curve 3). All lower portions of the curves are drawn with slope 3/2; the dashed portion is an extension of this slope. The symbol ■ denotes correction for organic-phase activity coefficients using the Debye-Hückel expression and an a = 6 Å.

Fig. 9. Water contents vs. $HAuCl_4$ (0.010M HCl) concentration in the organic phase (as the aqueous $HAuCl_4$ concentration increases) for a total TBP concentration of 0.37M in CCl_4. Line 1 is the total organic-phase water less the solvent water; line 2 is the total organic-phase water less both the solvent water and the water bound to TBP.

Fig. 10. Water content vs. $HClO_4$ concentration in the organic phase (as the aqueous $HClO_4$ concentration increases) for a total TEHP concentration of 0.21M in isooctane. Line 1 is the total organic-phase water less the solvent water; line 2 is the total organic-phase water less both the solvent water and the water bound to TEHP.

Fig. 11. Water content vs. HBr concentration in the organic phase (as the aqueous HBr concentration increases) for a total TBP concentration of 0.37M in CCl_4. Line 1 is the total organic-phase water less the solvent water; line 2 is the total organic-phase water less both the solvent water and the water bound to TBP.

Fig. 12. The infrared spectrum in the region 1300-4000 cm^{-1} for the $HAuCl_4$:TBP acid complex when equal volumes of 1.0M $HAuCl_4$ (aq.) and 0.367M TBP (CCl_4) are equilibrated (curve 1). TBP and TBP·H_2O lines have been deleted. Similarly, curve 2 is the resultant of contacting 4.0M $HClO_4$ (aq.) and 0.367M TBP (CCl_4), while curve 3 is the spectra of 7.0M HBr (aq.) and 0.367M TBP (CCl_4).

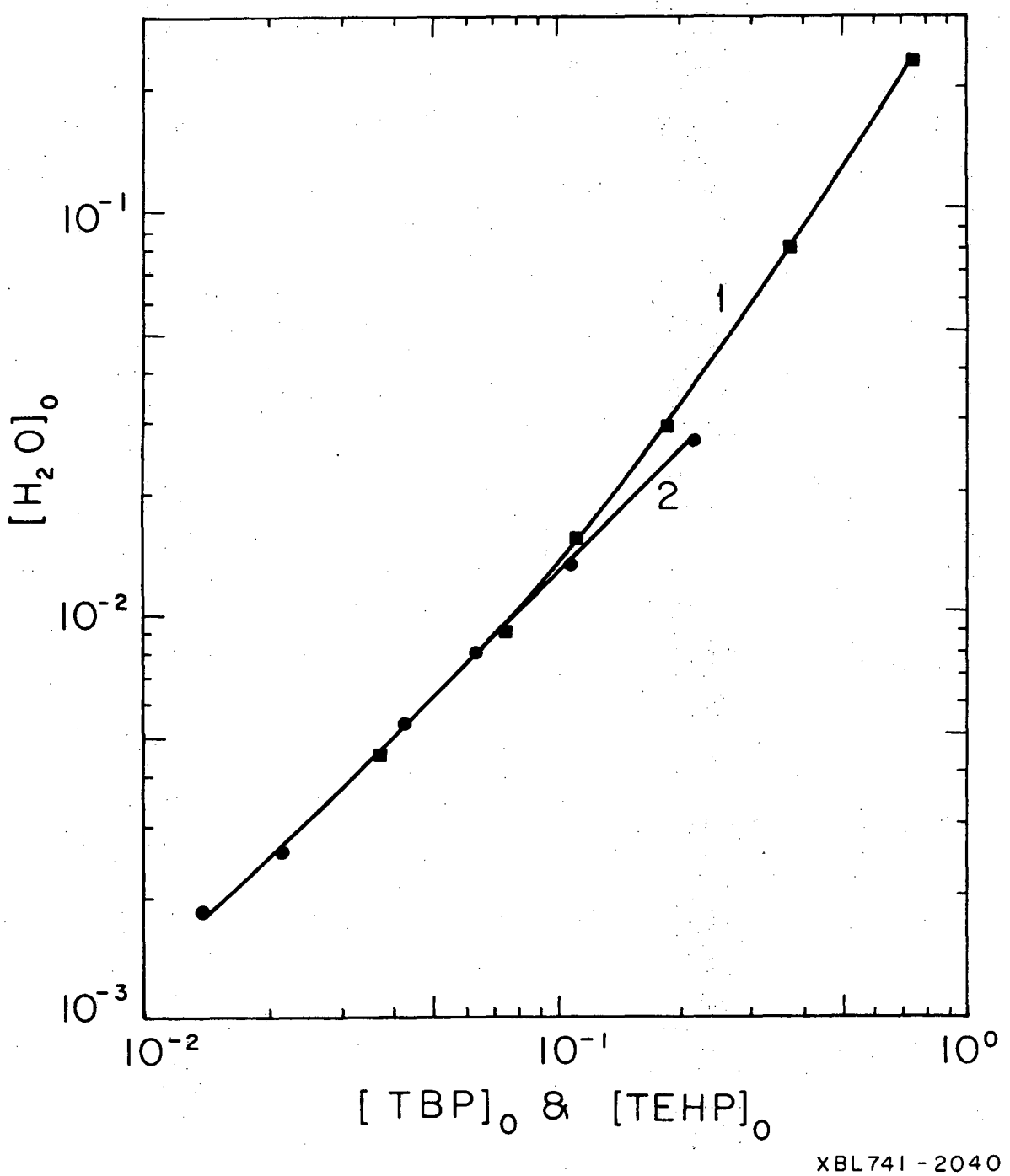


Fig. 1

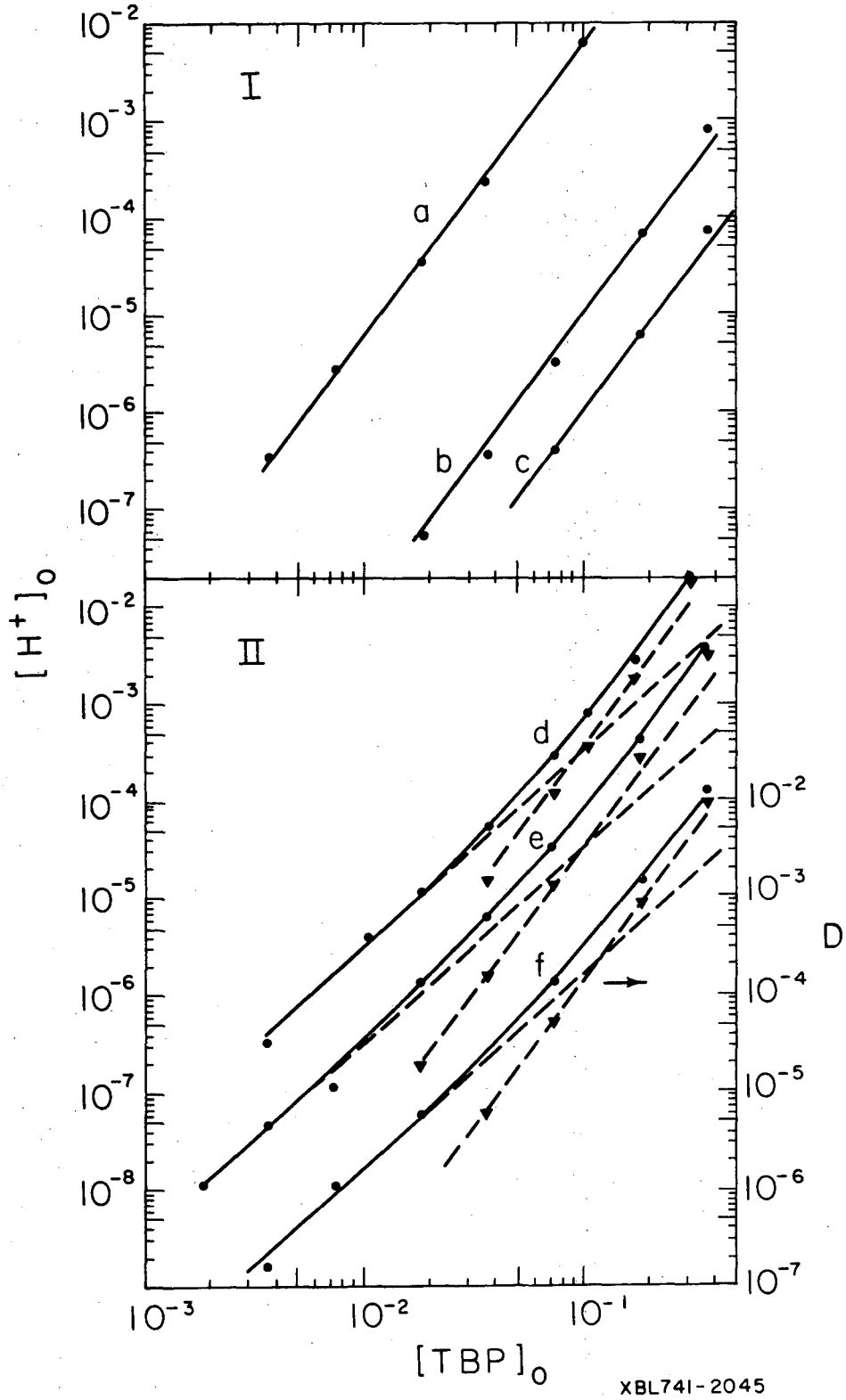

I
II
a
b
c
d
e
f
$[H^+]_o$
D
$[TBP]_o$
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-1}
XBL741-2045

Fig. 2

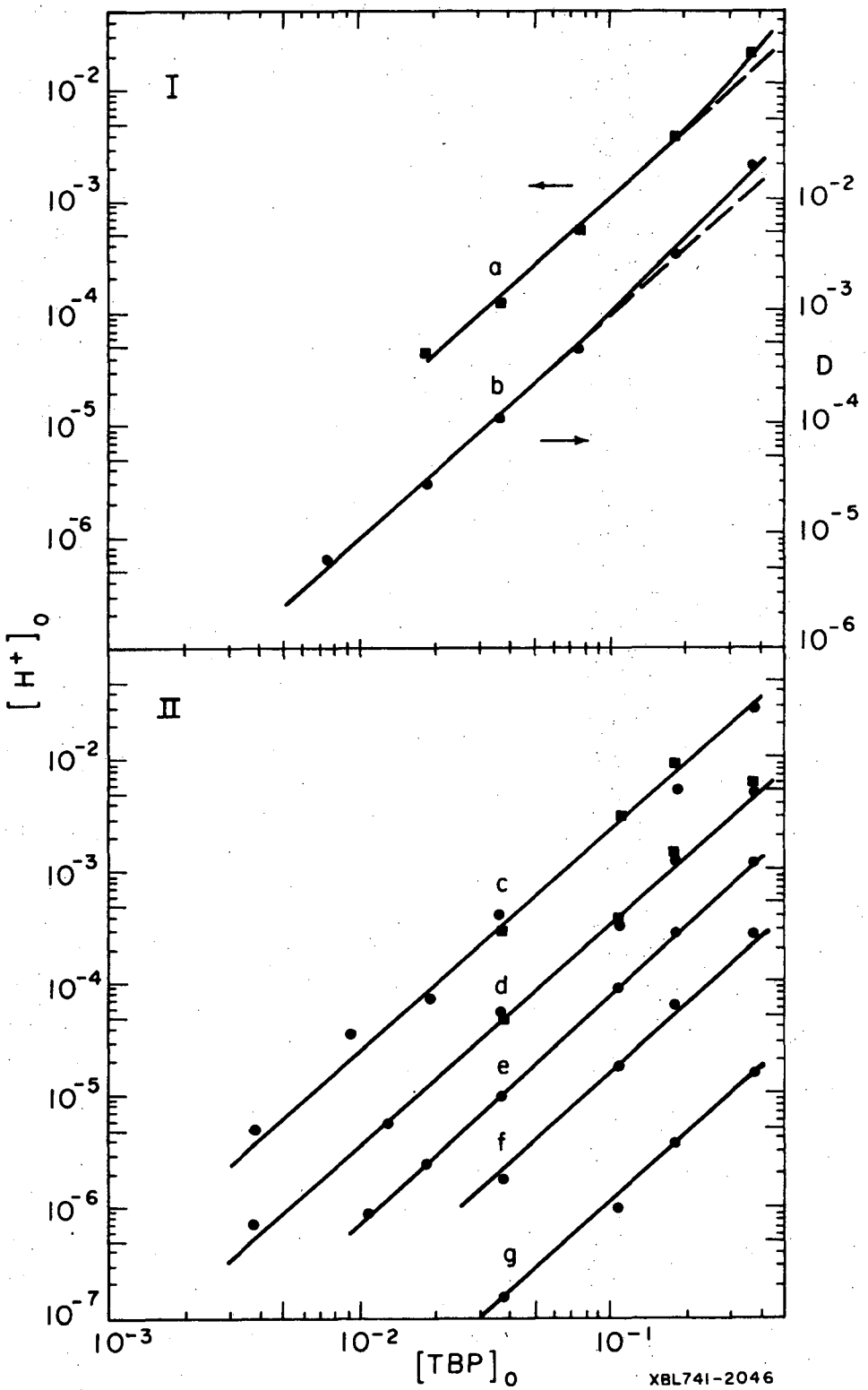


Fig. 3

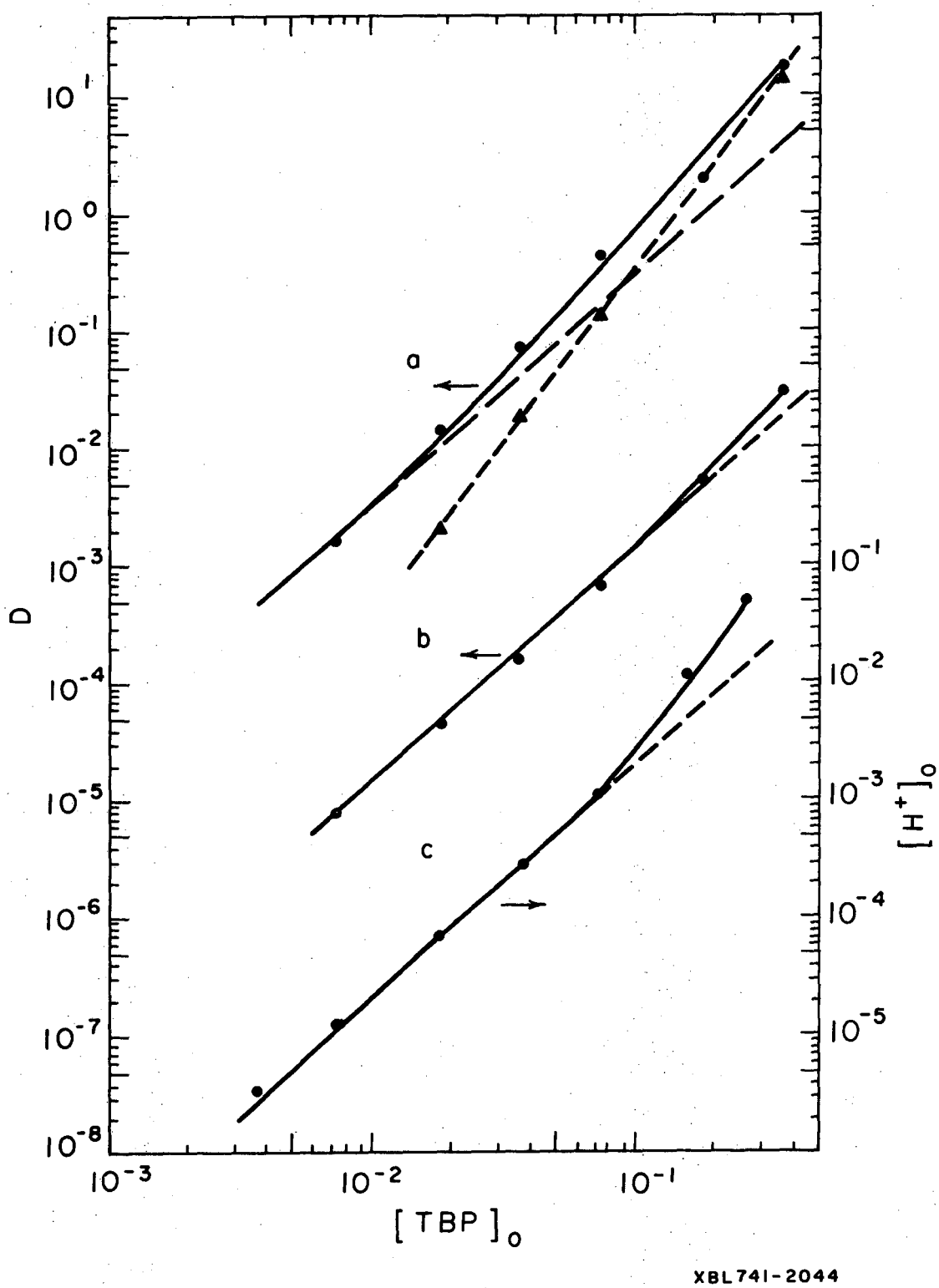

D
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
a
b
c
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
$[H^+]_o$
10^{-3}
10^{-2}
10^{-1}
$[TBP]_o$
XBL741-2044

Fig. 4

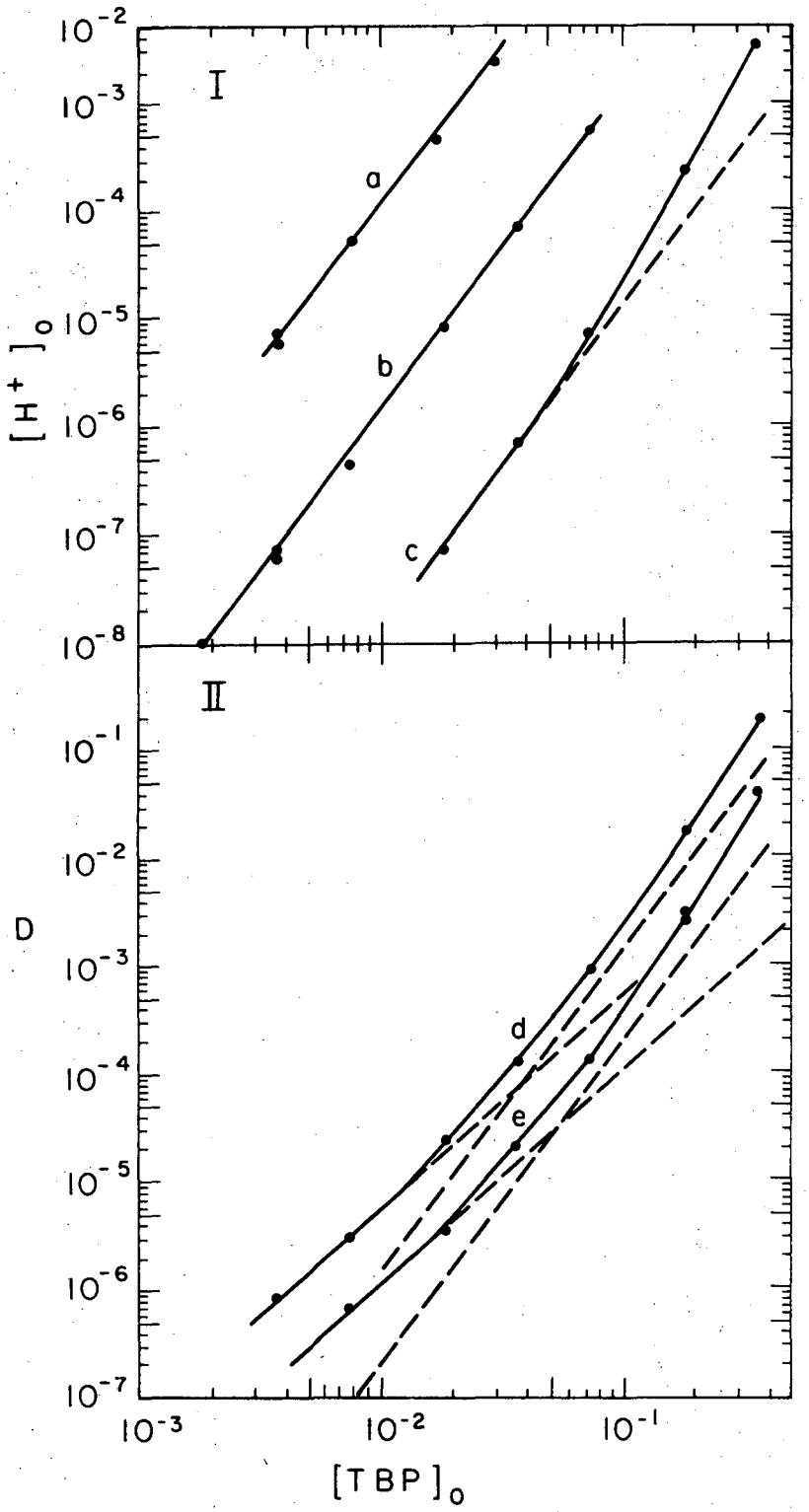


Fig. 5

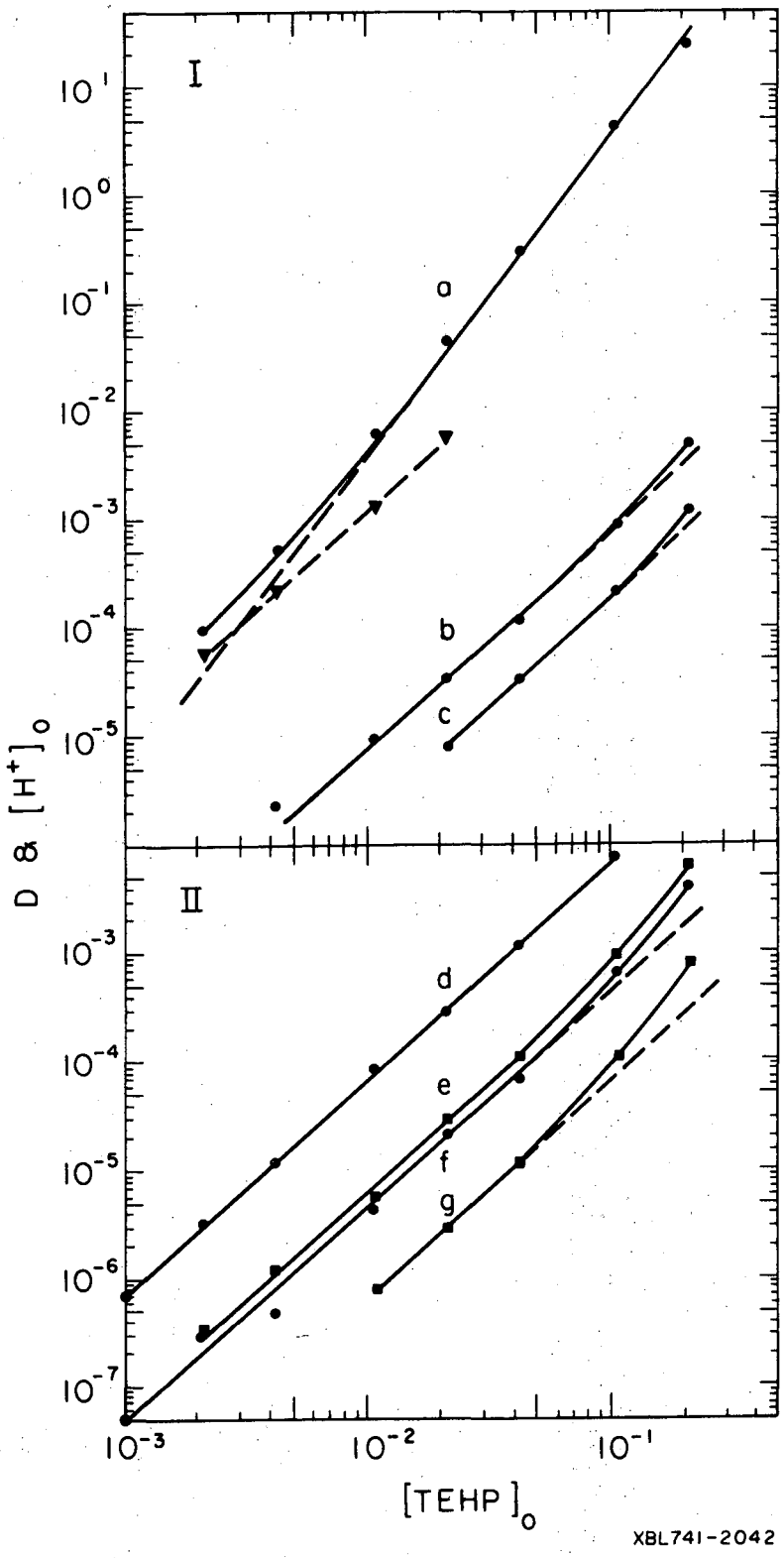

I
II
a
b
c
d
e
f
g
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
$D\,\delta\,[H^+]_o$
10^{-3}
10^{-2}
10^{-1}
$[TEHP]_o$
XBL741-2042

Fig. 6

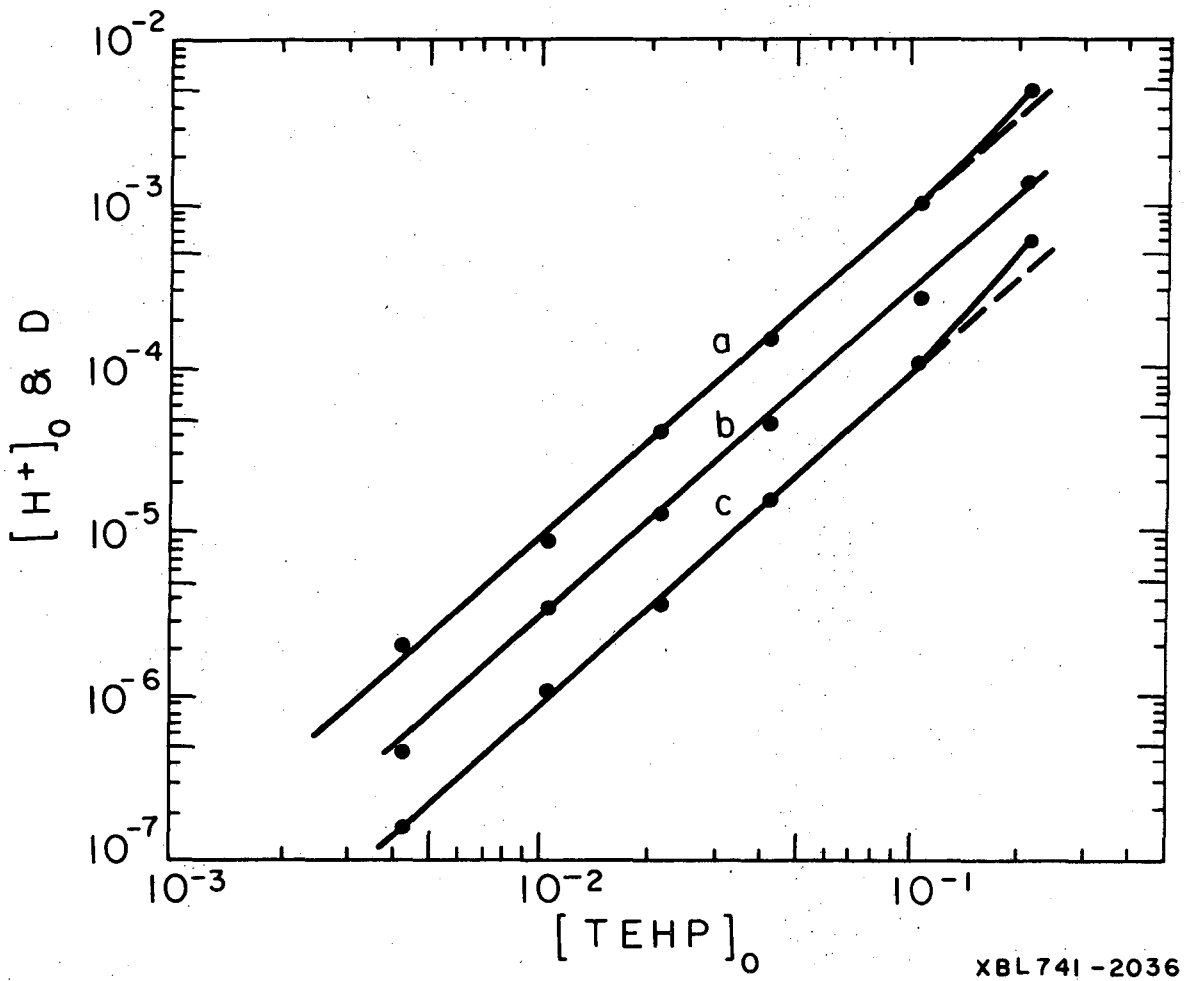


Fig. 7

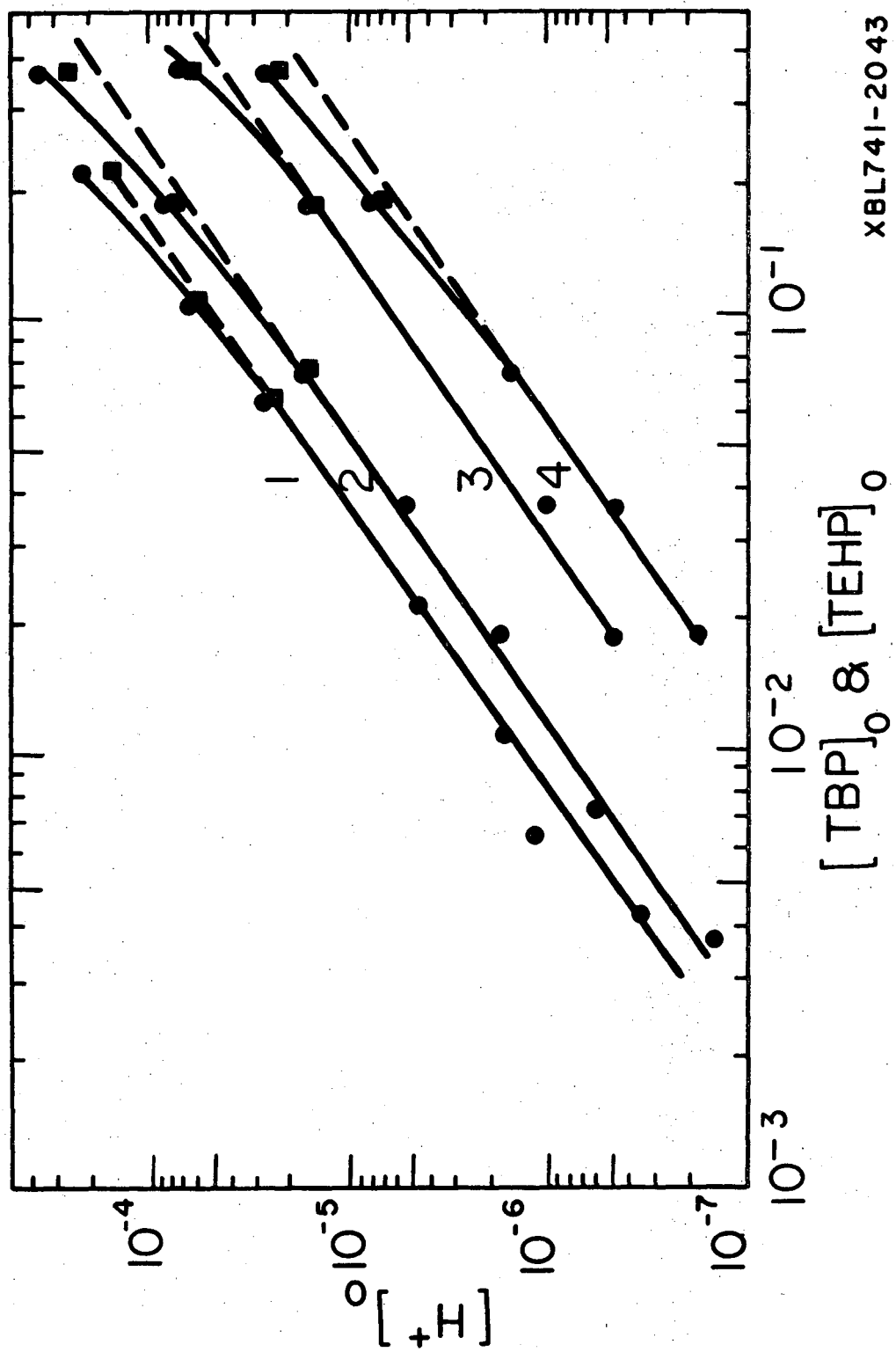
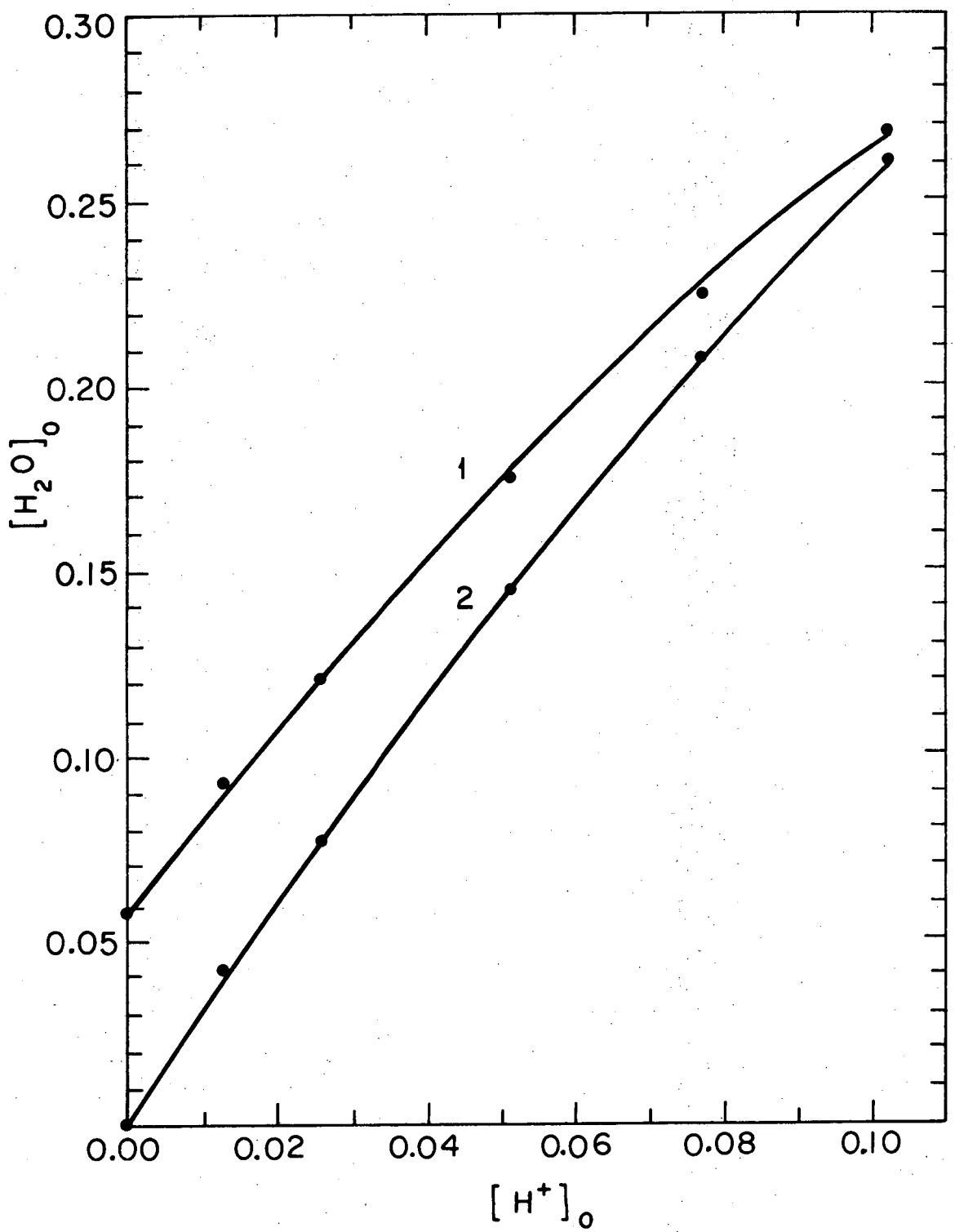


Fig. 8



XBL741-2039

Fig. 9

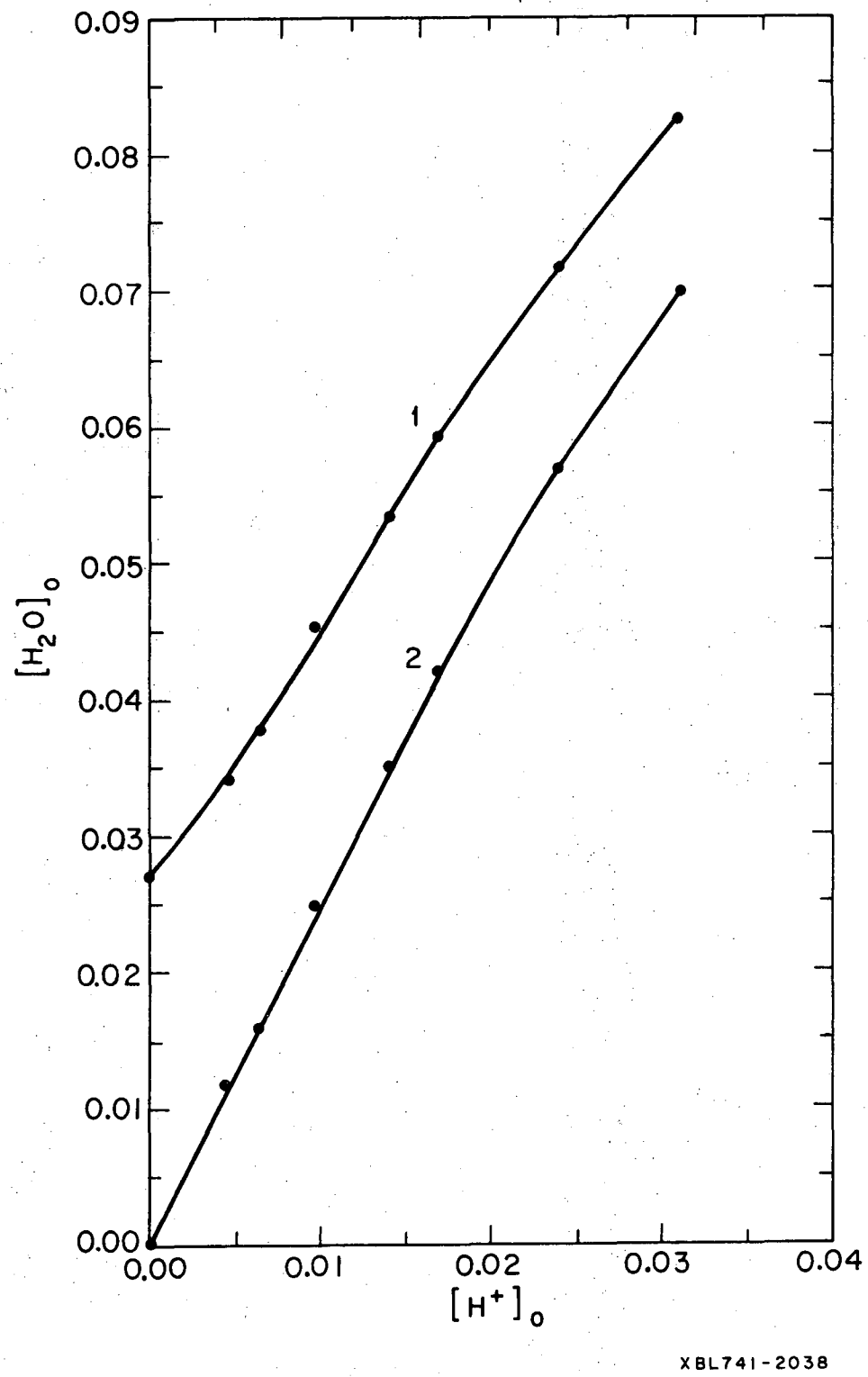
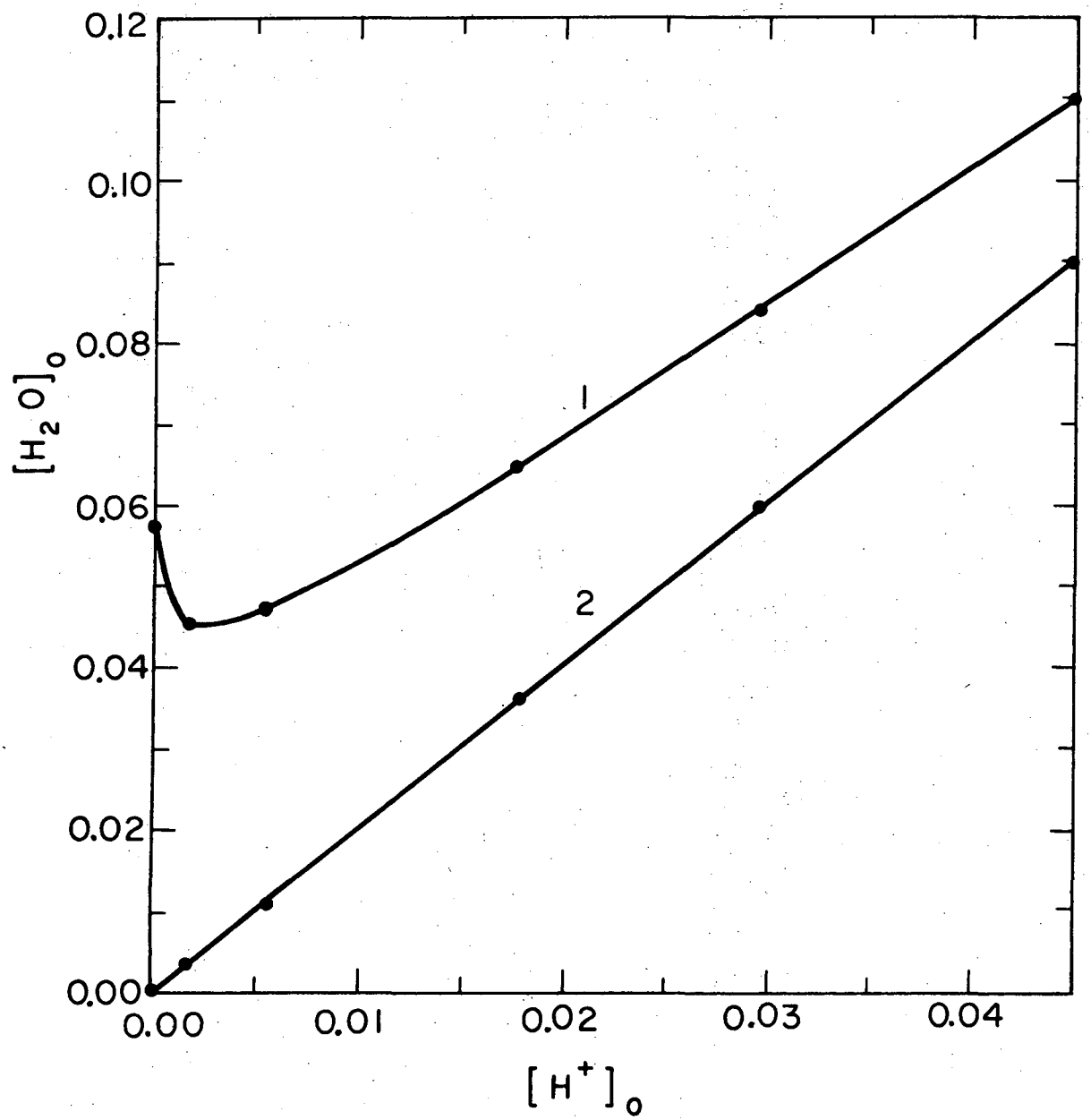

0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
$[H_2O]_o$
1
2
0.00
0.01
0.02
0.03
0.04
$[H^+]_o$
XBL741-2038

Fig. 10



XBL741-2037

Fig. 11

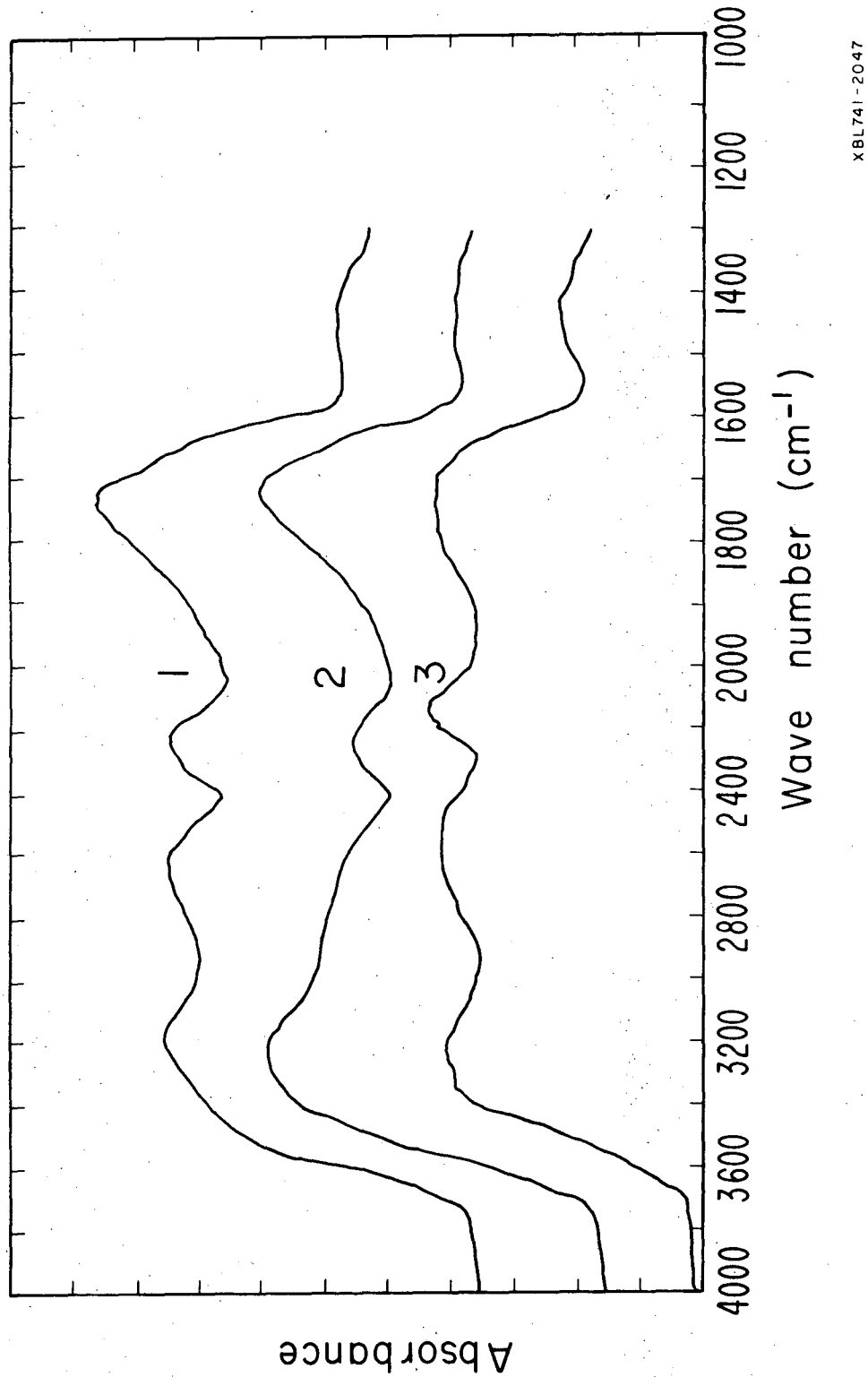

Absorbance
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
Wave number (cm⁻¹)
1
2
3
XBL741-2047

Fig. 12

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or 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.

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