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ABSTRACT

The extraction of HClO_4 or HReO_4 into dilute solutions of tributyl phosphate (TBP) in benzene, sym-triethyl benzene and chloroform has been studied. In the benzene and chloroform systems only a two-TBP acid complex was found; while in triethyl benzene a three-TBP acid complex was also found, depending upon the TBP concentration.

It is suggested that in all cases the extracting species is based upon a hydronium ion core which is ion paired to the anion, i.e., $n\text{TBP} \cdot \text{H}_3\text{O}^+ \cdot p\text{H}_2\text{O} \dots \text{ClO}_4^-$. In benzene, the value of $n = 2$ and p is ~ 2 . It is also suggested that the variation in coordination number and in extraction coefficients in these diluents and in those studied in the previous paper can be plausibly explained on the basis of the properties of the diluents.

Introduction

In the first part of this study² dealing with HClO_4 or HReO_4 extraction by tributyl phosphate (TBP), three types of diluents were used: isooctane, an example of a relatively inert hydrocarbon; CCl_4 , a halogenated diluent capable of moderate dispersion force interactions; and 1,2-dichloroethane, a solvent of relatively high dielectric constant. Although stepwise complexing, namely a $2\text{TBP}\cdot\text{acid}$ and a $3\text{TBP}\cdot\text{acid}$, occurred with isooctane and CCl_4 in the range of TBP concentrations employed, it was demonstrated that more than one mole of water co-extracted with each mole of acid, and it was suggested that the fundamental species extracting was a solvated hydronium perchlorate or perrhenate. The TBP and the additional water were thought to be bonded to the three positive sites of the H_3O^+ ion, and indeed, no complex higher than 3:1 was found in the TBP concentration range investigated. The diluent CCl_4 was better able to stabilize the 2:1 complex than could isooctane; the CCl_4 did this both indirectly by means of its interaction with TBP, which reduces the effective concentration of TBP, and directly through its solvation of the acidic cation by dispersion force interactions of the chlorine atoms. The solvent of high dielectric constant, 1,2-dichloroethane, permitted dissociation of the extracted ions. It was suggested that this loss of interaction with the anion required the hydronium cation to obtain its solvation more completely from the TBP, thus yielding only a 3TBP complex over the range of TBP concentrations examined.

In the present study the extraction of HClO_4 or HReO_4 with dilute TBP will be examined in two more types of diluents: benzene and 1,3,5-triethylbenzene, representing basic, aromatic diluents; and CHCl_3 , an acidic solvent.

The first type is expected to interact primarily with the acidic (2TBP·acid) cation, enhancing acid extraction, and the second type via its acidic hydrogen, should react mainly with the basic TBP molecule, thus depressing extraction. As before, ReO_4^- tracer was used to determine the organic-phase acid concentrations, and the data are presented in the form of log-log plots with the aim of determining whether the species is an ion pair or is dissociated, and what is the value of n , the TBP coordination number.

Experimental

Reagents: The HClO_4 and HReO_4 solutions were prepared and standardized as described in the previous paper.² The ^{186}Re tracer solution was prepared by irradiating KReO_4 with neutrons in the Vallecitos reactor and dissolving the product in distilled water. The benzene and chloroform were Baker and Adamson, Reagent grade. The 1,3,5-triethyl benzene was obtained from DuPont, and was purified by washing with conc. sulfuric acid, sodium carbonate, water, and was then distilled.

Procedure: Standardized solutions of either HClO_4 or HReO_4 containing radioactive $^{186}\text{ReO}_4^-$ were shaken for not less than one hour with diluted TBP solutions. After centrifugation, aliquots of both the organic and aqueous phases were taken for γ -counting in a well-type $\text{Na}(\text{Tl})\text{I}$ scintillation counter. Knowing the original concentration of acid and specific activity of the tracer, the measured counting rates yield the equilibrium concentrations of HClO_4 or HReO_4 in each phase. In some instances where sufficient acid extracted, acid-base titrations were used to determine the equilibrium acid content of each phase.

The organic-phase concentration of water bound by TBP and the amount of water coextracted with HClO_4 were analyzed by both the Karl Fischer method using a dead-stop end-point, and by means of tritiated water counted in a room-temperature liquid scintillation counter.

Results

The uncorrected experimental results are shown as log-log plots in Figs. 1-7. These data are indicated by circles and are connected by solid lines. Corrections made to the experimental points, as described in the Discussion section, are indicated in each of the plots by square symbols and are connected by dashed lines.

The log-log plots of organic-phase water concentration vs TBP concentration are shown in Figs. 1 and 2 for TBP-benzene and TBP- CHCl_3 systems, respectively, for a water activity of unity. 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 from these water concentrations (water solubility in benzene, 0.0314 M ; literature value, 0.031 M^3 at 23°C ; water solubility in CHCl_3 , 0.070 M , literature value, 0.070 M^3 at 24.5°C). Figure 3 is a log-log plot of organic-phase water concentration vs activity of water for 0.60, 0.30, and 0.10 M equilibrium TBP in CHCl_3 . The diluent water (corrected for both the water activity and the volume fraction) has again been subtracted.

The log-log plot in Fig. 4 is of organic-phase acid concentration vs the product of the aqueous activity of HClO_4 times the water activity to the appropriate power (described below) for 0.734 M , 0.367 M , and 0.183 M TBP in

benzene. Perrhenate tracer out of perchloric acid was used to determine the organic-phase concentrations for the 0.367 M TBP data, while acid-base titrations methods were used for the 0.734 M and 0.183 M TBP data.

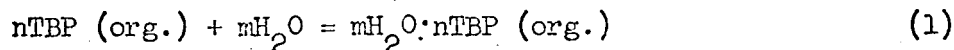
Figures 5 and 6 show the log-log dependence of the organic-phase acid concentration on the TBP concentration for benzene, CHCl_3 , and triethyl benzene. Perrhenate tracer out of perchloric acid was used in both the benzene and triethyl benzene systems, while perrhenate tracer out of perrhenic acid was used in the CHCl_3 case to determine the concentration of extracted acid.

The relationship between coextracted water and the organic-phase acid concentration is shown in Fig. 7 for benzene. The total amount of water extracted, exclusive of the diluent water, is shown by curves 1 and 2 for TBP concentrations of 0.734 M and 0.183 M. The difference between the organic-phase water concentration when acid is present and that which extracts into equivalent solutions of unbound TBP alone (but corrected to the appropriate water activity) is indicated by curve 3.

In those figures where ReO_4^- tracer was used as a marker for ClO_4^- , the values plotted for the organic-phase acid concentrations, $[\text{H}^+]_o$, may be up to a factor of two too high, as ReO_4^- extracts slightly better than ClO_4^- . But as long as the amount of TBP complexed with the extracted acid is small, correcting for this behavior would result only in a parallel displacement of the data and not a change of slope, so the apparent values of $[\text{H}^+]_o$ as determined from the ReO_4^- tracer are presented directly. When ReO_4^- tracer out of HReO_4 was used, the above problem does not arise, and the plotted values of organic-phase acid concentrations are the actual amounts.

Discussion

TBP-H₂O. The equilibrium for the distribution of water into a solution of TBP in an organic diluent may be written:



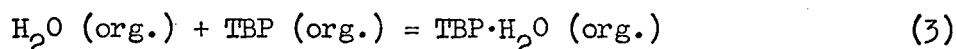
The corresponding equilibrium constant is

$$K_{\text{H}_2\text{O}} = \frac{(m\text{H}_2\text{O} \cdot n\text{TBP})_o}{(\text{H}_2\text{O})_o^m (\text{TBP})_o^n} = \frac{[m\text{H}_2\text{O} \cdot n\text{TBP}] y_{\text{H}_2\text{O}}}{(\text{H}_2\text{O})_o^m [\text{TBP}]_o^n y_{\text{TBP}}^n} = K_{\text{H}_2\text{O}} \frac{y_{\text{H}_2\text{O}}}{y_{\text{TBP}}^n} \quad (2)$$

where parentheses signify activity, brackets denote molar concentrations, and y is a molar activity coefficient. With the assumption that the ratio $y_{\text{H}_2\text{O}}/y_{\text{TBP}}^n$ is a constant in the dilute solutions used, as discussed and validated in the previous paper,² Eq. (2) suggests that a log-log plot of the organic-phase water concentration vs the equilibrium TBP concentration should generate a line of slope n , where n is the number of TBP molecules coordinated in each extracted water complex. Such plots are shown in Figs. 1 and 2 for the TBP-benzene and TBP-CHCl₃ systems at a water activity of unity. The data connected by a solid line results from plotting $[\text{H}_2\text{O}]_o$ vs initial concentration of TBP; the water extracted by the diluent alone has been subtracted. At TBP concentrations below 0.1 M in benzene and below 0.8 M in CHCl₃, it is seen that the plots yield a slope of unity. This suggests that a water complex with only one TBP molecule dominates at these and lower TBP concentrations. Correcting these data from initial TBP concentrations to equilibrium TBP values by subtracting the amount of TBP bound to water on the basis of one TBP per H₂O molecule extracted (see below), leads to the dashed lines in the figures.

By performing the complementary experiment of measuring $[\text{H}_2\text{O}]_o$ at a fixed TBP concentration but with varying a_w , it can be determined how many water molecules are involved in the TBP·water complex. In Fig. 3, data for $[\text{H}_2\text{O}]_o$ vs a_w for equilibrium concentrations of TBP of 0.10, 0.30, and 0.60 M in CHCl_3 are shown.⁴ Lines of unit slope can be drawn through each set and this indicates that $m = 1$; only one water molecule is involved. Because of the similarly low concentrations of water involved in the benzene-TBP system, we feel it likely that there too, only one water molecule is in the extracted complex at low TBP concentrations. Then we can calculate the value of $K_{\text{H}_2\text{O}}$ for the 1:1 TBP: H_2O complex ($n = m = 1$) below 0.1 M TBP in benzene as $0.28 (\text{mol/l.})^{-1}$, and below 0.8 M TBP in chloroform as $0.18 (\text{mol/l.})^{-1}$.

These equilibrium quotients involve species in two phases, TBP and TBP· H_2O in the organic phase, and water in the aqueous phase.⁵ Thus a number of equilibria are involved: the distribution of water between the aqueous and organic phases, and the competition of the diluent and extracted water for the TBP. If one wants to concentrate attention upon the latter competition, it is more meaningful to remove the effect of the distribution of water and to work with a quotient involving only organic-phase species. This can be done by dividing the mixed-phase quotient by the solubility of water in the diluent (column 2, Table I) to yield the equilibrium quotient for the organic-phase reaction.



These are given in column 4 of Table I, and it can be seen that in contrast to the range of only two in the mixed-phase quotients (column 3) between isoctane and chloroform, there is now a factor of 13. The order of the organic-phase

Table I. Constants for the bonding of H_2O by TBP in various diluents.

Diluent	Water solubility (molarity)	K_{H_2O} (Eq. (1))	\bar{K}_{H_2O} (Eq. (3))
isooctane	0.0035 ²⁾	0.12 ²⁾	34
CCl_4	0.008 ⁶⁾	0.15 ⁷⁾	18
benzene	0.031	0.28	9.1
$CHCl_3$	0.070	0.18	2.6

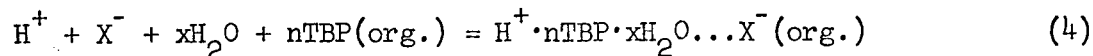
quotients reflects primarily the interaction of the diluent with TBP, whereas the mixed-phase quotients also directly involve the compensating effect of the diluents' interaction with water. Isooctane may be taken as the relatively "inert" standard diluent; since it provides poor solvation for water, the water solubility is low, and since it also provides poor solvation for TBP, the TBP and organic-phase water are free to complex with each other, yielding the largest value of \bar{K}_{H_2O} . At the other extreme, chloroform, through its weakly acidic hydrogen, interacts with water and thus has the highest water solubility, but it also interacts relatively strongly with TBP, reducing the latter's effective concentration. Both reasons produce a small \bar{K}_{H_2O} . It can be seen from Table I that benzene also has a low value for \bar{K}_{H_2O} , suggesting a significant interaction between benzene and TBP. This has been indicated before by activity coefficient measurements.⁸⁻¹³ We believe that this interaction involves the π -electron rings of benzene and the phosphoryl group of TBP. To a perhaps smaller extent, the electrons on the chlorine atoms of CCl_4 contribute to a similar interaction with TBP.

Thus, although the values of K_{H_2O} do not show a very great spread and are somewhat difficult to interpret because of the compensating behavior of the diluent interactions with water and with TBP, the values of \bar{K}_{H_2O} show a much greater spread and are interpretable in a plausible way.

At higher concentrations of TBP than the limits mentioned earlier, it can be seen (Figs. 1 and 2) that the data no longer follow the line of unit slope, but increase at a faster rate with increasing TBP. This result may indicate that a higher TBP-water species^{7,14} is forming or that the assumption of a constant activity coefficient ratio may no longer be valid. As was

suggested previously, both processes probably are occurring, but the present data are insufficient to establish which is the more important.

TBP-H₂O-HClO₄ and -HReO₄. The extraction of HReO₄ or HClO₄ by TBP solutions in low dielectric constant media where the extracted species are ion paired may be written



with the corresponding equilibrium constant

$$K_n^a = \frac{(H^+ \cdot nTBP \cdot xH_2O \dots X^-)_o}{(TBP)_o^n (H_2O)^x (H^+ X^-)} \quad (5)$$

If we make the reasonable assumption that the ratio of activity coefficients y_{HX}/y_{TBP}^n is a constant in the dilute organic-phase solutions employed in this study (the variation of both coefficients is initially of a similar nature), then where this assumption holds

$$K_n^a = \frac{[H^+ \cdot nTBP \cdot xH_2O \dots X^-]_o}{[TBP]_o^n (H_2O)^x (H^+ X^-)} \quad (6)$$

where K_n^a is the mixed equilibrium quotient and brackets indicate concentrations. Thus, if the TBP concentration is held constant, a log-log plot of the organic-phase acid concentration, $[H^+]_o$, vs the aqueous-phase activity product, $(H^+ X^-)(H_2O)^x \equiv a'_{HX}$, should yield a straight line and a value of unity for the slope, demonstrating that the extracting acid species is an ion pair. Such a plot for 0.734, 0.367, and 0.183 M TBP in benzene is shown in Fig. 4. Three is the value used for the number x, as described later. Over most of the range of extracted acid, the points lie on lines of unit slope, suggesting that the extracted complex is indeed an ion pair. At high concentrations of

$[H^+]_0$, where curvature in the plot becomes noticeable, an increasingly large fraction of the TBP is complexed with the extracted acid. Since such TBP is no longer free, this represents a serious departure from the required condition of a fixed $[TBP]$. The value of $[H^+]_0$ can be corrected to a fixed concentration of TBP by means of the following equation,

$$[H^+]_0' = [H^+]_0 [TBP]_0'^n / [TBP]_0^n \quad (7)$$

For benzene, $n = 2$, as is shown below. It can be seen that the points on the curved portion of the plots in Fig. 4 are thus brought onto the straight lines of unit slope extended from the dilute solution regions where corrections are not necessary.

Similar data were not collected for the TBP- $CHCl_3$ and TBP-triethyl benzene systems, but it is certainly expected that ion pairs would also be formed in these relatively low dielectric constant media. ($\epsilon = 4.81$ ¹⁵ at 20°C for $CHCl_3$; $\epsilon = 2.28$ ¹⁵ at 20°C for benzene and triethyl benzene).

It is now possible to determine the value of n , the number of TBP molecules coordinated in the extracted complex for each of the TBP-diluent systems. By examining log-log plots of extracted acid vs TBP concentration at a constant a_{HClO_4}' or a_{HReO_4}' , the slopes yield directly the value of n . As in Part I of this study, the concentrations of TBP in the plots are initial values rather than the equilibrium concentrations called for by Eq. (6). This does not lead to any error in the determination of n , because for concentrations below 0.1 M TBP, correction for the TBP bound to water, $[TBP \cdot H_2O]$, means only a shift in the TBP scale, and does not change the slope of the plot. Correction for the TBP bound up in the acid complex must be made, however, and such

corrected points are shown as squares in Fig. 5. This figure has plots for the extraction of HReO_4 tracer out of 1.60 M and 4.07 M HClO_4 into TBP solutions in benzene, and for 2.91 M HReO_4 into TBP solutions in CHCl_3 . Lines of slope two can be drawn through each set of data; the dashed lines are extensions to higher concentrations. Up to TBP concentrations of 0.1-0.15 M in benzene the agreement of the data points with the line suggests only a two-TBP coordinated complex is extracted. The upturn of the extraction curve at $[\text{TBP}] > 0.15 \text{ M}$ may indicate a 3TBP complex is forming, or, as was suggested in Part I of this study,² the breakdown of the dilute solution behavior (assumption of a constant organic-phase activity coefficient ratio) upon which the analysis is based. We cannot distinguish between these two possibilities; they both may be occurring.

But the main feature of the extraction into benzene as a diluent is the large range of TBP concentration over which a 2TBP complex dominates, and, as can be seen in Table II, the fact that the value of K_2^a is larger than for any other diluent studied. Certainly benzene interacts with TBP itself; activity coefficient measurements show there are attractive interactions leading to negative deviations from ideality.⁸⁻¹³ If the π -electrons are responsible, as we believe, we might expect stronger interactions between benzene and an acidic species than with a basic species such as TBP. This should be true especially with a 2TBP complex of the hydronium ion, as one positive site of the hydronium ion core would be relatively open to basic electron-donating molecules. The 3TBP complex is essentially coordinatively saturated and should be less affected. While the TBP-benzene interaction contributes indirectly to an extended region of a 2TBP·acid complex by lowering the effective concentration of TBP compared to isooctane as diluent, such solvation of TBP should also

Table II. Equilibrium quotients for extraction of tracer HReO_4 .

Diluent	Macro acid	K_2^a	K_3^a
Benzene	HClO_4	2.9×10^{-2}	----
triethyl benzene	HClO_4	1.3×10^{-2}	1.7×10^{-1}
CHCl_3	HReO_4	8.2×10^{-4}	$< 1 \times 10^{-3}$
CCl_4	HReO_4	1.7×10^{-3}	2.0×10^{-2}
isooctane	HClO_4	5.0×10^{-3}	8.3×10^{-1}

lower the value of K_2^a . The direct interaction of benzene with the $2\text{TBP}\cdot\text{HClO}_4$ complex should stabilize the 2TBP complex, leading to an enhanced region of existence, but should increase the magnitude of K_2^a over that in isooctane, as is observed experimentally. So the latter interaction dominates in the benzene system. If so, we can provide a test by using triethyl benzene, rather than benzene, as diluent. Because of the ethyl groups, the density of π -electrons per unit volume is only about one-half of that in benzene, and these electrons are probably also partially blocked from coordinating with acidic receptors by the side-chains. For both of these reasons, we would expect triethyl benzene interactions to be less important. As Fig. 6 and Table II show, this is the behavior observed. For triethyl benzene the log-log plots of $[\text{H}^+]_0$ vs $[\text{TBP}]$ at fixed aqueous concentrations of 1.60 M and 4.12 M HClO_4 can be resolved into two lines (dashed) having slopes of two and three. This indicates both 2TBP and 3TBP complexes are being formed in the same stepwise fashion as earlier observed for isooctane and CCl_4 ,² and the TBP concentration where both species are in equal abundance is at about 0.035 M , compared to 0.09 M for CCl_4 and 0.008 M for isooctane. Because of the reduced ability of triethyl benzene to solvate the acid complexes, particularly the 2:1 species, the value of K_2^a is more than 2 times lower than in benzene. But because triethyl benzene still interacts more strongly with TBP than does isooctane, the 3:1 complex, though observable in the range of TBP concentrations studied, has a constant 5 times smaller than in isooctane.

We have also included a weakly acidic diluent, CHCl_3 , in those studied. From work dealing with the activities in the binary system, $\text{TBP}-\text{CHCl}_3$,^{10,11} and the system $\text{TBP}-\text{CHCl}_3-\text{H}_2\text{O}$,¹³ large negative deviations from ideality are

found. That is, through its acidic hydrogen, CHCl_3 coordinates relatively strongly with the basic TBP molecule,¹⁶ effectively reducing the latter's concentration. But we expect CHCl_3 to interact less strongly with the extracted acidic species, as such interaction could only be through the static bond moments and induced moments of its chlorine atoms, much as such interactions occur with CCl_4 . The result would be a lowered extraction of all acidic species in this diluent, and because of the reduction in the effective concentration of TBP, an extension of the region of 2TBP complex to higher stoichiometric TBP concentrations than in our standard comparison diluent, isooctane. The results shown in Fig. 5 and in Table II confirm this expectation. At an aqueous HReO_4 concentration of 2.91 M, the log-log plot of $[\text{H}^+]_o$ vs $[\text{TBP}]^a$ shows essentially only a slope of two, indicating a 2:1 TBP: HReO_4 species, and the value of K_2^a obtained is the lowest of any of the diluents studied. If we ascribe the slight upward curvature at high TBP concentrations to the formation of a 3:1 complex, we may determine an upper limit (some, if not all, of this effect is probably due to a change in the activity coefficients) for that complex, and this limit is 800 times lower than the measured quotient in isooctane.

The relationship between extracted acid and coextracted water is shown in Fig. 7 for 0.734 and 0.183 M TBP in benzene. Lines 1 and 2 show the total organic-phase water concentration less diluent water; while line 3 is the result of subtracting from 1 and 2 the calculated amount of water extracted by the remaining TBP. (For purposes of calculating this amount it was assumed only 2TBP-acid complexes were formed.) The slope of line 3 is a little greater than three. Thus sufficient water is coextracted to allow formation of the

proposed central unit of the acid complex, the hydronium ion. The additional water probably bridges between H_3O^+ and the coordinated TBP and bonds to the third unoccupied site of the hydronium core. It has not been proved, however, that the perchlorate or perrhenate anion is anhydrous, although this is likely.

It should be noted that measurements of the activities of TBP⁸⁻¹³ in benzene and CCl_4 yield very similar values. Yet from Table II, it is clear that the 2TBP complex is considerably better extracted into benzene than into CCl_4 . The range of the 2TBP complex also goes to a higher stoichiometric TBP concentration in benzene than in CCl_4 . We take this to mean that the benzene molecule, because of its π -electrons, can better solvate the extracted acid complexes, especially the more open 2TBP complex, than can CCl_4 . Both solvents, however, show better solvation of the acid complexes than does isooctane, an example of an aliphatic hydrocarbon diluent. The poor solvating characteristics of isooctane with respect to both TBP and the acid complexes makes more important their mutual interactions, and so favor the formation of the coordinatively saturated 3TBP acid complex. Triethyl benzene is intermediate between an aliphatic hydrocarbon and benzene in the efficacy of its solvent interaction via its (somewhat diluted and hindered) π -electrons. The range of 2TBP complex is greater in this diluent than in isooctane, but less than in CCl_4 or benzene. The principal result of the use of $CHCl_3$ as a diluent is its hydrogen-bonded interaction with TBP. This binding of the TBP results in the low values of the equilibrium quotients for $CHCl_3$ given in Table II, and also favors the 2:1 complex indirectly by reducing the effective concentration of the TBP. Such behavior contrasts with that in benzene where direct enhancement of the 2:1 species occurs by interaction of the acidic cation with the basic aromatic diluent.

It is concluded that the extraction complex in all these systems is built around a hydronium, or partially-hydrated hydronium, ion core. The number of TBP molecules coordinated to this core can vary from three to two over the range of TBP concentrations examined, and which of the complexes dominates at a given TBP concentration is determined by diluent chemical interactions which also hinder or enhance the extraction of the acid. It is suggested that this behavior can be qualitatively explained, even predicted, on the basis of known properties of the diluents.

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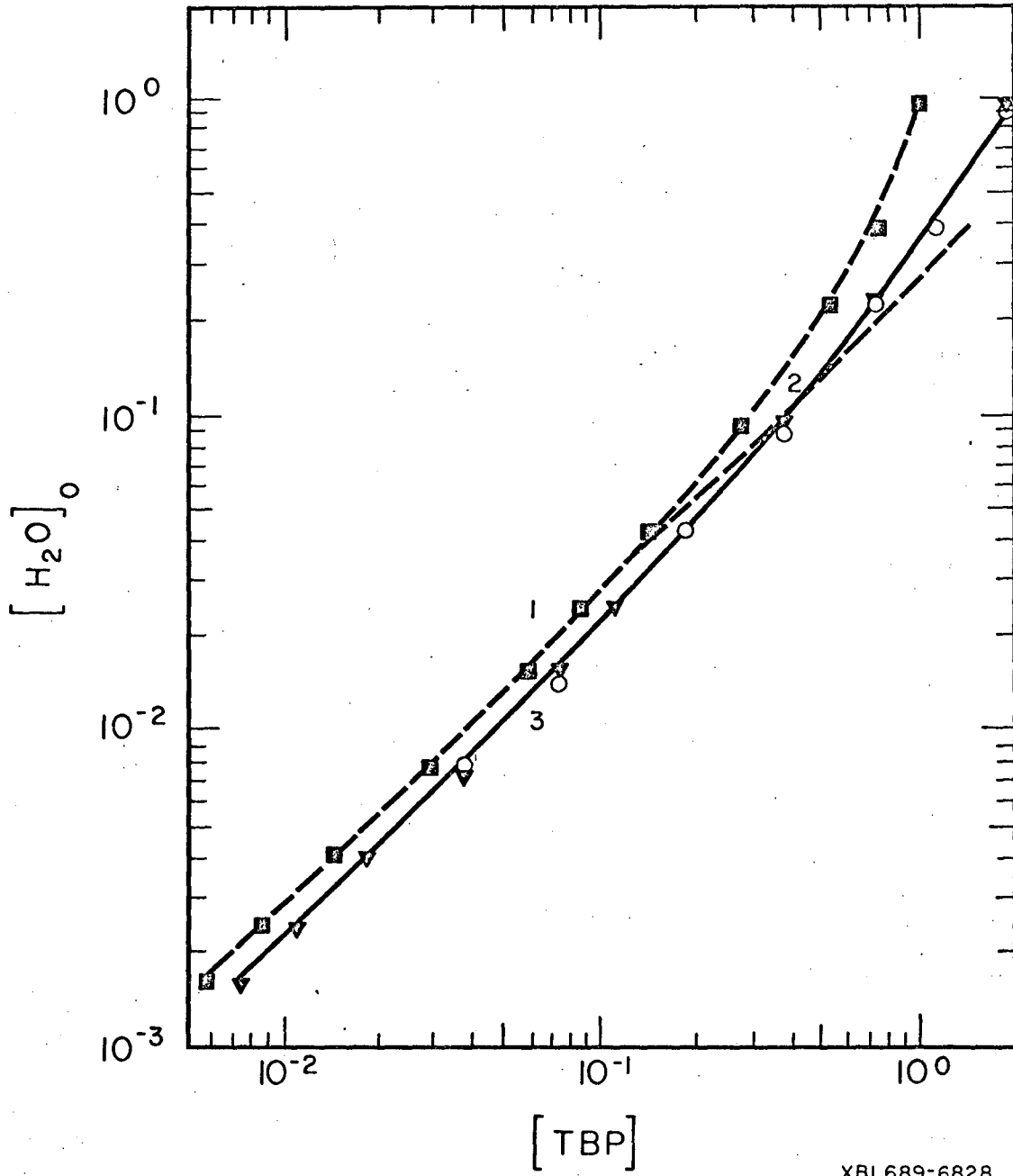
Figure Captions

- Fig. 1 Variation of water content of organic phase with TBP concentration in benzene. ($[H_2O]_o$ = total H_2O-H_2O dissolved by diluent.) Line 1, \blacksquare , is $[H_2O]_o$ vs equilibrium TBP ($[TBP]_o$ = total TBP- $[H_2O]_o$). Line 2 is a continuation of the line of unit slope. Line 3, ∇ , is $[H_2O]_o$ vs initial TBP concentration. ∇ , denotes results using tritium as a tracer; \circ , denotes results from Karl Fischer titrations.
- Fig. 2 Variation of water content of organic phase with TBP concentration in $CHCl_3$. ($[H_2O]_o$ = total H_2O-H_2O dissolved by diluent.) \blacksquare , is $[H_2O]_o$ vs equilibrium TBP ($[TBP]_o$ = total TBP- $[H_2O]_o$). \bullet , is $[H_2O]_o$ vs initial TBP concentration. The straight dashed line is drawn with unit slope.
- Fig. 3 Variation of water content of organic phase with activity of water at various equilibrium TBP concentrations in $CHCl_3$. Line 1 is at 0.60 M equilibrium TBP; line 2 is at 0.30 M equilibrium TBP; and line 3 is at 0.10 M equilibrium TBP. All lines are drawn with unit slope.
- Fig. 4 Variation of acid content of organic-phase with the product of the $HClO_4$ activity and the cube of the water activity for 0.183 M TBP (line 5) and for 0.734 M TBP in benzene (line 3) as measured by acid-base titration; and for 0.367 M TBP in benzene (line 4) as measured by ReO_4^- tracer out of $HClO_4$ acid. \bullet , uncorrected data; \blacksquare , data corrected for used-up TBP. Lines 1 and 2 show the effect of using n equal to three and two respectively. Line 2, dashed portions of lines 4 and 5, as well as lower portions of lines 3 and 5 are drawn with unit slope.

Fig. 5 Variation of acid content of organic phase with TBP concentration in benzene for aqueous HClO_4 concentration of 4.07 M (line 1) and for 1.60 M HClO_4 (line 2); and with TBP concentration in CHCl_3 for aqueous HReO_4 of 2.91 M (line 3). \odot , uncorrected data; \square , data corrected for used-up TBP. Dashed and lower portions of lines 2 and 3, as well as line 1 are drawn with slope two.

Fig. 6 Variation of acid content of organic phase with TBP concentration in triethyl benzene for aqueous HClO_4 concentration of 4.12 M (upper curve) and for 1.60 M (lower curve). \odot , uncorrected data; ∇ , resolved $n = 3$ lines; other dashed lines, $n = 2$; \square , data corrected for used-up TBP.

Fig. 7 Water content vs HClO_4 concentration in the organic phase (as the aqueous HClO_4 concentration increases) for total TBP concentrations of 0.183 M and 0.734 M in benzene. Lines 1 and 2, \odot , are the total organic-phase water less the diluent water; line 3, \square , ∇ , is the total organic phase water less both the solvent water and the water bound to TBP.



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Figure 1

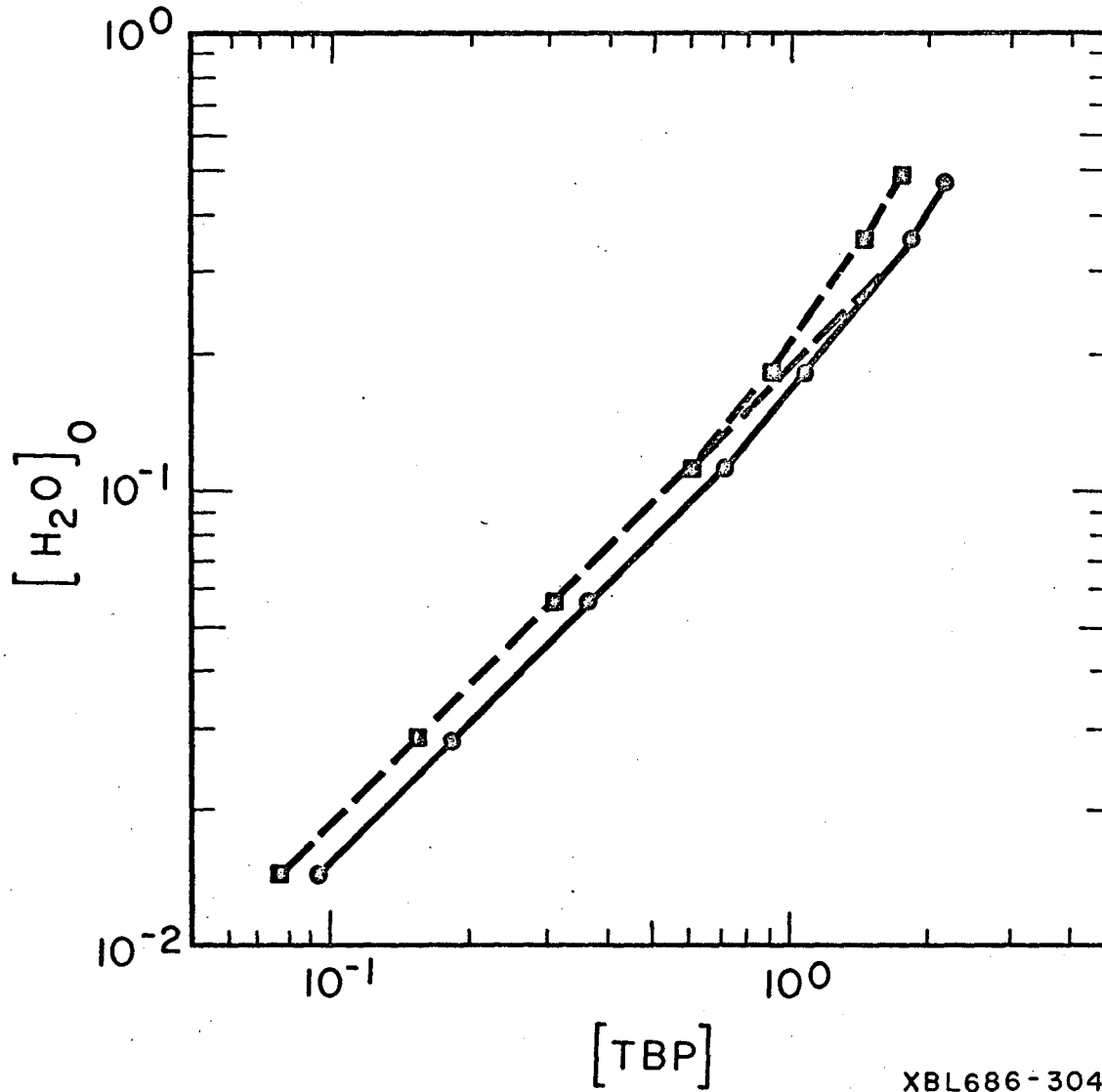
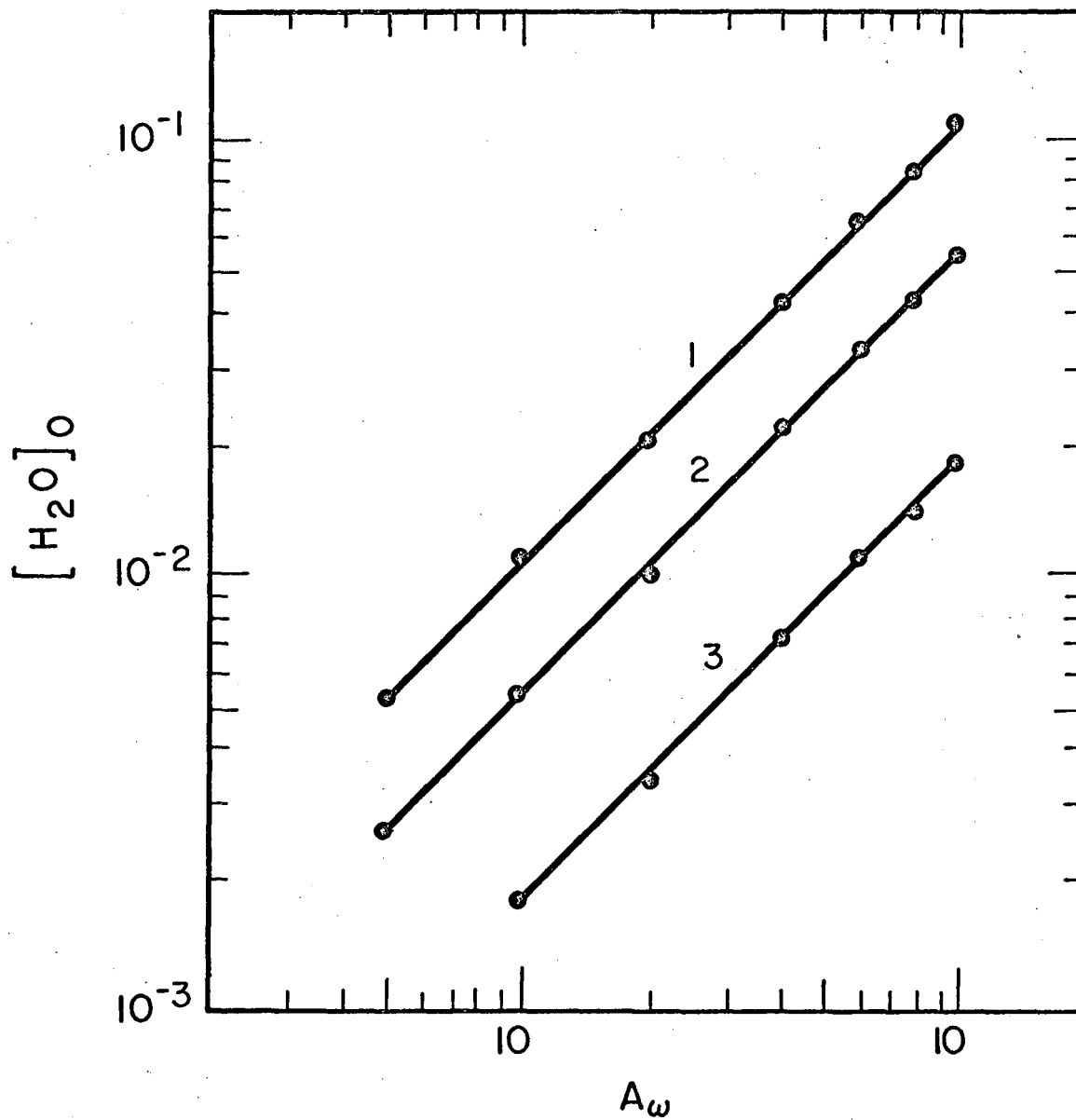


Figure 2

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Figure 3

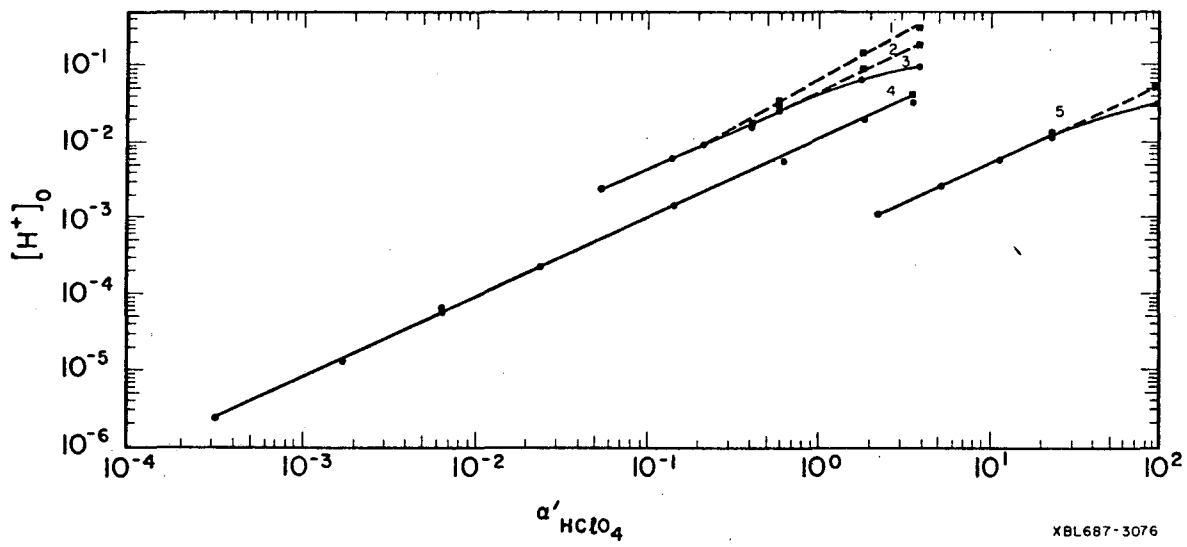
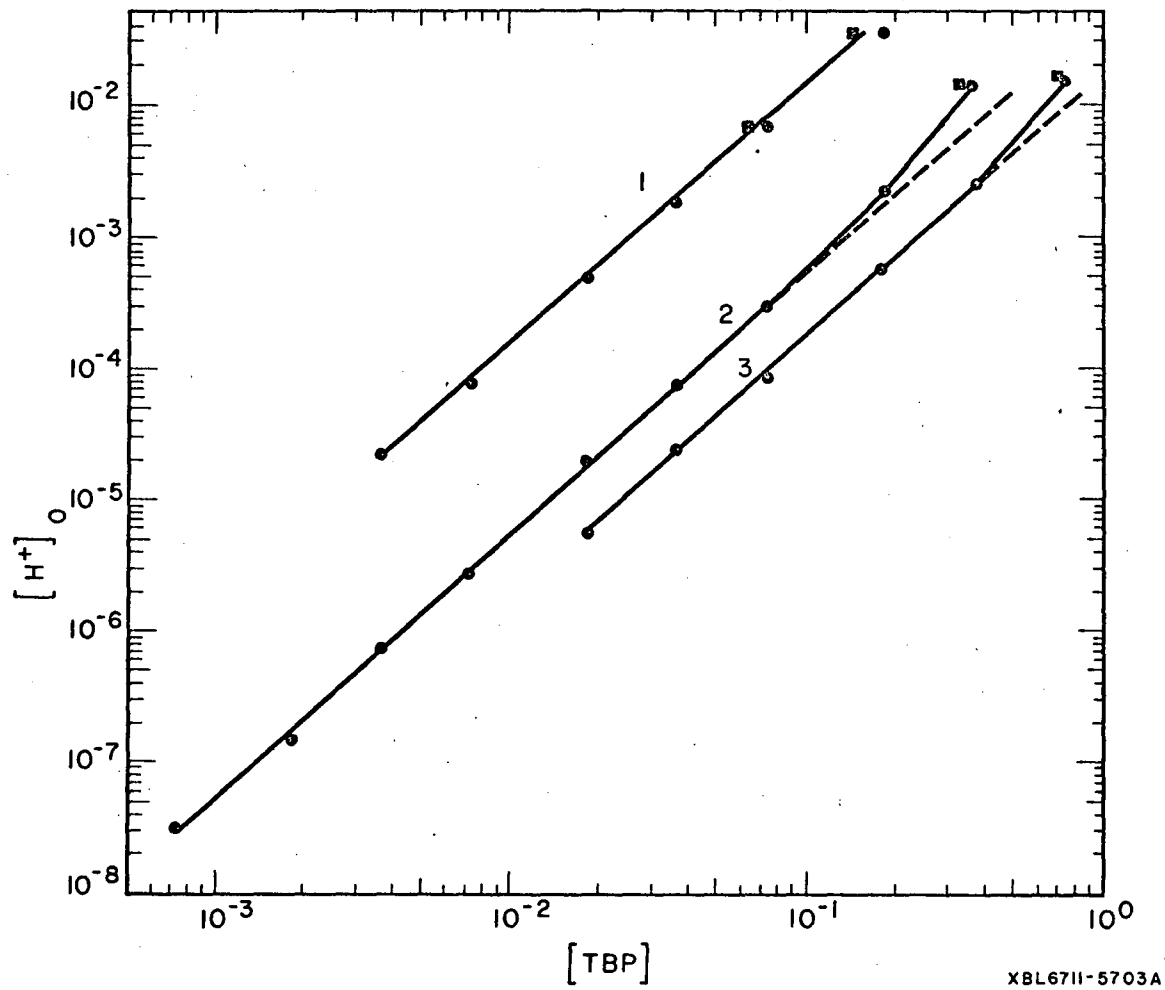
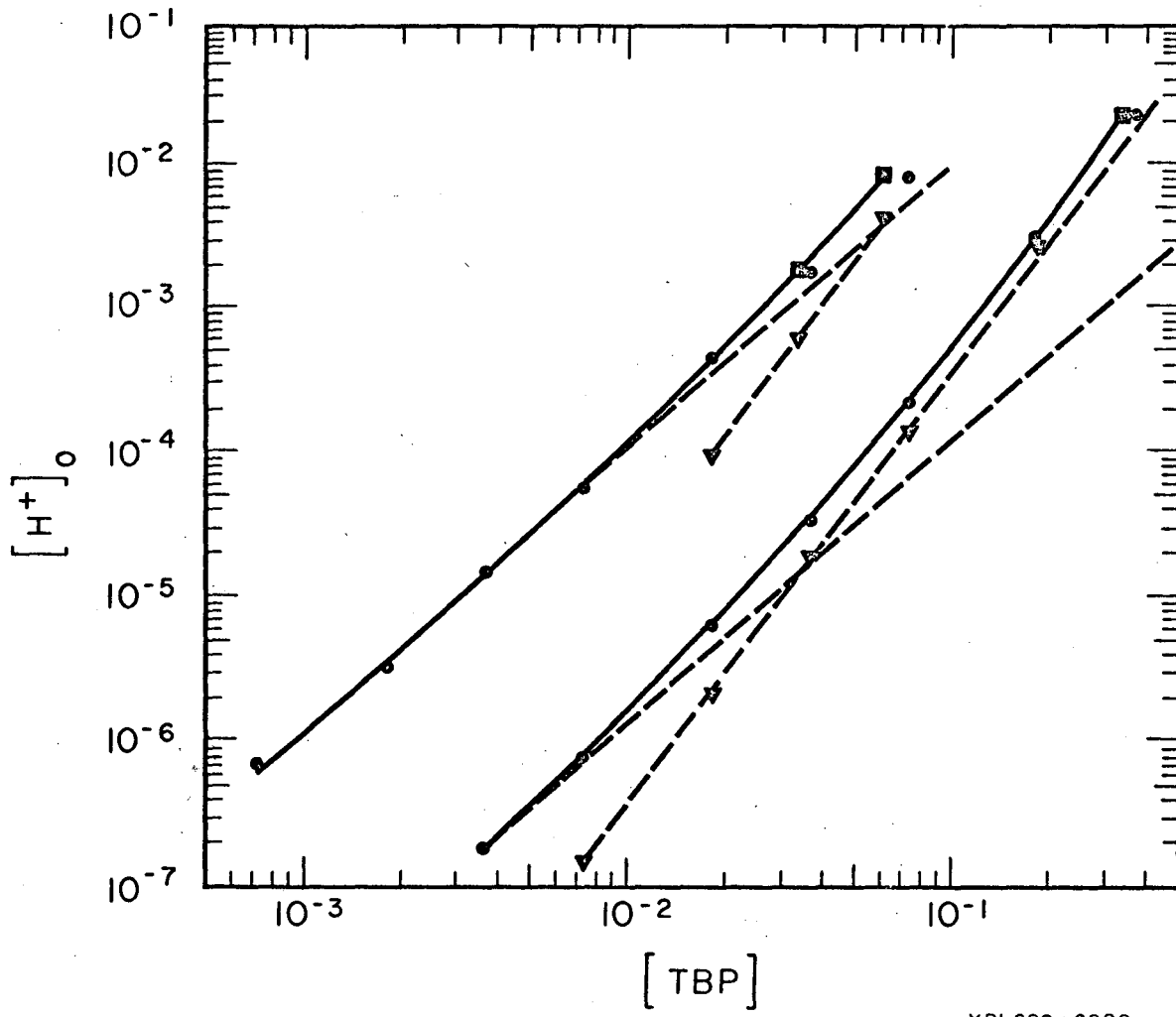


Figure 4



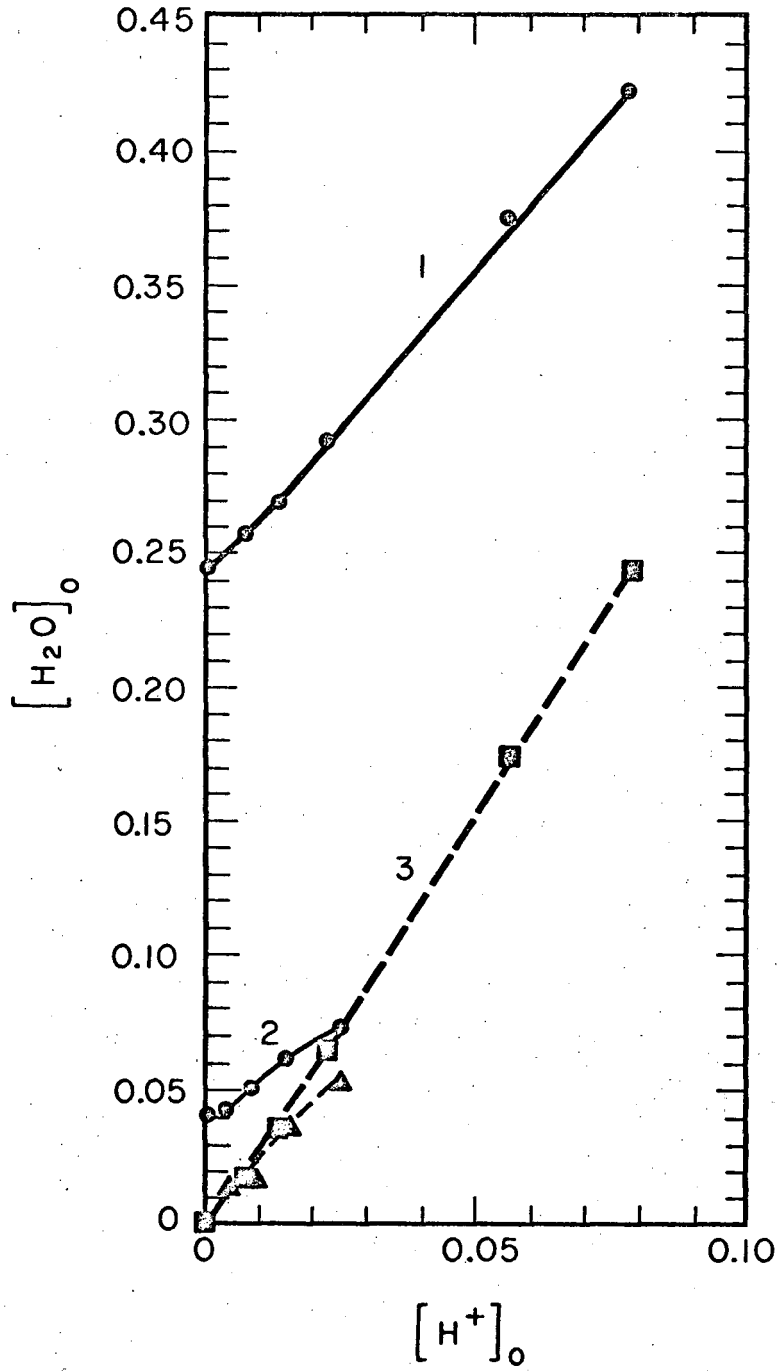
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Figure 5



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Figure 6



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Figure 7