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EXTRACTION OF HClO₄ AND HReO₄ BY DILUTE SOLUTIONS OF TRIBUTYL PHOSPHATE IN CCl₄, ISOCTANE AND 1,2-DICHLOROETHANE

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EXTRACTION OF HCLO₄ AND HReO₄ BY DILUTE SOLUTIONS OF TRIBUTYL PHOSPHATE IN CCl₄, ISOOCTANE AND 1,2-DICHLOROETHANENE

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Abstract

The extraction of HReO₄ or HCLO₄ into dilute solutions of tributyl phosphate (TBP) in CCl₄, isoctane and 1,2-dichloroethane has been studied, and the extracting species have been determined. A previous study of TBP in CCl₄, where the TBP concentrations were 0.03 to 0.3 M and the stoichiometric ratio TBP/H⁺ was > 3, indicated the only extracting species were the molecular adduct TBP·H₂O and the hydronium ion species 3TBP·H₂O⁺. pH₂O ... ClO₄⁻, an ion pair, where 0 ≤ p ≤ 1.5. In this study even more dilute TBP solutions in CCl₄ were examined, and a two-TBP acid complex, in addition to the three-TBP complex, was found. In the isoctane system either a two- or three-TBP acid complex, depending upon TBP concentration, was found to predominate. With 1,2-dichloroethane-TBP and at the organic-phase acid concentrations examined, only a dissociated three-TBP complex was found. In addition to an anion effect, it is suggested solvent effects upon both TBP and the extraction complex are changing to a greater or lesser extent, the TBP coordination number of the extracted hydronium ion from three to two.
Introduction

A previous study of HC104 extraction by dilute solutions of tributyl phosphate (TBP) in CC14 indicated that the proton was coordinated with three TBP molecules in the organic phase. This study also showed that at least one water molecule was always coextracted. From these two results a model for the extracted species was suggested; the complex has a hydronium ion core to which the three TBP molecules are coordinated. It was also suggested that this model could have general application as a guide for understanding acid extraction by dilute solutions of other weakly basic organic extractants as well as by other TBP-diluent systems.

To test the validity of this proposed model the extraction of HC104 by TBP in other diluents was investigated. In this paper, the first of a two-part study, the use of isoctane and of 1,2-dichloroethane as diluents was investigated. Isoctane was chosen to illustrate the extraction process in a solvent which possesses relatively weak solvating properties and so can be considered relatively "inert". This system will be used as a reference against which the other TBP-diluent systems can be compared. The solvent 1,2-dichloroethane was chosen for its relatively high dielectric constant; this property may allow dissociation of the extraction complexes into independent ions, thus freeing the cation from any close interaction with the anion.

Instead of using acid-base titration methods for determining the amount of extracted acid, as was mainly done in the previous TBP-CC14 investigation, radioactive perrhenate (ReO4-) tracer was employed. Since the molecular structure and charge of ReO4- is similar to ClO4- it is found that this tracer anion can be used successfully as a marker for ClO4- although it is not
identical in behavior. Because this radioactive tracer technique allows accurate determination of much lower organic-phase acid concentrations than those previously obtained, the TBP-HClO₄(HReO₄)-CCl₄ system was also reexamined over a greater range of dilute TBP concentrations.

Experimental

Reagents.—The HClO₄ solutions were prepared by dilution with distilled water of G. F. Smith reagent grade HClO₄, 70 to 72%. The stock 70-72% solution was standardized by titration with sodium hydroxide to the bromothymol blue endpoint. HReO₄ solutions were made by dilution from a stock solution, standardized in the same way, and prepared by dissolving Re₂O₇ in water. The 186ReO₄⁻ tracer solution was prepared by irradiating KReO₄ with neutrons in the Vallecitos reactor and dissolving the product in distilled water. The CCl₄ was Baker and Adamson reagent grade; the isoctane was "spectro" grade obtained from Matheson, Coleman and Bell; and the 1,2-dichloroethane was Matheson, Coleman and Bell, reagent grade.

Procedure.—Procedures for sample preparation, measurements and data analysis are essentially the same as already noted elsewhere.²,³ Additions or changes are as follows: 1) When using 1,2-dichloroethane as a diluent, shaking times of 5-6 hours were necessary to obtain reproducible results; 2) the volume ratios of organic to aqueous phases were not always kept one-to-one as before; 3) endpoint determination in the Karl Fischer water titrations was by the dead-stop instead of a visual endpoint technique. All extractions were performed at 23 ± 2°C.
Results

The experimental results are shown as log-log plots in Figures 1-7. The raw data are indicated by circles and are connected by solid lines. Corrections made to the experimental points, as described below, 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 Figures 1 and 2 for the TBP-isooctane and TBP-1,2-dichloroethane systems at a water activity of unity ($a_w = 1$). The amount of water extracted by the diluent alone, calculated as the product of the molar solubility in the diluent, times the volume fraction of diluent, has already been subtracted from the water concentrations plotted (water solubility in isooctane, 0.0035 M; literature values, 0.002 M - 0.006 M at 25°C; water solubility in 1,2-dichloroethane, 0.125 M; literature value, 0.129 M at 25°C).

The log-log plots in Figures 3 and 4 are of organic-phase acid concentration vs. aqueous activity of acid times the water activity to the appropriate power (described below) for 0.073 M and 0.367 M TBP in isooctane; for 0.367 M TBP in CCl₄; and for 0.367 M TBP in 1,2-dichloroethane. Perrhenate tracer out of perchloric acid was used to determine the concentrations in both the isooctane and CCl₄ systems shown in Figure 3; ReO₄⁻ tracer out of perrhenic acid was used for the 1,2-dichloroethane system, Figure 4.

Figures 5, 6 and 7 show the log-log dependence of organic-phase acid concentration vs. concentration of TBP in CCl₄, isooctane, and 1,2-dichloroethane, respectively. Perrhenate tracer out of perrhenic acid was used in both the CCl₄ and 1,2-dichloroethane systems and for one set of data in the isooctane
system; for the other set of data in isooctane, perrhenate tracer out of perchloric acid was employed.

The relationship between coextracted water and the organic-phase acid concentration is shown in Figure 8 for isooctane. The total amount of water extracted, exclusive of that in the diluent itself, is shown by line 1 for (initial) 0.73 M TBP and by line 2 for 0.183 M TBP. The difference between organic-phase water concentration when the acid is present and that which extracts into equivalent solutions of TBP alone (but corrected to the appropriate water activity) is indicated by line 3.

In those systems where ReO₄⁻ tracer was used as a marker for ClO₄⁻, the plotted organic-phase acid concentrations, [H⁺]₀, may be up to a factor of two higher than the actual HClO₄ concentrations, as ReO₄⁻ extracts somewhat better than ClO₄⁻ out of HClO₄. As long as the correction for the amount of TBP complexed with extracted acid is small, this causes no error in the slope analyses used in this paper, as it produces only a parallel displacement of the curves and no change in slope. But at high concentrations of extracted acid, where corrections for that fraction of the TBP complexed to the acid become important, a knowledge of the actual concentrations of organic-phase HClO₄ is needed, and these were obtained by direct two-phase titrations. In those systems where data were obtained using ReO₄⁻ tracer out of macro-perrhenic acid, no problem arises, and the values of [H⁺]₀ plotted are the correct ones.
Discussion

TBP-H₂O. The equilibrium for the distribution of water into a solution of TBP in an organic diluent is maintained independently of any other extraction equilibria, and may be written:

\[ n_{\text{TBP(org.)}} + m_{\text{H}_2\text{O}} = m_{\text{H}_2\text{O}} \cdot n_{\text{TBP(organ.)}} \]  \hspace{1cm} (1)

The corresponding equilibrium constant is:

\[ K_{\text{H}_2\text{O}} = \frac{(m_{\text{H}_2\text{O}} \cdot n_{\text{TBP}})}{(m_{\text{H}_2\text{O}})^n (n_{\text{TBP}})} = \frac{[m_{\text{H}_2\text{O}} \cdot n_{\text{TBP}}]_a}{(H_2O)^m [TBP]^n y_{\text{H}_2\text{O}}} \]  \hspace{1cm} (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 these dilute solutions, eq. 2 suggests a log-log plot of the organic-phase water concentration (corrected for water uptake of the diluent), \([H_2O]_o\), vs. the equilibrium TBP concentration, \([\text{TBP}]_o\), should generate a line of slope \( n \), where \( n \) is the number of TBP molecules bound to each extracted water complex. Such plots are shown in Figures 1 and 2 for isooctane and 1,2-dichloroethane, respectively. In these figures, the data connected by a solid line results from plotting \([H_2O]_o\) vs. the initial TBP concentration. It can be seen that for values below 0.2 M in dichloroethane and below 0.07 M in isooctane a line of slope one can be drawn through the points. This suggests that a water complex containing only one TBP molecule occurs at these (and lower) TBP concentrations, at least when \( a_w = 1 \); the majority of the TBP molecules, however, remain
unhydrated. Without determining $[H_2O]$ as a function of $a_w$, it cannot be
definitely asserted how many water molecules are involved in the complex.
However, from published $^2,7,8$ and unpublished studies $^9$ made upon similar
extractant-solvent systems, it is clear that the assumption of only one water
molecule being involved is reasonable. That is, at or below $0.2 \text{ M}$ in
dichloroethane and $0.07 \text{ M TBP}$ in isoctane and at or near $a_w = 1$, the
TBP-water species present is a predominantly 1:1 ($n = m = 1$) complex.
Correcting the TBP concentrations to equilibrium values, $[\text{TBP}]_0$, on this
basis of as many TBP molecules complexed as there are extracted waters, leads
to the dashed curves in Figures 1 and 2, and values of $K_{H_2O}$ for the dichloro-
ethane and isoctane systems of 0.44 and 0.12 (mol/L)$^{-1}$, respectively.

For higher concentrations of TBP, the experimental points deviate
from the line of unit slope. This result probably indicates a higher TBP-
water complex is being formed, but we must also consider how the activity
coefficients of the TBP and of the complex are varying. At some point, as
the TBP concentration is increased, the properties of the solution begin to
deviate significantly from those of the pure diluent. The individual
activity coefficients of the TBP and TBP·$H_2O$ species change from their infinitely
dilute solution values.$^{10,11}$ But experience indicates that the coefficients
of such similar species change in the same direction, that the assumption of
a constant activity coefficient ratio is still valid. Such "compensation"
of activity coefficient effects in extraction systems has been described by
other authors.$^{12,13}$ However, at some higher concentration of TBP, even the
ratio of coefficients may no longer remain constant, and then deviations from
the straight line determined at lower concentration may occur even though no
new species is formed. Experience with a number of extraction systems seems to indicate that such behavior does not occur much below about 5 volume % TBP (0.2M). Thus the deviations observed in isooctane starting below 0.07 M probably do indicate a new species. Definite corroboration of the existence of at least one additional water complex (in more concentrated solutions) has been obtained from N.M.R. studies made on TBP-CCl₄ systems. But over most of the range of TBP concentrations in isooctane used in this work, and for all the 1,2-dichloroethane solutions, the 1:1 TBP:H₂O complex is the dominant hydrated species.

A study of [H₂O]₀ for the TBP-CCl₄ system, using both Karl Fischer titrations and normalized infra-red intensities, has been published previously. The data presented is quite similar in form to that found in Figure 1. A 1:1 TBP:H₂O complex occurs up to a TBP concentration of 0.1 M. Beyond this concentration the water extraction curve again indicates the formation of an additional water:TBP complex. The K₇H₂O for the 1:1 complex was 0.15 (mol/l.)⁻¹.

TBP-H₂O-HClO₄ or-HReO₄. The extraction of HClO₄ or HReO₄ by solutions of TBP in a diluent may be expressed as

\[ H^+ + X^- + xH₂O + nTBP = H^+ . nTBP . xH₂O ... X^-(org.) \]

with the corresponding equilibrium constants

\[ \kappa_a = \frac{[H^+ . nTBP . xH₂O ... X^-]}{[TBP]_o^n [HClO₄]_o X(HClO₄)} \]

\[ \kappa_d = \frac{[H^+ . nTBP . xH₂O]_o [X^-]}{[TBP]_o^n [HClO₄]_o X(HClO₄)} \]

(4)

(4')
From log-log plots of the organic-phase acid concentration, \([H^+]_o\) vs. the aqueous-phase activity product \((HClO_4)(H_2O)^x = a_{HClO_4}\), with the TBP concentration held constant, it can be determined whether the extracting species is an ion pair (eq. 4) or a pair of dissociated ions (eq. 4'). Such log-log plots are shown in Figure 3 for 0.367 M and 0.073 M solutions in isooctane and for 0.367 M TBP-solutions in \(CCl_4\). (Experimentally, \(x\) has values near three and five for TBP-\(CCl_4\) and TBP-isooctane, respectively, as described below.) At low concentrations of extracted acid all the points lie on lines of unit slope, suggesting that the extraction complex is associated as ion pairs. At higher concentrations, where curvature of the plot becomes pronounced, an increasingly large fraction of 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 equilibrium concentration of extractant. The value of \([H^+]_o\) can be corrected to a fixed concentration of TBP by means of eq. 5.

\[
[H^+]' = [H^+]_o [TBP]'^n / [TBP]^n_0
\]  

(5)

Here primed quantities refer to the condition of a fixed (initial) equilibrium concentration, and unprimed quantities denote the experimental values, among which \([TBP]_o\) can be obtained from the relationship

\[
[TBP]_o = [TBP]_{initial} - [TBP\cdot H_2O]_o - n[H^+]_o
\]  

(6)

By using the value \(n = 3\) (whose origin is justified later) in applying equations 5 and 6 to correct the data in Figure 3, it can be seen that the points on the curved portions of the plots are brought onto the straight line
of unit slope extended from the dilute solution regions where corrections are not necessary.

A similar plot for the system TBP-1,2-dichloroethane is given in Figure 4. With this diluent the slope observed is closer to 0.5 than to unity, suggesting the presence of a dissociated species (eq. 1'). If so, the value of \([H^+]_0\) should be corrected by an electrostatic, or Debye-Hückel, mean ion activity coefficient. An estimate of these coefficients, perhaps a tenuous one for a solvent with a dielectric constant of only 10.5, was made by using the Mayer-Poirier expression.\(^{14}\) The computed values of \(y_\pm\) were applied to the raw extraction data and gave the results indicated by the square symbols plotted in Figure 4. Clearly the application of the calculated \(y_\pm\) values to the higher \([H^+]_0\) concentrations lowers these data onto the line of slope 0.5. This line has already been determined by the points at lower concentrations where activity coefficients are negligibly different from unity. Thus, it may be concluded that over the entire range of extracted acid concentrations studied, the extraction complex in 1,2-dichloroethane is principally dissociated into two independent ions. This result is not unreasonable; Fuoss's equation for ion-pairing would predict approximately seventy percent free ions at the highest \([H^+]_0\) in Figure 4, for an ə = 7A.\(^{15}\) At yet higher organic-phase acid concentrations, however, the above conclusions may not still be true.

It is possible to determine the value of \(n\), the number of TBP molecules coordinated in the extracted complex, for each diluent-TBP system. From log-log plots of the extracted acid vs. TBP concentration at a constant \(a'_\text{HClO}_4\) or \(a'_\text{HReO}_4\), the slopes of the curves directly equal \(n\) for ion-paired
complexes or 0.5 $m$ for dissociated complexes. The TBP concentrations so used
in Figures 5, 6, and 7 are not equilibrium TBP but initial TBP concentrations
corrected for the amount of TBP bound in the acid complex. Except for the
case where an appreciable amount of TBP is involved in the acid complex,
correcting the data for the amount of TBP bound by water would only result
in a parallel displacement of the curve and would not change the values
of the slopes found in the slope analysis techniques employed in this paper.

The above outlined procedure is shown in Figure 5 for TBP-CCl$_4$ at two
fixed concentrations of perrhenic acid, 1.60 M and 2.91 M. The plots of the
raw data (solid lines) do not have a unique slope over the range of TBP
concentrations used. It is evident, however, that a limiting slope equal to
two (n=2) can be obtained at the lower end. Extension of this line of slope
two (dashed line) to higher TBP concentrations and subsequent subtraction
from the raw data yields a line whose slope is three (n=3). It thus appears,
for TBP concentrations in CCl$_4$ less than 0.1 M, a two-TBP one-HReO$_4$ complex
predominates, and that above 0.1 M a three-TBP complex takes over. But above
about 0.2 M TBP it may become questionable to use this type of slope
analysis; activity coefficient ratios may not remain constant, as already
mentioned in the TBP$\cdot$H$_2$O discussion, and such behavior would lead to
(unknown) curvature in the lines.

In a previous study of HClO$_4$ extraction by TBP-CCl$_4$ only a three-TBP
coordinated complex was found, in disagreement with the present finding of
a 2TBP complex, as well as a 3TBP species. The previous result, however, is
due to the experimental limitation of using TBP concentrations $\geq 0.0367$ M.
With that restriction the present data would also yield a good fit to a
value of \( n = 3 \) alone. It is only when more dilute TBP solutions are examined by means of \( \text{ReO}_4^- \) tracer that the existence of a \( 2 \text{TBP} \) complex is clearly evident.

Another example of this behavior is shown in Figure 6. The lower curve is a log-log plot of \([H^+]_0\) vs. TBP in isoctane for 0.874 \( \text{M} \) \( \text{HReO}_4 \), and shows only a slope of 3 for the range of TBP concentrations studied, namely 0.3 \( \text{M} \) - 0.02 \( \text{M} \). But when a higher acid concentration is used so as to be able to carry the study to smaller TBP concentrations, evidence for a lower complex appears. The curve for 4.00 \( \text{M} \) \( \text{HClO}_4 \) shown in Figure 6 covers the range of TBP concentrations from \( 7 \times 10^{-4} \) to \( 7 \times 10^{-2} \) \( \text{M} \) and clearly can be resolved into two components; predominantly a 3:1 complex above \( 7 \times 10^{-3} \) \( \text{M} \) TBP and a 2:1 complex below that concentration. It may be noted that this cross-over point is at an order of magnitude lower concentration in isoctane than in \( \text{CCl}_4 \), as will be discussed later.

In Figure 7 the TBP dependence data are shown for TBP-1,2-dichloro-ethane. In this case the extracted species is dissociated into two ions; the value of the slope in the log-log plot is 0.5 \( n \) and the raw data must be corrected by Debye-Hückel type activity coefficients. At the higher organic-phase acid concentrations where these activity coefficient corrections become noticeable, the corrected points are shown as open squares. A slope of 1.5 is obtained at both acid concentrations, so that over the range of TBP concentrations from \( 3 \times 10^{-3} \) \( \text{M} \) to \( 3 \times 10^{-1} \) \( \text{M} \) a dissociated 3TBP complex is extracted. There is no evidence for a 2TBP complex in the range of TBP concentrations employed.
The amount of water associated with the extracted acid complex in TBP-isooctane is shown in Figure 8. The slope of line 3 in this figure indicates that four-to-five water molecules are coordinated to the ion-paired 3TBP complexes formed at the TBP concentrations investigated. A previous study of the TBP-CCl₄-HClO₄-H₂O system² found a smaller number (~2.5) of water molecules coordinated to the acid complex. While the different amounts of water coextracted in these two solvent systems probably has significance, it will only be noted now that both systems have more than one water per acid. That is, both systems have sufficient coextracted water to allow the formation of a hydronium ion. It is this last fact, in addition to the finding of a 3TBP complex in CC₄, which led to the previously suggested model for interpreting acid extraction data in these moderately basic organic systems.

However, with the observation in this study of a 2TBP complex in addition to the 3TBP complex, the question arises whether the previously suggested extraction model is appropriate. Unfortunately, we cannot determine the water coextracted by the 2TBP complex so as to prove that at least one water molecule is still involved with it; the concentrations where this species predominates are too low for satisfactory Karl Fischer determinations. But we believe the hydronium core model is still necessary to explain the present data. In each of the three diluent systems, over some range of TBP concentrations, a 3TBP complex is found. Without the existence of a hydronium ion, with its three positive charge sites, it is difficult to conceive how TBP coordination numbers of three could be obtained. It is suggested that the appearance of a 2TBP species at lower TBP concentrations is a natural consequence of the stepwise formation of coordination complexes, rather than an indication
of the breakdown of the proposed model. This is analogous to the behavior found with metal complexes, where lower complexes appear in the more dilute solutions of the complexing reagent and the (higher) saturated complex occurs in more concentrated solutions.

Another interesting result of this study is the difference in TBP concentration at which a 2TBP complex becomes dominant. In isooctane, the lower complex predominates only up to TBP concentrations of 0.007 M, while it is the major species to almost 0.1 M in CC1₄. Clearly in the CC1₄ system one or more factors are operating to stabilize the 2TBP complex over the 3TBP complex with respect to the situation in isooctane. It is probable that the main factor is the CC1₄ molecule itself, providing solvation for both the TBP molecule and the extracted 2TBP-acid complex by means of dispersion force interactions via its chlorine atoms. Interaction of CC1₄ with the TBP molecules is confirmed by activity coefficient measurements on TBP in both TBP-CC1₄¹⁰,¹⁶ and TBP-CC1₄-H₂O¹¹ systems. These show that the value of y_TBP initially decreases and then becomes constant at a reduced value as the amount of CC1₄ in the solution increases; there is a marked negative deviation from ideal behavior. The result of this interaction between CC1₄ and TBP corresponds to a reduction in the effective concentration of the latter (y_TBP < 1), leading to reduced extraction of the acid (see Table 1) and a higher range of (stoichiometric) TBP concentration for which the 2:1 acid complex dominates. But we must also consider the interaction of CC1₄ with the extracted acid complexes. Although the situation is not exactly the same, it can be pointed out that the UO₂(NO₃)₂·2TBP complex has also been shown to have attractive interactions with CC1₄¹³,¹⁶,¹⁷ as diluent. We think it is most reasonable that the hydronium-TBP complex would behave in a similar
manner. This should be particularly true for the 2:1 complex, with its exposed site, the third hydronium hydrogen, and so would reduce the need of that complex for a third TBP molecule. The result is to again help increase the range of existence of the 2:1 complex. Thus the interactions of \( \text{CCl}_4 \) with TBP and with the acid complex both tend to favor the lower complex, and the former interaction decreases all acid extraction while the latter helps extraction of the 2:1 complex mainly.

The situation is just the opposite with isooctane as the diluent. Activity coefficient data for TBP (and for the \( \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP} \) complex) in hexane indicate that the hydrocarbons are not very effective in solvating these species.\(^{10,17}\) The coefficients of TBP (and \( \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP} \)) increase in magnitude with increasing proportion of hexane. This time the deviations from ideality are positive. The effective concentration of TBP in isooctane is greater than that indicated by the stoichiometric value \( (y_{\text{TBP}} > 1) \), and at any given TBP concentration the higher TBP-acid complex should be favored over the 2:1 species compared to \( \text{CCl}_4 \) as a diluent. This trend is reinforced by the relatively poorer ability of isooctane to solvate the 2:1 acid complex. The differences in behavior of 2:1 and 3:1 acid complexes in \( \text{CCl}_4 \) and isooctane thus can be reasonably explained.

A comparison of the extraction data with 1,2-dichloroethane and with isooctane points to still another factor which may be important in the extraction process. It is noted that only a 3TBP-acid complex is found in 1,2-dichloroethane at TBP concentrations equal to or lower than those which in isooctane show evidence for a 2TBP complex. It would surely be expected that 1,2-dichloroethane would provide free TBP and the extracted complex with "chemical solvation" at least equal to that of isooctane. An estimate of the direction of change for the TBP activity coefficient in 1,2-dichloroethane can
be obtained from a distribution experiment into water from 0.183 M TBP in 1,2-dibromoethane, where rather strong negative non-ideality is indicated. \(^\text{12}\) It might then be expected that the interaction of 1,2-dichloroethane with TBP and with the extraction complex should yield behavior along the lines already found for the TBP-CCl\(_4\) system. The existence of a lower (2:1) complex might therefore be expected to be observed with 1,2-dichloroethane at an equal or higher TBP concentration than with isooctane. The two systems, however, have a major difference. In 1,2-dichloroethane, the extracted acid is dissociated; the ReO\(_4^-\) anion is free of the cation complex, while in isooctane the anion is electrostatically bound to it. It may be that in isooctane and CCl\(_4\) the oppositely charged anion gives sufficient electrostatic solvation to the hydronium complex to help displace one of the coordinating TBP molecules, to help stabilize the lower coordination complex. But in dichloroethane, the lack of interaction of the dissociated anion with the hydronium cation reinforces the latter's need for more complete coordination with TBP. Hence the 3:1 complex would be favored down to still lower TBP concentrations than in isooctane, as is observed experimentally.

It is evident that the resolved lines of slope two or three in Figures 5-7 only fit the data up to concentrations of about 0.2 M, and have fallen below the experimental points at 0.3 M and higher TBP concentrations. From slope analysis this would indicate a still higher TBP complex. But the coordination of additional TBP molecules to the hydrated hydronium cation should be more difficult, though it is conceivable. It is unlikely that TBP could coordinate to ClO\(_4^-\) or ReO\(_4^-\). We believe the enhanced extraction of acid at TBP concentrations above 0.2 M is due mainly to the change in the
nature of the diluent. It is no longer isoctane or CCl₄ or 1,2-dichloroethane, but an isoctane-TBP or CCl₄-TBP, etc., mixture with a significant proportion of TBP. The consequent changes in the physical and chemical properties of the diluent mixture naturally affect its extraction properties, and these changes probably are reflected in the breakdown of the assumption of a constant activity coefficient ratio $y_{H^+}^TBP / y_{TBP}^n$. This would mean that in CCl₄, $y_{H^+}^TBP$ increases less rapidly with increasing TBP concentration than does $y_{TBP}^n$, and in isoctane, $y_{H^+}^TBP$ decreases more rapidly than $y_{TBP}^n$. In the more concentrated TBP solutions, the extracted acid complex(es) obtain better solvation relative to the TBP molecules themselves, than in the dilute solutions.

The equilibrium constants for the extraction of HReO₄ tracer by TBP dissolved in isoctane, CCl₄, and 1,2-dichloroethane as found in this study are listed in Table 1. They are not true equilibrium constants, as concentrations, rather than activities, have been used for the organic-phase species. But since the ratio of organic-phase activity coefficients appears to be constant in dilute solutions of TBP, the substitution of concentrations for activities in dilute solution should not lead to serious error. However, we shall use a different symbol, $K_{m}^{a,d}$, instead of $\chi$. The superscript indicates whether the species in question is associated (a) or dissociated (d) and the subscript indicates whether a 2:1 or 3:1 complex is involved. The TBP concentrations used in evaluating the K's are equilibrium values, corrected for the TBP bound in the acid complex and to water. Finally, for calculating the aqueous activity of perrhenic acid, the activity coefficient of perchloric acid at the same concentration was used.
Several points can be made from this table. It can be seen that the value of $K_2^a$ in isooctane is ~40 times larger than that in $\text{CCl}_4$. We believe that this is mainly due to the stronger interaction of $\text{CCl}_4$ with TBP, effectively decreasing the concentration of TBP available to the acid complex and so hindering its extraction in $\text{CCl}_4$. The 3:1 acid complex is essentially coordinatively saturated by the TBP, and so is not greatly influenced by the nature of the diluent. But this is not true for the 2:1 complex which has an open hydronium hydrogen, and so $\text{CCl}_4$ can solvate this complex better than can isooctane. This enhanced solvation by $\text{CCl}_4$ just about compensates for the effect of the enhanced interaction of $\text{CCl}_4$ with TBP itself, and so the values of $K_2^a$ are almost alike in the two diluents. The diluent 1,2-dichloroethane also must interact with TBP more strongly than does isooctane, thus hindering extraction of the acid complex, but its
most important property is its relatively high dielectric constant, which favors extraction and leads to dissociated ions in the extracted species. No evidence for a 2:1 species was found in this system in the concentration range studied, and we believe that the loss of interaction with the anion in the dissociated species requires a more complete solvation of the cation by the TBP, thus favoring the 3:1 complex.

In this paper we have shown that the hydronium-TBP complex can have lower complexes than the saturated 3:1 species, and that the nature of the diluent employed affects both the magnitude of the extraction and the nature of the extracted complex in a reasonable way. Several other studies of $\text{HClO}_4$, $\text{HCIO}_4$, or $\text{HReO}_4$ extraction by TBP or TBP-diluent systems have been made. These studies, however, are either at higher concentrations of TBP than used in this study or use a different diluent, so that comparisons with the present work are difficult. In the next paper, this type of study will be extended to chloroform and to aromatic diluents.
Footnotes and References

(1) This work was done under the auspices of the U.S. Atomic Energy Commission.


(4) T. I. Berkengiim, Zorochkaya Lab., 10, 592 (1941).


(9) J. J. Bucher, A. Beck, and R. M. Diamond, unpublished work.


Figure Captions

Fig. 1. Variation of water content of organic phase with TBP concentration in isooctane. ([H$_2$O]$_o$ = total H$_2$O-H$_2$O dissolved by diluent). Line 1, ■, is [H$_2$O]$_o$ vs. equilibrium TBP ([TBP]$_o$ = total TBP-[H$_2$O]$_o$). Line 2, ●, is [H$_2$O]$_o$ vs. initial TBP concentration. Line 3 is a continuation of the line of unit slope.

Fig. 2. Variation of water content of organic phase with TBP concentration in 1,2-dichloroethane. ([H$_2$O]$_o$ = total H$_2$O-H$_2$O dissolved by diluent). Line 1, ■, is [H$_2$O]$_o$ vs. equilibrium TBP ([TBP]$_o$ = total TBP-[H$_2$O]$_o$). Line 2 is a continuation of the line of unit slope. Line 3, ●, is [H$_2$O]$_o$ vs. initial TBP concentration.

Fig. 3. Variation of acid content of organic phase with aqueous HClO$_4$ activity for 0.073 M TBP in isooctane (line 3) and for 0.367 M TBP in isooctane (line 1) as measured by ReO$_4^-$ tracer out of HClO$_4$ acid; and for 0.367 M TBP in CCl$_4$ (line 2) as measured by ReO$_4^-$ tracer out of HClO$_4$ acid. ●, uncorrected data; ■, data corrected for used-up TBP. Dashed lines drawn with slope unity.

Fig. 4. Variation of acid content of organic phase with aqueous HReO$_4$ activity for 0.367 M TBP in 1,2-dichloroethane. ●, uncorrected data; ■, data corrected for activity coefficients.

Fig. 5. Variation of acid content of organic phase with TBP concentration in CCl$_4$ for aqueous HReO$_4$ concentrations of 1.60 M (●) and of 2.91 M (○); ▲, △, resolved n = 3 line; other dashed line, n = 2; □, data corrected for used-up TBP.
Fig. 6. Variation of acid content of organic phase with TBP concentration in isooctane for aqueous HReO$_4$ concentration of 0.870 M (●), and for aqueous HC1O$_4$ concentration of 4.00 M (○); △, resolved n = 3 line; other dashed line, n = 2.

Fig. 7. Variation of acid content of organic phase with TBP concentration in 1,2-dichloroethane for aqueous HReO$_4$ concentrations of 0.0100 M and of 0.100 M (○); ■, data corrected for activity coefficients.

Fig. 8. Water content vs. HC1O$_4$ concentration in the organic phase (as the aqueous HC1O$_4$ concentration increases) for total TBP concentrations of 0.183 M and 0.73 M in isooctane. Lines 1 and 2, ○, and ●, are the total organic-phase water less the solvent water; line 3, □, is the total organic-phase water less both the solvent water and the water bound to TBP.
Fig. 1.
Fig. 3.
Fig. 4.
Fig. 5.
Fig. 6.
Fig. 7.
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