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Authors

Bucher, J. J.
Diamond, R. M.

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University of California

Ernest O. Lawrence
Radiation Laboratory

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EXTRACTION OF $HClO_4$ AND $HReO_4$ BY DILUTE
SOLUTIONS OF TRIBUTYL PHOSPHATE IN
CCl_4, ISOOCTANE AND 1,2-DICHLOROETHANE[1]

J. J. Bucher and R. M. Diamond

Lawrence Radiation Laboratory
University of California
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Abstract

The extraction of $HReO_4$ or $HClO_4$ into dilute solutions of tributyl

phosphate (TBP) in CCl_4, isooctane and 1,2-dichloroethane has been studied,

and the extracting species have been determined. A previous study of TBP

in CCl_4, where the TBP concentrations were 0.03 to 0.3 $\underline{M}$ and the stoichio-

metric ratio TBP/H^+ was > 3 , indicated the only extracting species were

the molecular adduct $TBP \cdot H_2O$ and the hydronium ion species $3TBP \cdot H_3O^+ \cdot$

$pH_2O \ldots ClO_4^-$, an ion pair, where $0 \leq p \leq 1.5$. In this study even more

dilute TBP solutions in CCl_4 were examined, and a two-TBP acid

complex, in addition to the three-TBP complex, was found. In the isooctane

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 $HClO_4$ extraction by dilute solutions of tributyl phosphate (TBP) in CCl_4[2] 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 $HClO_4$ by TBP in other diluents was investigated. In this paper, the first of a two-part study, the use of isooctane and of 1,2-dichloroethane as diluents was investigated. Isooctane 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-CCl_4 investigation,[2] radioactive perrhenate (ReO_4^-) tracer was employed. Since the molecular structure and charge of ReO_4^- is similar to ClO_4^- it is found that this tracer anion can be used successfully as a marker for ClO_4^- 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-$HClO_4$($HReO_4$)-CCl_4 system was also reexamined over a greater range of dilute TBP concentrations.

Experimental

Reagents.—The $HClO_4$ solutions were prepared by dilution with distilled water of G. F. Smith reagent grade $HClO_4$, 70 to 72%. The stock 70-72% solution was standardized by titration with sodium hydroxide to the bromothymol blue end-point. $HReO_4$ solutions were made by dilution from a stock solution, stand-ardized in the same way, and prepared by dissolving Re_2O_7 in water. The $^{186}ReO_4^-$ tracer solution was prepared by irradiating $KReO_4$ with neutrons in the Vallecitos reactor and dissolving the product in distilled water. The CCl_4 was Baker and Adamson reagent grade; the isooctane 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 $23 \pm 2°C$.

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 $\underline{M}$; literature values, 0.002 $\underline{M}$[4] - 0.006 $\underline{M}$[5] at 25° C; water solubility in 1,2-dichloroethane, 0.125 $\underline{M}$; literature value, 0.129 $\underline{M}$[6] 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 $\underline{M}$ and 0.367 $\underline{M}$ TBP in isooctane; for 0.367 $\underline{M}$ TBP in CCl_4; and for 0.367 $\underline{M}$ TBP in 1,2-dichloroethane. Perrhenate tracer out of perchloric acid was used to determine the concentrations in both the isooctane and CCl_4 systems shown in Figure 3; ReO_4^- 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 CCl_4, isooctane, and 1,2-dichloroethane, respectively. Perrhenate tracer out of perrhenic acid was used in both the CCl_4 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 per-

chloric 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 $\underline{M}$ TBP and by line 2 for 0.183 $\underline{M}$ 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 ReO_4^- tracer was used as a marker for ClO_4^-,

the plotted organic-phase acid concentrations, $[H^+]_o$, may be up to a factor

of two higher than the actual $HClO_4$ concentrations, as ReO_4^- extracts

somewhat better than ClO_4^- out of $HClO_4$. 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 $HClO_4$ is needed, and these were obtained by direct two-phase

titrations. In those systems where data were obtained using ReO_4^- tracer

out of macro-perrhenic acid, no problem arises, and the values of

$[H^+]_o$ plotted are the correct ones.

Discussion

TBP-H_2O. 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:

$$nTBP(org.) + mH_2O = mH_2O \cdot nTBP(org.) \tag{1}$$
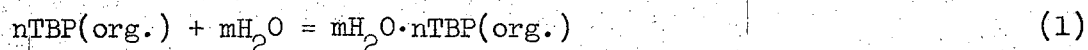
The corresponding equilibrium constant is:

$$\mathcal{K}_{H_2O} = \frac{(mH_2O \cdot nTBP)_o}{(H_2O)^m (TBP)_o^n} = \frac{[mH_2O \cdot nTBP]_o \; y_{H_2O}}{(H_2O)^m [TBP]_o^n y_{TBP}^n} \tag{2}$$

where parentheses signify activity, brackets denote molar concentrations,

and y is a molar activity coefficient. With the assumption that the ratio

y_{H_2O}/y_{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, $[TBP]_o$,

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 dichloro-

ethane 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

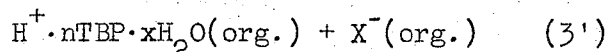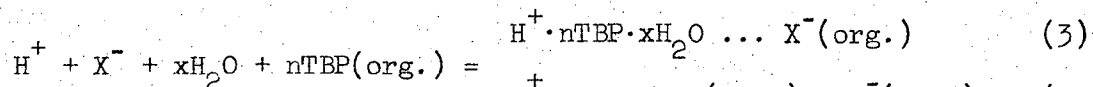$a_w \cong 1$; the majority of the TBP molecules, however, remain

unhydrated. Without determining $[H_2O]_o$ 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 $\underline{M}$ in

dichloroethane and 0.07 $\underline{M}$ TBP in isooctane 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, $[TBP]_o$, 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 isooctane 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 $TBP \cdot H_2O$ 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 (0.2$\underline{M}$). Thus the deviations observed in isooctane starting below 0.07 $\underline{M}$
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[8,9] made on TBP-CCl$_4$ 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:H$_2$O complex
is the dominant hydrated species.

A study of $[H_2O]_o$ for the TBP-CCl$_4$ system, using both Karl Fischer
titrations and normalized infra-red intensities, has been published
previously.[2] The data presented is quite similar in form to that found in
Figure 1. A 1:1 TBP:H$_2$O complex occurs up to a TBP concentration of 0.1 $\underline{M}$.
Beyond this concentration the water extraction curve again indicates the
formation of an additional water:TBP complex. The K_{H_2O} for the 1:1 complex
was 0.15 (mol/l.)$^{-1}$.

TBP-H$_2$O-HClO$_4$ or-HReO$_4$. The extraction of HClO$_4$ or HReO$_4$ by solutions of TBP
in a diluent may be expressed as

$$H^+ + X^- + xH_2O + nTBP(org.) = \begin{cases} H^+ \cdot nTBP \cdot xH_2O \ldots X^-(org.) & (3) \\ H^+ \cdot nTBP \cdot xH_2O(org.) + X^-(org.) & (3') \end{cases}$$

with the corresponding equilibrium constants

$$\mathcal{K}^a = [H^+ \cdot nTBP \cdot xH_2O \ldots X^-]_o \, y_{HX} / [TBP]_o^n \, y_{TBP}^n (H_2O)^x (HX) \qquad (4)$$

$$\mathcal{K}^d = [H^+ \cdot nTBP \cdot xH_2O]_o [X^-]_o \, y_\pm^2 / [TBP]_o^n \, y_{TBP}^n (H_2O)^x (HX) \qquad (4')$$

From log-log plots of the organic-phase acid concentration, $[H^+]_o$

vs. the aqueous-phase activity product $(HClO_4)(H_2O)^x \equiv a'_{HClO_4}$, 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.

$$[H^+]_o' = [H^+]_o \, [TBP]_o'^n \,/\, [TBP]_o^n \tag{5}$$

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

$$[TBP]_o = [TBP]_{initial} - [TBP \cdot H_2O]_o - n[H^+]_o \tag{6}$$

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 $[H^+]_o$ 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 $[H^+]_o$ 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 con-
centrations 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 $[H^+]_o$ in Figure 4, for an $\overset{o}{a} = 7A$.[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'_{HClO_4} or a'_{HReO_4}, the slopes of the curves directly equal $\underline{n}$ for ion-paired

complexes or 0.5 $\underline{n}$ 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 $\underline{M}$ and 2.91 $\underline{M}$. 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 $\underline{M}$, a two-TBP one-$HReO_4$ complex

predominates, and that above 0.1 $\underline{M}$ a three-TBP complex takes over. But above

about 0.2 $\underline{M}$ 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·H_2O discussion, and such behavior would lead to

(unknown) curvature in the lines.

In a previous study of $HClO_4$ extraction by TBP-CCl_4[2] 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 $\underline{M}$.

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 ReO_4^- tracer that the existence of a 2TBP complex is clearly evident.

Another example of this behavior is shown in Figure 6. The lower curve

is a log-log plot of $[H^+]_o$ vs. TBP in isooctane for 0.874 M $HReO_4$, and shows

only a slope of 3 for the range of TBP concentrations studied, namely 0.3 M -

0.02 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 M $HClO_4$ shown in Figure 6 covers the range of TBP concentrations

from 7×10^{-4} to 7×10^{-2} M and clearly can be resolved into two components;

predominantly a 3:1 complex above 7×10^{-3} 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 isooctane than in 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.[14] 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 con-

centrations from 3×10^{-3} M to 3×10^{-1} 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-CCl$_4$-HClO$_4$-H$_2$O system[2] 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 CCl$_4$, which led to the previously suggested model for inter-
preting 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 step-
wise 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 $\underline{M}$, while

it is the major species to almost 0.1 $\underline{M}$ in CCl_4. Clearly in the CCl_4 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 CCl_4 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 CCl_4 with the

TBP molecules is confirmed by activity coefficient measurements on TBP in

both TBP-CCl_4[10,16] and TBP-CCl_4-H_2O[11] systems. These show that the value of

y_{TBP} initially decreases and then becomes constant at a reduced value as the

amount of CCl_4 in the solution increases; there is a marked negative deviation

from ideal behavior. The result of this interaction between CCl_4 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 CCl_4 with

the extracted acid complexes. Although the situation is not exactly the same, it can

be pointed out that the $UO_2(NO_3)_2 \cdot 2TBP$ complex has also been shown to have

attractive interactions with CCl_4[13,16,17] 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 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 $UO_2(NO_3)_2 \cdot 2TBP$ complex) in

hexane indicate that the hydrocarbons are not very effective in solvating these

species.[10,17] The coefficients of TBP (and $UO_2(NO_3)_2 \cdot 2TBP$) 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 ($y_{TBP} > 1$), and

at any given TBP concentration the higher TBP-acid complex should be favored

over the 2:1 species compared to 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 CCl_4 and iso-

octane 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 acitivity coefficient in 1,2-dichloroethane can

be obtained from a distribution experiment into water from 0.183 $\underline{M}$ TBP in
1,2-dibromoethane, where rather strong negative non-ideality is indicated.[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 rein-
forces 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 $\underline{M}$, and have fallen
below the experimental points at 0.3 $\underline{M}$ 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 $\underline{M}$ is due mainly to the change in the

nature of the diluent. It is no longer isooctane or CCl_4 or 1,2-dichloroethane,

but an isooctane-TBP or CCl_4-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^+}/y_{TBP}^n . This would mean that in CCl_4, y_{H^+} increases

less rapidly with increasing TBP concentration than does y_{TBP}^n , and

in isooctane, y_{H^+} 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 $HReO_4$ tracer by TBP

dissolved in isooctane, CCl_4, 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 $\mathcal{K}$. 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[18]

at the same concentration was used.

Table I.

Constants for the extraction of $HReO_4$.

Diluent	Macro-acid	K_2^a	K_3^a
isooctane	$HClO_4$	$5._0 \times 10^{-3}$	$8._3 \times 10^{-1}$
	$HReO_4$	---	$7._6 \times 10^{-1}$
CCl_4	$HReO_4$	$1._7 \times 10^{-3}$	$2._0 \times 10^{-2}$
			K_3^d
1,2-dichloroethane	$HReO_4$	---	$2._4 \times 10^{-4}$

Several points can be made from this table. It can be seen that the value of K_3^a in isooctane is ~40 times larger than that in CCl_4. We believe that this is mainly due to the stronger interaction of CCl_4 with TBP, effectively decreasing the concentration of TBP available to the acid complex and so hindering its extraction in 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 CCl_4 can solvate this complex better than can isooctane. This enhanced solvation by CCl_4 just about compensates for the effect of the enhanced interaction of 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,[17] 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 $HClO_4$[19,20]

or $HReO_4$[21] 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.

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Figure Captions

Fig. 1. Variation of water content of organic phase with TBP concentration in isooctane. ($[H_2O]_o$ = total H_2O-H_2O dissolved by diluent). Line 1, ■, is $[H_2O]_o$ vs. equilibrium TBP ($[TBP]_o$ = total TBP-$[H_2O]_o$). Line 2, ●, is $[H_2O]_o$ 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. ($[H_2O]_o$ = total H_2O-H_2O dissolved by diluent). Line 1, ■, 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.

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 $\underline{M}$ (●), and for aqueous

$HClO_4$ concentration of 4.00 $\underline{M}$ (○); △ , 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 $\underline{M}$ and

of 0.100 $\underline{M}$ (○); ▓ , data corrected for activity coefficients.

Fig. 8.   Water content vs. $HClO_4$ concentration in the organic phase (as the

aqueous $HClO_4$ concentration increases) for total TBP concentrations of

0.183 $\underline{M}$ and 0.73 $\underline{M}$ 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.

XBL685-2802

Fig. 1.

Fig. 2.

XBL685-2801

Fig. 3.

Fig. 4.

Fig. 5.

XBL6711-5704

XBL6711-5702

Fig. 6.

XBL6711-5709

Fig. 7.

XBL685-2800

Fig. 8.