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ABSTRACT

The extraction of $HClO_4$ into dilute solutions of tributyl phosphate (TBP) in CCl_4 has been studied, and the extracting species and extraction mechanism have been determined. It has been found that so long as the TBP concentration is < 0.1 $\underline{M}$ and the stoichiometric ratio TBP/H^+ is > 3 the only extracting species are the molecular adduct $TBP \cdot H_2O$ and the solvated hydronium ion $3TBP \cdot H_3O^+ \cdot xH_2O \ldots ClO_4^-$, an ion pair, where $0 \leqslant x \leqslant 1$. For $1 < TBP/H^+ < 3$ there are several possible species, whereas at $TBP/H^+ = 1$ the only species present in the organic phase is the salt $TBPH^+ \ldots ClO_4^-$. These results are interpreted in terms of a proposed general model for such strong acid-basic solvent extraction systems.

THE EXTRACTION OF ACIDS BY BASIC ORGANIC SOLVENTS[*]

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In the field of inorganic solvent extraction a type of system of great interest is that composed of a strong acid, water, and a basic organic compound, either pure or diluted with an inert organic liquid. By strong acid is meant not only the simple mineral acids such as $HClO_4$, HNO_3, H_2SO_4, and the hydrogen halides, but also the complex metal acids such as $HFeCl_4$, $HAuCl_4$, and $HInBr_4$. A basic organic solvent is a compound that contains an electron pair available for coordination with an acidic species; the most prominent types are those involving a basic oxygen or nitrogen atom. Examples, in approximate order of decreasing base strength, are the trialkyl amines, trialkyl phosphine oxides, trialkyl phosphates, triaryl phosphates, ketones, and ethers.

The aim, in the series of investigations of which this is the first report, is to determine the nature and composition of the extracted species and see how these vary with the basicity and steric availability of the organic coordinating group, the water activity, and the base strength of the acid anion. The ultimate goal is to determine the most important factors influencing the extraction, to explain why acids extract so much better than the alkali metal salts, and to understand the general mechanism of extraction.

With any such system as described above, the extraction involves a competition among the anion, the water, and the basic organic extractant for the proton. In this paper the acids chosen for study were $HClO_4$ and $HReO_4$, as with these strong acids the anion is too weak a base to enter successfully into the competition and only the competition between the water and the organic extractant needs to be considered.

With the use of a very basic extractant, such as the trialkyl amines, the proton is almost completely captured by the organic base, leading to a very low residual concentration of acid in the aqueous phase and to a very high distribution ratio, defined as

$$D = \frac{\text{concentration of acid in organic phase}}{\text{concentration of acid in aqueous phase}} .$$

The extracted species is the substituted ammonium salt, $R_3NH^+ X^-$, with little or no water involved. If a less basic extractant is used, it cannot compete as well with water for the proton. The latter is preferentially taken up by a water molecule, and the organic molecules and the water are then in competition for solvating the resulting ion. An extracting species containing both water and organic molecules might then be expected, as well as a lower distribution ratio than with the amines.

The extractant used in this study, tri-n-butyl phosphate (TBP), is less basic than the amines and is known to extract strong acids with the accompaniment of water.[1,2] TBP is an ester of phosphoric acid and butyl alcohol and has the structure

$$
\begin{array}{l}
C_4H_9\ O \\
\qquad\qquad \backslash \\
C_4H_9\ O\text{-}P = O. \\
\qquad\qquad / \\
C_4H_9\ O
\end{array}
$$
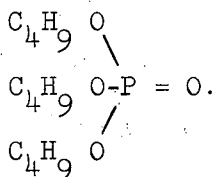
There are four basic sites in the molecule, corresponding to the four oxygen
atoms, but the terminal oxygen atom of the P=O bond far exceeds the other
oxygen atoms in base strength and can thus be considered to be the principal
coordinating site for acidic species (possible exceptions to this for very
high acid concentrations are presented in the final section of the Results and
Discussion). Since TBP and ClO_4^- are both bases, that is, they both contain
electron donor groups, no significant amount of coordination would be expected
between them and it will be assumed that none exists.

A considerable amount of work has already been published on the $HClO_4$
-TBP and $HReO_4$-TBP extraction systems.[3-9] Where these data and those of our
work overlap, there is agreement. But much of the earlier work is either
incomplete for the present purpose or deals only with extraction into either
pure or concentrated TBP solutions. As pointed out by Hesford et al.,[10-12]
one must be very cautious in drawing conclusions from calculations involving
organic phase concentrations (as opposed to activities) in such solutions,
as they are nonideal mixtures of (solvated) ions, water, and TBP.

One way to avoid this problem is to limit the concentration of the
extractant to less than a few tenths molar in some inert organic liquid, and
to choose the experimental conditions such that only a few percent of the
extractant molecules are involved in the extracted complex. Thus, the organic
phase essentially retains the properties of the inert diluent, and changing the
concentration of the extractant, acid, or water in that phase will have only a
slight effect on the activity coefficients of these species. However, the
resulting variation in the extraction will then yield the dependence of the
extracting species on the particular component varied (all others held constant),
and hence its part in the complex. After establishing in this manner the nature
of the extracting species in the dilute extractant solutions, it is possible

to extend the studies to the more concentrated solutions by making use of spectro-scopic methods. This is the approach used throughout this series of investigations.

EXPERIMENTAL METHODS

Reagents

The $HClO_4$ solutions were prepared by dilution of G. F. Smith reagent-grade $HClO_4$, 70 to 72%, with distilled water, and were standardized by titration with standard base to the phenolphthalein end point. The 12.5 $\underline{M}$ $HClO_4$ solution was G. F. Smith constant-boiling $HClO_4$, 73.6%, and was used as purchased. The $HReO_4$ was prepared by dissolving 50 g $KReO_4$ (Varlacoid Corp., New York, N.Y.) in 6 liters of distilled water and passing this solution through 100 ml of Dowex AG 50 X12, 50-100 mesh (Bio-Rad Laboratories, Richmond, Cal.) which had been thoroughly washed with 3 $\underline{M}$ $HClO_4$ and distilled water. The effluent was evaporated down to approx. 100 ml and the $HReO_4$ solutions were made by accurate dilution of this 1.74 $\underline{M}$ $HReO_4$ with distilled water. Analysis showed < 1% $KReO_4$ in the $HReO_4$. The Re^{186} tracer was prepared by irradiating $KReO_4$ with neutrons in the Livermore Pool-Type Reactor and dissolving the product in distilled H_2O. Approximately 10^{-11} mole of tracer was used per 5 ml of $HReO_4$ solution. The CCl_4 was Baker and Adamson reagent grade; infrared spectro-photometric analysis showed a slight trace of $CHCl_3$ as the only impurity. The 2,2,4-trimethylpentane ("octane") was Eastman SpectroGrade. The TBP was Matheson, Coleman, and Bell reagent grade, and was purified by repeated washing with 0.04 $\underline{M}$ NaOH and H_2O, the final rinse water being approximately pH 6. The TBP was dried by heating under vacuum, after which it was stored in a glass-stoppered bottle over Drierite (W. C. Hammond Drierite Co., Xenia, Ohio). All dilutions of TBP were made on a volume-percent basis using volumetric glassware, and these dilute solutions were also stored over Drierite. The

D_2O (99.5% pure) was obtained from Bio-Rad Laboratories, Richmond, Calif.
The Karl Fischer reagent was Matheson, Coleman, and Bell stabilized premixed
single solution. The methanol used in the Karl Fischer blank was Baker and
Adamson Electronic Grade, < 0.1% H_2O content; the pyridine was Baker and
Adamson reagent grade, 0.1% H_2O content.

Procedure

Infrared measurements were made on a Bechman IR-5 double-beam recording
spectrophotometer using as a reference CCl_4 or dry TBP solution of the same
concentration as the sample, both solutions being contained in matched 2- or 1-
mm cells with CaF_2 windows, 0.5-mm cells with AgCl windows, or 0.1-mm cells
with Irtran-2 windows. Samples were prepared either by injecting with a
micropipet a known amount of water or aqueous acid solution into a much larger
known volume of TBP solution and shaking for 1 hour, or by shaking together
equal volumes of water or aqueous acid solution and TBP solution for 1 hour,
separating the layers by centrifugation, and withdrawing the organic portion
with a pipette. All samples were stored in ground-glass-stoppered bottles to
prevent evaporation; no changes were observed over a period of several weeks
in water-TBP solutions stored in this manner. Water in the organic phase was
determined by the Karl Fischer method, using a direct visual end point and
a 10% pyridine-in-methanol solvent and blank.[13] Acid content in the organic
phase was determined by addition of a known excess of .01000 M NaOH and back
titration with .01000 M HCl to the phenol red end point.[14] Aqueous acid
concentrations were corrected where necessary for the amount of acid extracted.
Distribution ratios (D's) for the $HReO_4$ in TBP-octane solutions were determined
by γ-counting 2-ml aliquots of each phase in a well-type Na(Tl)I scintillation
counter. All experimental work was done at room temperature, 23 ± 2°C.

RESULTS AND DISCUSSION

TBP-H$_2$O

     As a prelude to the investigation of the species present in the extraction of HClO$_4$ and H$_2$O into dilute TBP solutions, the extraction of water alone was studied. The equation for this reaction can be written

$$nTBP_{(o)} + H_2O = H_2O \cdot nTBP_{(o)}, \tag{1}$$
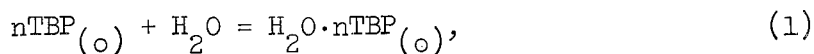
where (o) indicates the organic phase.

The corresponding equilibrium constant is

$$K_{H_2O} = \frac{(H_2O \cdot nTBP)}{(H_2O)(TBP)^n}, \tag{2}$$

where parentheses ( ) signify activity. The assumption was made that the ratio of the activity coefficients in the organic phase, $\gamma_{H_2O \cdot nTBP}/\gamma_{TBP}^n$, is a constant, since the two species are in dilute solution in CCl$_4$. Taking logarithms and rearranging, one obtains

$$\log [H_2O \cdot nTBP] = n\log [TBP] + \log (H_2O) + \log K'_{H_2O}, \tag{3}$$

where brackets [ ] signify concentration. Thus if the log of the H$_2$O concentration in the organic phase is plotted vs the log of the equilibrium TBP concentration, a line of slope n should result which determines the number of TBP molecules per H$_2$O molecule in the extracting water complex.

     Solutions ranging in TBP concentration from 0.1 to 60% by volume (.00366 to 2.20 $\underline{M}$) in CCl$_4$ were equilibrated with H$_2$O and the water content of the organic phase determined by using the Karl Fischer method. The values so obtained were corrected for the amount of H$_2$O extracted by CCl$_4$ and the results are shown in Fig. 1. It is seen that a straight line of slope n = 1.0 is obtained from 0.003 to .1 $\underline{M}$ TBP. Beyond this region the line curves

upward, indicating a greater relative uptake of H_2O by the more concentrated

TBP solutions, in agreement with the behavior found by Alcock et al.[15] This

change of slope can be interpreted as signifying either the presence of a

second kind of TBP-H_2O complex or a breakdown of the assumption that the

ratio of the organic species' activity coefficients is a constant; both effects

may be occurring simultaneously. However, in the region below 0.1 $\underline{M}$ TBP

(corresponding to an original solution 3.5 % TBP by volume), the straight

line of unit slope indicates that the assumption of a constant organic phase

activity coefficient ratio was correct and that the extracting species is the

simple molecular complex, $H_2O \cdot TBP$. The value of K'_{H_2O} in Eq. (3) is 0.15

(provided $\log (H_2O) \approx 0$), so that only about 13% of the TBP molecules are bound

to H_2O in this dilute, near-ideal region, as opposed to the pure TBP case in

which the stoichiometric TBP/H_2O ratio is 1.

In an effort to determine the reasons for the deviation from the

straight line at higher TBP concentrations, and also to aid in the interpretation

of the acid-extraction data, a method was developed for determination of H_2O

in the organic phase by infrared analysis. The infrared spectrum of water in

the gas phase or dissolved in nonpolar solvents shows absorption peaks for the

fundamental stretching modes of vibration at 2.70 and 2.75 microns (Fig. 2a).

Water dissolved in dilute TBP in CCl_4 solutions shows peaks at 2.72 and 2.90

microns (Fig. 2b), the shift in position of the peaks presumably being due to

the presence of hydrogen bonding between H_2O and TBP (the small peak at 3.12 μ

is the first harmonic of the H-O-H bending mode, not shown, which occurs at 6.17

μ). On the basis of these shifts, it seems reasonable to assign the 2.72-μ peak

to the free -O-H stretch and the 2.90-μ peak to the bonded -O-H stretch. These

peaks were all ascertained to be due to H_2O by observation of the shift in

wavelength by a factor of 1.35 when D_2O was used in place of H_2O.[16]
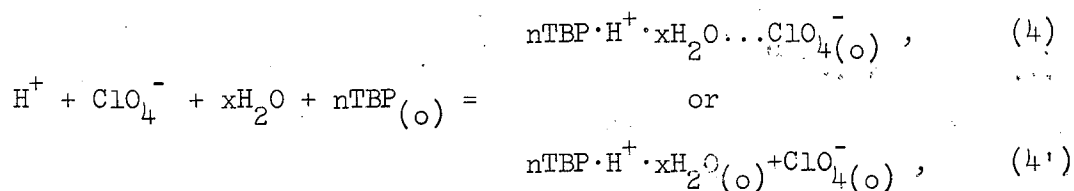
Standard samples of H_2O in TBP were prepared by injecting into dry
TBP solutions known amounts of H_2O ranging from barely perceptible on the
infrared spectrum up to saturation of the TBP solution being used. As a
check on the water content of these samples, aliquots were titrated by the
Karl Fischer method; the water content so determined was within 5% of the
amount injected. The infrared spectra of these solutions were taken and
standard calibration curves of absorbance vs H_2O concentration were constructed
for both the 2.72-μ and 2.90-μ peaks.

The infrared absorption spectra of the previously described water-
saturated solutions of 0.1 to 60% TBP in CCl_4 were also taken and the H_2O
content determined from the calibration curves; these results are also shown
in Fig. 1. It is seen that they are in agreement with the Karl Fischer values
until the TBP concentration reaches 0.1 $\underline{M}$, after which there is a divergence
between the amounts of H_2O present as determined by the two different absorp-
tion peaks. Specifically, the 2.90-μ peak increases more rapidly than the
2.72-μ one, until at 60% TBP in CCl_4 the latter has become almost completely
engulfed by the former (Fig. 2c). These spectra can be seen to be approaching
that for pure water (Fig. 2d), and indicate that above 0.1 $\underline{M}$ TBP the H_2O
molecules, on the average, are becoming more highly hydrogen-bonded. This
suggests that some water molecules can dissolve without bonding directly to TBP
but bonding to water already present in the organic phase. It should be
noted that the H_2O concentration as determined by the 2.72-μ peak remains
linear all the way to 60% TBP, indicating that this peak measures only
terminal H_2O bonded to TBP; further evidence for this hypothesis is seen in
the next section. However, from the behavior of the 2.90-μ peak and Karl
Fischer water data, it appears that a change in the extracting water species
occurs above 0.1 $\underline{M}$ TBP, and in order to retain the advantages of dilute

solutions it is necessary that the TBP concentration not exceed this amount.
(In actual fact, any solution 10% (0.3 $\underline{M}$) or less by volume in CCl_4 was con-
sidered to be dilute, since the slight loss in ideality was more than over-
balanced by the large increase in extraction afforded by the greater TBP
concentration.)

TBP—H_2O—dilute $HClO_4$ ($HReO_4$)
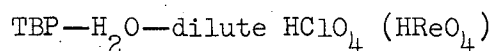
The general equation for the extraction of $HClO_4$ (or $HReO_4$) from
dilute aqueous solutions ($\lesssim 6$ $\underline{M}$) into dilute solutions of TBP may be written

$$H^+ + ClO_4^- + xH_2O + nTBP_{(o)} = \begin{cases} nTBP \cdot H^+ \cdot xH_2O \ldots ClO_4^-{}_{(o)} \ , & (4) \\ \text{or} \\ nTBP \cdot H^+ \cdot xH_2O_{(o)}{}^+ClO_4^-{}_{(o)} \ , & (4') \end{cases}$$

the products being written either as an ion pair (4) or as separate ions (4').
The equilibrium constant can be written

$$K_{HClO_4} = \frac{[nTBP \cdot H^+ \cdot xH_2O \ldots ClO_4^-] \ \gamma}{(HClO_4)(H_2O)^x[TBP]^n \gamma_{TBP}^n} \tag{5}$$

or

$$K_{HClO_4} = \frac{[nTBP \cdot H^+ \cdot xH_2O] \ \gamma_+[ClO_4^-] \ \gamma_-}{(HClO_4)(H_2O)^x[TBP]^n \gamma_{TBP}^n} \ , \tag{5'}$$

where brackets [ ] signify concentration and parentheses ( ) signify activity.

In order to determine whether (5) or (5') is the correct expression,
i.e., whether the extracting species is an ion pair or dissociated ions, all
the terms in the expression may be held constant except $(HClO_4)$ and the con-
centration of the extracting species; the dependence of the latter on $(HClO_4)$
will yield the desired information. Expressions (5) and (5') may be simplified

if one notes that for (5) $[nTBP \cdot H^+ \cdot xH_2O...ClO_4^-]\gamma = [H^+]_{(o)}\gamma$ while for (5')

$[nTBP \cdot H^+ \cdot xH_2O]\gamma_+[ClO_4^-]\gamma_- = [H^+]^2_{(o)}\gamma^2_{\pm}$, where $[H^+]_{(o)}$ is the organic acid

concentration. These may be combined by writing the species as $[H^+]^m_{(o)} \gamma^m_{H^+}$

where m = 1 for the ion pair and m=2 for the separate ions; an evaluation of m

will then distinguish between the two cases.

The organic phase, being a dilute solution, is again assumed near

enough ideal so that the organic phase activity-coefficient ratio $\gamma^m_{H^+}/\gamma^n_{TBP}$ is

a constant. Also, it is convenient to combine the aqueous phase water and acid

activities; this is done by defining $\underline{a}'_{HClO_4} = (HClO_4)(H_2O)^x$, where x ranges

between 1.4 and 2.5, as seen in a subsequent part of this section. Under these

conditions, taking logarithms yields

$$m\log[H^+]_{(o)} = \log \underline{a}'_{HClO_4} + \log K'_{HClO_4} , \qquad (6)$$

and a plot of $\log [H^+]_{(o)}$ vs $\log \underline{a}'_{HClO_4}$ should yield a straight line of slope

1/m.

Such a plot is shown in Fig. 3, and it can be seen that the slope 1/m

is 1.0 throughout the range shown, i.e., 1 to 10% TBP in CCl_4 and 0.5 to 6 $\underline{M}$

aqueous $HClO_4$; thus it appears that the extracted perchloric acid in the dilute

CCl_4 solutions is in the form of an ion pair. This result is altogether

reasonable, since the low dielectric constant of the CCl_4 solutions would tend

to repress any dissociation in the organic phase. These results are also in

agreement with those found by Hesford and McKay[5] for $HClO_4$ extracted into

dilute solutions of TBP in benzene, where the dissociation as measured by

electrical conductivity was found to be negligibly small, although in pure

TBP the $HClO_4$ was almost completely dissociated.

In order that the conditions set forth in the derivation of Eq. (6)

be obeyed, it was necessary to correct $[H^+]_{(o)}$ so that it represented the same

equilibrium concentration of TBP for all the points on a given line. The

corrected values were obtained from the relationship $[H^+]'_{(o)} = [H^+]_{(o)}[TBP]'^3/$

$[TBP]^3$; the reason for this relationship will become apparant in the next

paragraph. The magnitude of the corrections varied from negligibly small at

low a'_{HClO_4} to a factor of 6 for the highest a'_{HClO_4}; the fact that the corrected

points fall on the line whose slope is determined by those points where no

correction is needed indicates this method is the appropriate one to use.

Now that Eqs. (4) and (5) have been established as the correct

representation of the extraction, these equations may be used in establishing

the dependence of the extraction on the TBP concentration. The same assumption

regarding the constancy of the ratio of the organic-phase activity coefficients

for dilute solution may be made as in the previous case, but now a'_{HClO_4} will be

held constant while [TBP] is varied. Again representing the extracting species

as $H^+_{(o)}$ and taking logarithms, one obtains the expression

$$\log[H^+]_{(o)} = n\log[TBP] + \log K''_{HClO_4}. \tag{7}$$

In Fig. 4 there appears a plot of $\log [H^+]_{(o)}$ vs $\log [TBP]$ at eight different

a'_{HClO_4} corresponding to the range from 1.69 to 5.92 $\underline{M}$ $HClO_4$. It can be seen

that n is 3.0 over this entire range. It must be pointed out that [TBP] is the

equilibrium concentration of TBP and does not include the amount of TBP bonded

to H_2O or, more importantly, included in the extracting complex. The correction

for $TBP \cdot H_2O$ is small and will be discussed in a later paragraph dealing with

the determination of the H_2O/H^+ ratio. The correction for acid-complexed TBP

was determined by noting that for those cases in which the amount of acid ex-

tracted was so small that the equilibrium TBP concentration was a constant--

i.e., in which the stoichiometric H^+/TBP ratio was less than 10^{-2}-- the value

of n was 3.0; thus it was concluded that the correction is equal to $3 \times [H^+]_{(o)}$.

Using this correction factor yielded straight lines of slope 3.0 until at least 80% of the total TBP was incorporated into the bonding of the extracting acid species. Correction factors of 2 and 4 times $[H^+]_{(o)}$ were also tried in order to determine whether such a procedure would yield straight lines of slopes other than 3.0; no such line with slope 2 or 4 was found.

The acid concentration range was extended down to 0.109 $\underline{M}$ through the use of $HReO_4$ containing radioactive ReO_4^- (Re^{186}, $t_{1/2}=90$ hr) in place of $HClO_4$ and replacing CCl_4 with octane, the latter enhancing the extraction approximately 30-fold. $HReO_4$, with an ionic structure and size similar to $HClO_4$, might be expected to yield similar results, and as can be seen in Fig. 5, there is practically no change in behavior when $Re^{186}O_4^-$ tracer is extracted by using 1.7 $\underline{M}$ $HClO_4$ instead of 1.7 $\underline{M}$ $HReO_4$ as the carrier acid. Figure 5 also shows that no significant deviation from the slope of 3.0 occurs at these lower acid concentrations, so again it appears that the species with a 3-to-1 ratio of TBP to H^+ is the only species formed in the region where it is stoichiometrically possible. That is, as long as the stoichiometric ratio TBP/H^+ is more than 3 in the organic phase, the extracting complex which has a ratio of 3 TBP molecules per hydrogen ion (to be hereafter referred to by the species designation $3TBP \cdot H^+$) will be the only acid species present. The behavior at and above the stoichiometric limit for this species will be discussed in a subsequent section.

This TBP/H^+ ratio of 3 to 1 for the extracting species strongly suggests that the complex is built up around a core that is capable of forming three separate (hydrogen) bonds; it seems reasonable to assign this role to the hydronium ion, H_3O^+.

Several discussions of the hydronium ion and of its hydration in aqueous solution have appeared in the literature[1,8,17-21] and are not repeated here. However, direct evidence for the existence of a discrete hydration shell for the hydronium ion has been published recently and should be mentioned, since

it pertains directly to the extraction results found in this section. Beckey,[22] by the use of a mass spectrometer with a field emission source, has detected singly charged species which have masses corresponding to H_3O^+, $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$, and none with higher masses. Also, as the field strength is decreased, and the disruptive forces on the complex ions are diminished, the higher-mass species tend to be favored at the expense of the lower ones, suggesting that $H_9O_4^+$ would be a considerably more important species in the absence of the field. As a result of the evidence of Beckey and the other workers cited above, it may be concluded that in moderately dilute acid solutions the proton is present as the trihydrated hydronium ion, which is further, but more weakly, hydrated by additional shells of water molecules, until the most distant waters of hydration blend into the normal hydrogen-bonded water structure. Since the acid species that extracts into TBP is also trisolvated, it is reasonable to predict that such a species might have a similar type of structure.
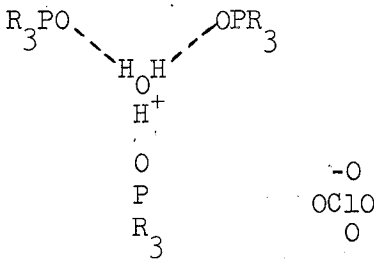
In order to determine whether such a model as described above is consistent with experimental data, an investigation of the H_2O content in the organic phase, and more particularly the H_2O/H^+ ratio therein, was undertaken. Four solutions of 1.05, 1.75, 3.50, and 10.0% by volume TBP in CCl_4 were equilibrated with aqueous $HClO_4$ solutions ranging from 0.571 to 12.5 $\underline{M}$ and the H_2O and H^+ concentrations in the organic phase were measured; the results are shown in Fig. 6a and 6b. In order to obtain the amount of H_2O actually associated with the proton it was necessary to subtract from the total amount of H_2O (as determined by Karl Fischer titration) the amount dissolved in the CCl_4 and the amount contained in the $TBP \cdot H_2O$ complex. The former correction is small and is merely the solubility of H_2O in CCl_4. The size of the latter correction was deduced from the observation that as more acid entered the organic phase the infrared spectra showed a regular decrease in the absorption of the 2.72-μ peak

until at a stoichiometric TBP/H^+ ratio of 3:1 it completely disappeared. This

ratio, as shown earlier, is the upper limit for the existence of the species

3 TBP·H^+, and it is reasonable to assume that when this limit is reached all

or nearly all of the TBP in the organic phase is involved in the extracted

species. This leaves very little, if any, TBP available to form TBP·H_2O, and

since this point also marks the disappearance of the 2.72-μ peak, it was

assumed that its absorption is a measure of the TBP·H_2O. This assumption is

supported by the spectral behavior of the water-saturated TBP solutions, as

described in the section on TBP-H_2O where the absorbance of the 2.72-μ peak

appeared to measure only that portion of the H_2O in the organic phase which

could be accounted for by Eq. (1), i.e., only the species TBP·H_2O, as long as

the TBP concentration was 0.1 $\underline{M}$ or less. As an additional check on the validity

of this method of correction, the concentration of TBP·H_2O was calculated from

Eq. (3). The values obtained from these calculations were within 10% of those

given by the absorbance of the 2.72-μ peak over the entire range of solutions

studied. (For the 10% TBP solutions it was necessary to further correct for the

amount of H_2O not shown by the 2.72-μ peak, as seen in Fig. 1, in order that

the line in Fig. 6a begin at the origin.) Since the magnitude of these corrections

decreases as the acid content of the organic phase increases, the accuracy was

considered sufficient to permit the determination of the initial slopes in

Fig. 6a and 6b.

The initial slopes (H_2O/H^+) for the four total TBP concentrations 10,

3.5, 1.75, and 1.05 % are respectively 2.5, 1.9, 1.6, and 1.4. It appears

that a slope of 1.0, i.e., the species H_3O^+, is being approached with increasingly

dilute TBP solutions; extrapolation of a plot of the measured slopes vs total

TBP concentration (Fig. 7) yields a ratio of 1.0 at 0% TBP.[23] This behavior

is reasonable, since as the TBP concentration is lowered the nonpolar CCl_4 would
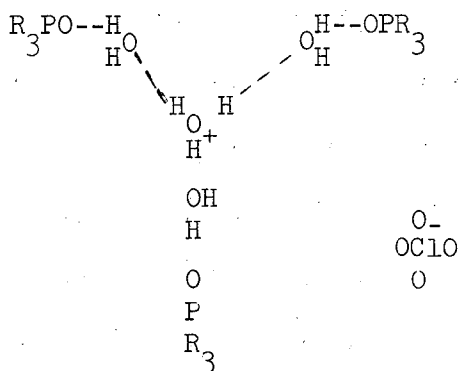
tend to discriminate against more highly hydrated and more polar species. An

extrapolation of the curve in Fig. 7 toward higher TBP concentrations seems to

approach a value greater than 3 for the slope, although drawing conclusions for

such concentrated solutions from so few data is not really justified, especially

in light of the nonideal nature of such solutions. But a reasonable prediction,

based on the behavior of the proton in water, is that this ratio might reach a

limiting value of 4, corresponding to the extraction of the hydronium ion plus

its primary hydration shell. A fair amount of experimental data is available

for pure $TBP-HClO_4-H_2O$ systems, and indeed slopes of approx. 4 have been seen,[5,7,8]

as is also true for the hydrohalic acids.[19] However, in pure TBP no information

is yet available on the distribution of the H_2O among TBP, H^+, and H_2O dissolved

in the organic phase, and it is thus not easy to conclude exactly what species are

present for this case.

On the basis of the foregoing considerations, a possible structure for

the extracting species which can be formulated for very dilute TBP solutions

(< 1%) is the hydronium ion hydrogen-bonded to a solvation shell of three TBP

molecules:

$$R_3PO \diagdown \qquad \diagup OPR_3$$
$$\diagdown H \diagup O H \diagup$$
$$H^+$$
$$O$$
$$P \qquad\qquad\quad {}^-O$$
$$R_3 \qquad\qquad\quad OClO$$
$$\qquad\qquad\qquad\quad O$$

where R is the butoxy group, C_4H_9O. As the TBP concentration rises, H_2O

molecules are able to enter the species and act as bridges between the hydronium

ion protons and the TBP molecules, until for very concentrated TBP solutions

the hydronium ion is quite possibly surrounded by a complete primary H_2O shell

of three molecules, which is in turn hydrogen-bonded to three TBP molecules as

a secondary solvation shell:

$$R_3PO\text{--}H \quad \underset{H}{O} \quad \cdots \quad \underset{H}{O}H\text{--}OPR_3$$

$$H_3O^+$$

$$OH$$
$$H$$
$$O$$
$$P$$
$$R_3$$

$$O\text{-}$$
$$OClO$$
$$O$$

The extracting species can thus be written, in the general case, as

$[3TBP \cdot H_3O^+ \cdot xH_2O \ldots ClO_4^-]$, where x is between 0 and 3.

TBP—H_2O— Concentrated $HClO_4$

The foregoing section has dealt with the case in which the extraction

takes place as shown in Eqs.(4) and (5), where n = 3, x = 1.4 to 2.5, and the

species is an ion pair. It is found, however, that $HClO_4$ extracts into TBP even

after the organic-phase hydrogen ion contration becomes greater than 1/3 the TBP

concentration, and in fact it extracts up to and a small amount past the point

where $[H^+]_{(o)} = [TBP]_{total}$ (Fig. 8). In order for this to occur there must be a

change in the extracting species when the stoichiometric ratio TBP/H^+ drops

below 3. An indication that this is the case is seen in Fig. 9, where $\log[H^+]_{(o)}$

is plotted vs log $(HClO_4)$ for four different total TBP concentrations; it may

be noted that the break in each curve occurs at a TBP/H^+ ratio of 3. Other

experimental data that support this change are the decrease in the H_2O/H^+ ratio,

as seen in Figs. 6a and 6b, and the decrease in slopes when $\log[H^+]_{(o)}$ is plotted

vs log $[TBP]_{total}$ for increasing aqueous $HClO_4$ concentrations (Fig. 9).

It must be realized that in the region where the ratio TBP/H^+ goes below 3 Eqs. (4) and (5) no longer apply and ideal-solution calculations such as those done in the previous section cannot be made. Thus any statements about the species present must be inferred from the total (stoichiometric) concentration of each component, unless a different species is identified and defined by some spectroscopic method. With this kept in mind, it is still possible to make several qualitative statements regarding the region of high aqueous (and organic) acid concentrations.

At very high external $HClO_4$ concentrations (approx.10 $\underline{M}$) the H_2O/H^+ ratio in the organic phase starts dropping very rapidly and approaches 0 for the highest $[H^+]_{(o)}$ (Figs. 6a and 6b). When the external acid is 11.6 $\underline{M}$, the TBP/H^+ ratio is exactly 1.00 over a TBP concentration range of 10^3 (Fig. 9). Thus the stoichiometric ratio of the components yields $TBP \cdot H^+ \cdot ClO_4^-$ as the extracting species at these very high acid concentrations. An interpretation of this behavior is that the greatly reduced H_2O activity (< 0.05) allows TBP to compete more favorably as a base for the proton and, in face, to become the primary solvating molecule. (This would be very similar to the case of a more basic trialkyl amine forming an ammonium salt.) The species can then be written $TBPH^+ \ldots ClO_4^-$.

For the extraction from 12.5 $\underline{M}$ aqueous $HClO_4$ into 3.5 and 10% TBP the TBP/H^+ ratio actually falls below 1.0. This may be due to extra $HClO_4$ present in the organic phase as an ion association with $TBPH^+ \ldots ClO_4^-$ and not bonded directly to TBP. More likely, however, it is due to the attraction of the proton to the ether oxygens of the TBP, since their relative basicity has also been enhanced by the reduction of the H_2O activity to the point at which they too may compete as solvating groups in the organic phase.

It is difficult to determine what other species are present in the transition region between 6 and 10 $\underline{M}$ aqueous $HClO_4$. From the fact that the water concentration remains relatively constant (Figs. 6a and 6b) it appears that some kind of hydrated species of lower TBP content than the previously considered $3TBP \cdot H_3O^+ \cdot xH_2O \ldots ClO_4^-$ must be present; possible examples of such species include $2TBP \cdot H_3O^+ \cdot H_2O \ldots ClO_4^-$, $2TBP \cdot H_3O^+ \ldots ClO_4^-$, $TBP \cdot H_3O^+ \ldots ClO_4^-$, and $TBPH^+ \cdot H_2O \ldots ClO_4^-$. None of the data presented herein give any indication which, if any, of these forms is correct; but nuclear magnetic resonance studies and a detailed analysis of the infrared spectra of these solutions, both of which are in progress, may give some insight into this problem.

CONCLUSIONS

If the extraction system is defined as $HClO_4$—H_2O—dilute TBP (0.1 $\underline{M}$ or less), the following definite statements may be made concerning the extracting species.

a. When the $HClO_4$ concentration is zero, the only species present are TBP and the simple molecular adduct $TBP \cdot H_2O$.

b. When the $HClO_4$ concentration is < 6 $\underline{M}$, i.e. when the stoichiometric ratio of TBP to $H^+_{(o)}$ is greater than 3:1, the only acidic species present is $3TBP \cdot H_3O^+ \cdot xH_2O \ldots ClO_4^-$, an ion pair, where $0 \leqslant X \leqslant 1.0$.

c. When the $HClO_4$ concentration is > 6 $\underline{M}$, there may be several possible acidic species, all with smaller TBP/H^+ and H_2O/H^+ ratios than the one in case (b), but all tend to go to the salt form $TBPH^+ \ldots$ ClO_4^-, as the aqueous acid concentration approaches 12 $\underline{M}$.

From the fact that a ratio of 3 solvent molecules per hydrogen ion has been observed for a variety of strong acids extracting into several different

moderately basic solvents (e.g., $HReO_4$, $HClO_4$, HBr, $HAuCl_4$, and $HAuBr_4$ into

TBP,[24,25] $HReO_4$, $HClO_4$, and $HAuCl_4$ into trioctyl phosphine oxide,[25,26] and

$HFeCl_4$ into dibutyl ether[27]), it might be predicted that the hydronium ion is

the basis for all such extractions.

However, this is not true when either the acid anion or the organic

extractant molecule is more basic than water. Examples of these two cases

are the $TBP-H_2O-HNO_3$[15] and butyl ether$-H_2O-HNO_3$[28] systems and the trialkyl-

amine$-H_2O-HClO_4/HReO_4$[29] and $-HCl$[30] systems, respectively, in which the

dependence of the extracted acid on the extractant concentration is first

power, not third, for dilute extractant solutions, and little water is co-

extracted.

ACKNOWLEDGMENTS

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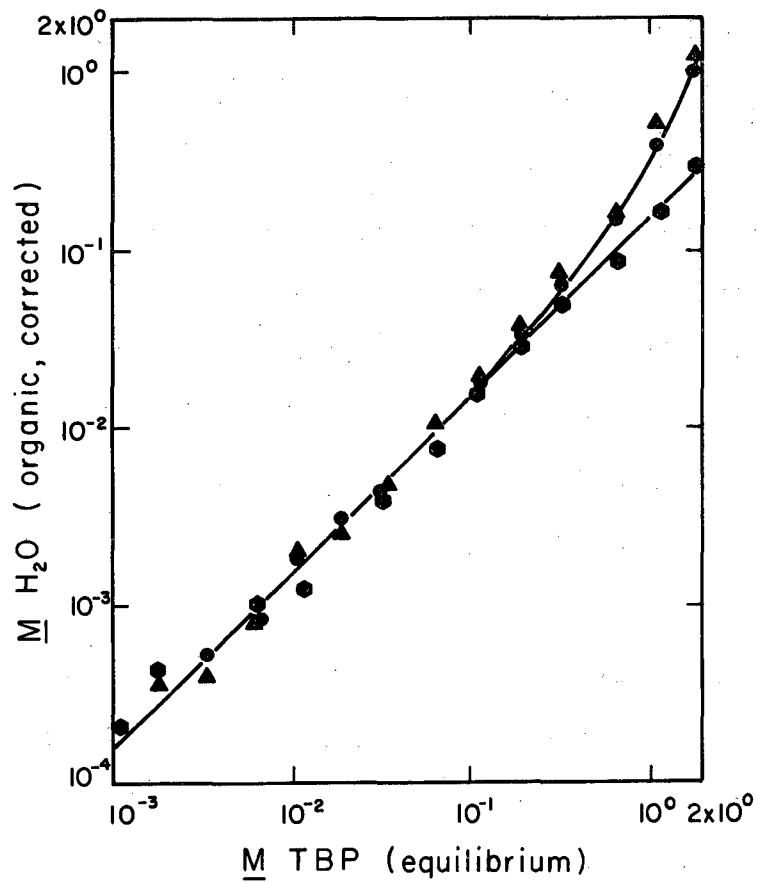
Fig. 1. Variation of water content of organic phase, with TBP concentration.
($\underline{M}$ H_2O = total $\underline{M}$ H_2O - $\underline{M}$ H_2O dissolved by CCl_4; $\underline{M}$ TBP = total $\underline{M}$ TBP
- $\underline{M}$ TBP·H_2O.) ●, $\underline{M}$ H_2O by Karl Fischer method; ◆, 2.75-μ peak;
▲, 2.90-μ peak.

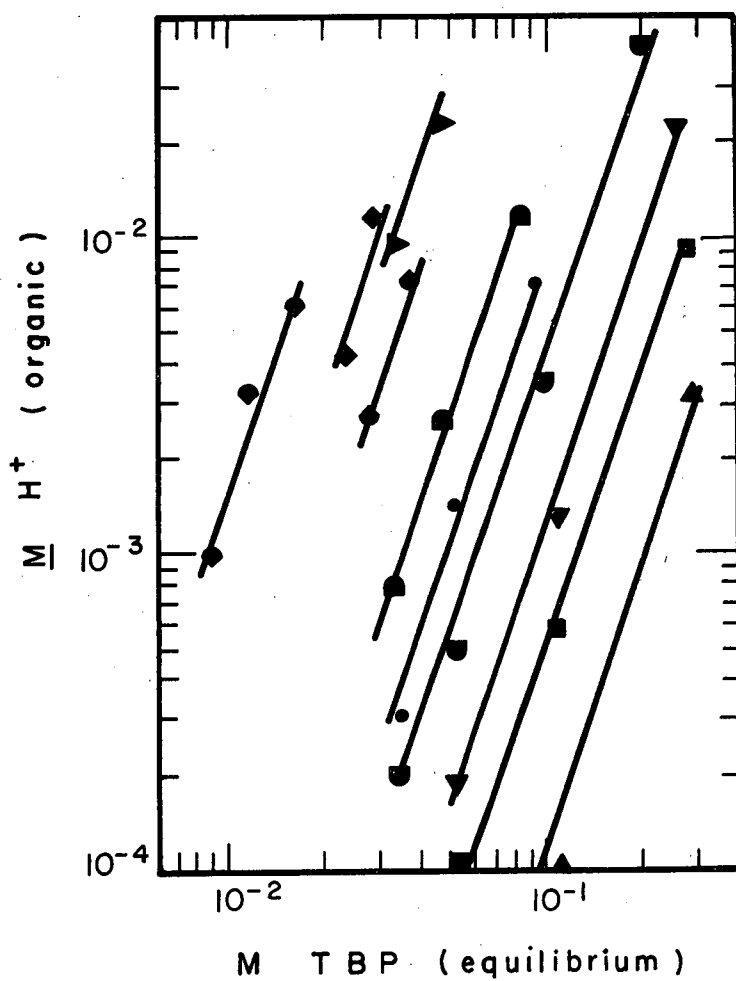Wave   number   (cm⁻¹)

Wave   length   (μ)
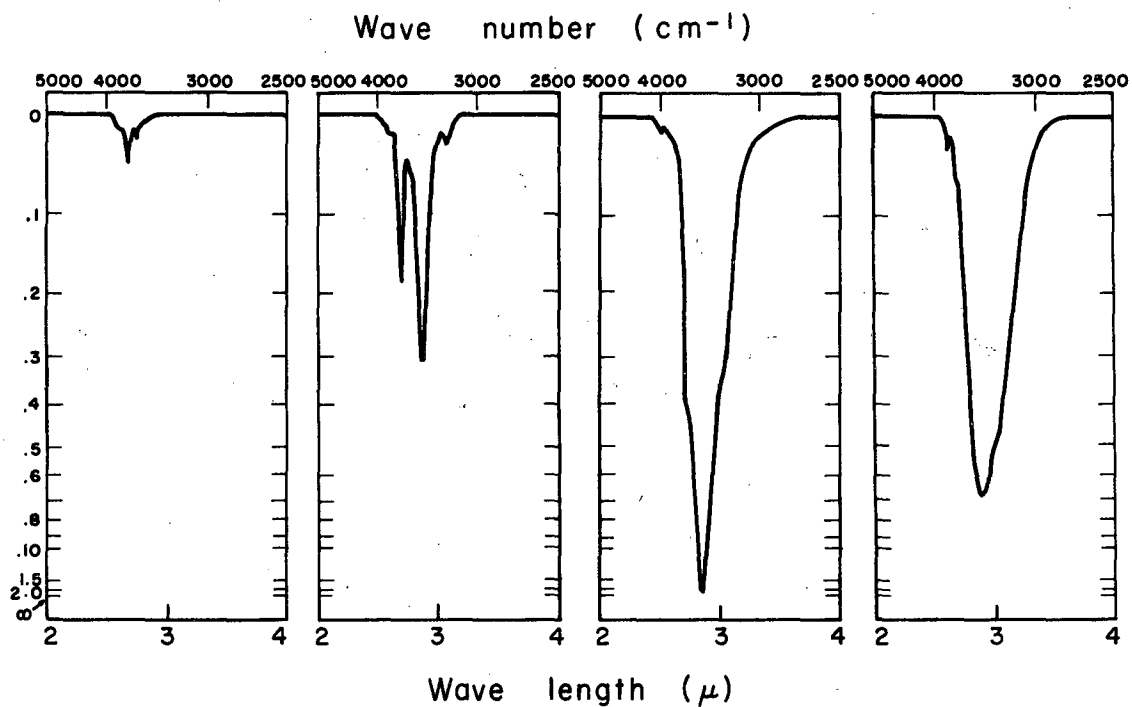
MU-26575

Fig. 2. Infrared spectra of (left to right) (a) water-saturated CCl₄,
   (b) water-saturated 0.128 M TBP, (c) water-saturated 2.11 M TBP,
   (d) pure liquid H₂O.
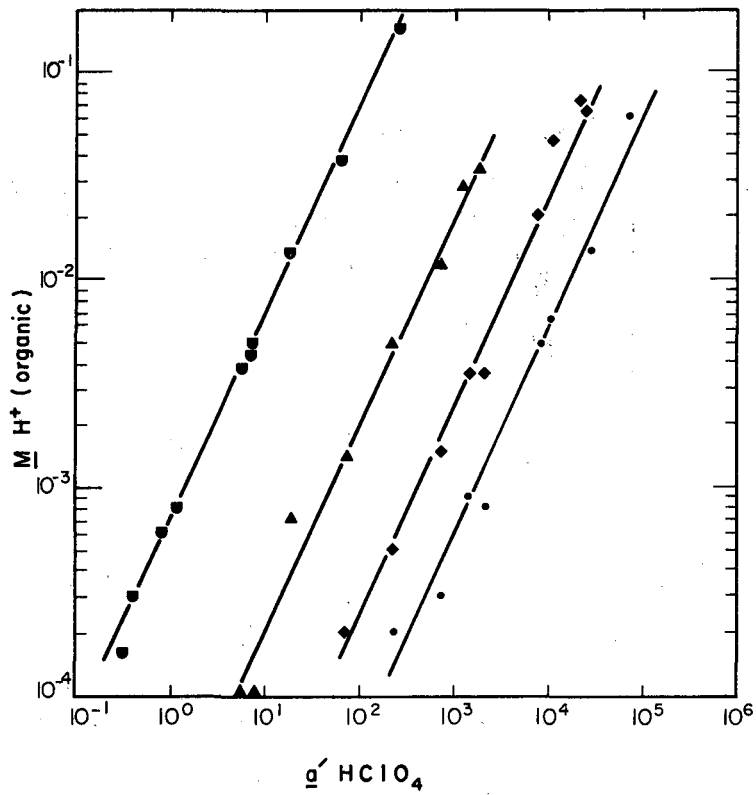
MU-25455

Fig. 3. Variation of acid content of organic phase with $\underline{a}'_{HClO_4}$ ($=\underline{a}_{HClO_4}$ times $(\underline{a}_{H_2O})^x$, $1.4 < x < 2.5$) for equilibrium TBP concentrations:

● , 0.0345 $\underline{M}$; ◆ , 0.0535 $\underline{M}$; ▲ , 0.109 $\underline{M}$; and ▼ , 0.307$\underline{M}$. All lines drawn with slope 1.0.

MU-25457

Fig. 4. Variation of acid content of organic phase with equilibrium TBP concentration for aqueous $HClO_4$ activities (molarities):
▲ , 5.57 (1.69 $\underline{M}$); ■ , 18.3 (2.64 $\underline{M}$); ▼ , 66.8 (3.40 $\underline{M}$); ▼ , 223 (407 $\underline{M}$); ● , 701 (4.69 $\underline{M}$); ● , 1.38 x 10^2 (5.05 $\underline{M}$); ◆ , 8.06 x 10^3 (5.92 $\underline{M}$); ◆ , 1.17 x 10^4 (6.08 $\underline{M}$); ◆ , 2.96 x 10^4 (6.94 $\underline{M}$). All lines drawn with slope 3.0.
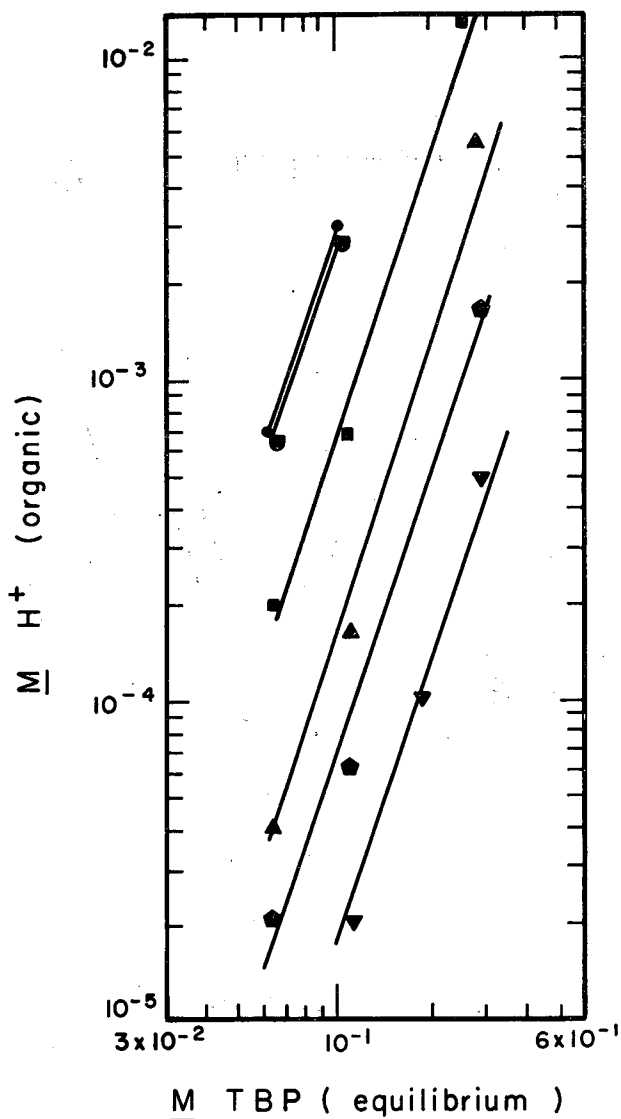
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Fig. 5. Variation of acid content of organic phase with equilibrium
TBP concentration for aqueous acid molarities:
▼ , 0.109 $\underline{M}$ HReO$_4$; ◆ ,0.217 $\underline{M}$ HReO$_4$; ▲ ,0.43 $\underline{M}$ HReO$_4$;
▩ , 0.87 $\underline{M}$ HReO$_4$; ▨ ,1.74 $\underline{M}$HReO$_4$; ● ,1.63 $\underline{M}$ HClO$_4$.
All lines drawn with slope 3.0.
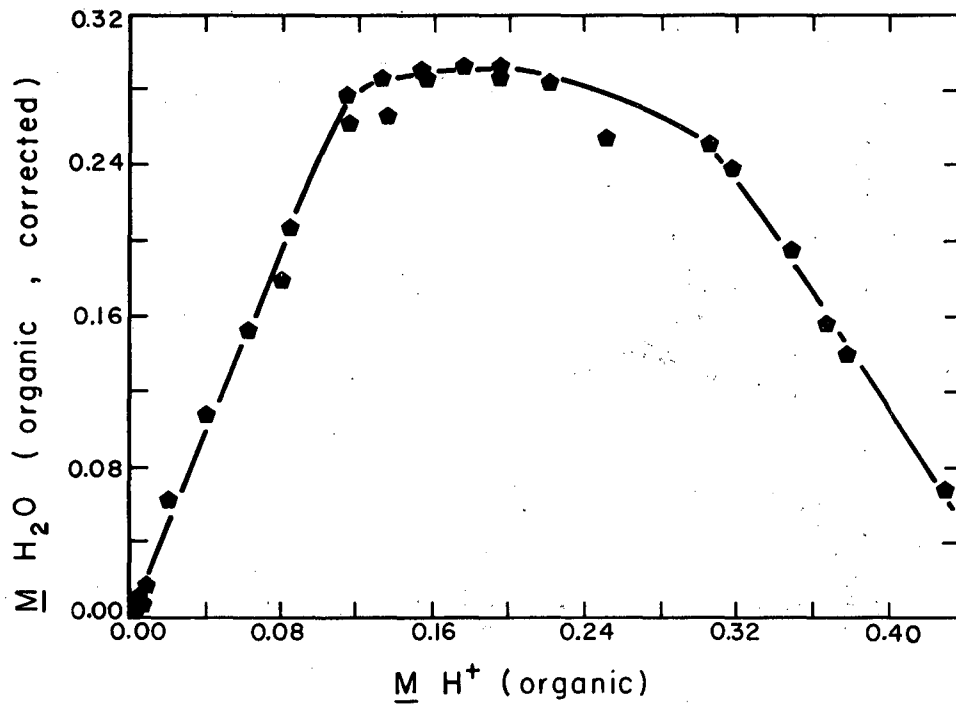
Fig. 6a. Water content vs HClO$_4$ concentration in the organic phase
(as the aqueous HClO$_4$ concentration increases) for total TBP
concentration ⬟ 0.366 $\underline{M}$. $\underline{M}$ H$_2$O does not include the water
dissolved by CCl$_4$ or complexed as TBP·H$_2$O.
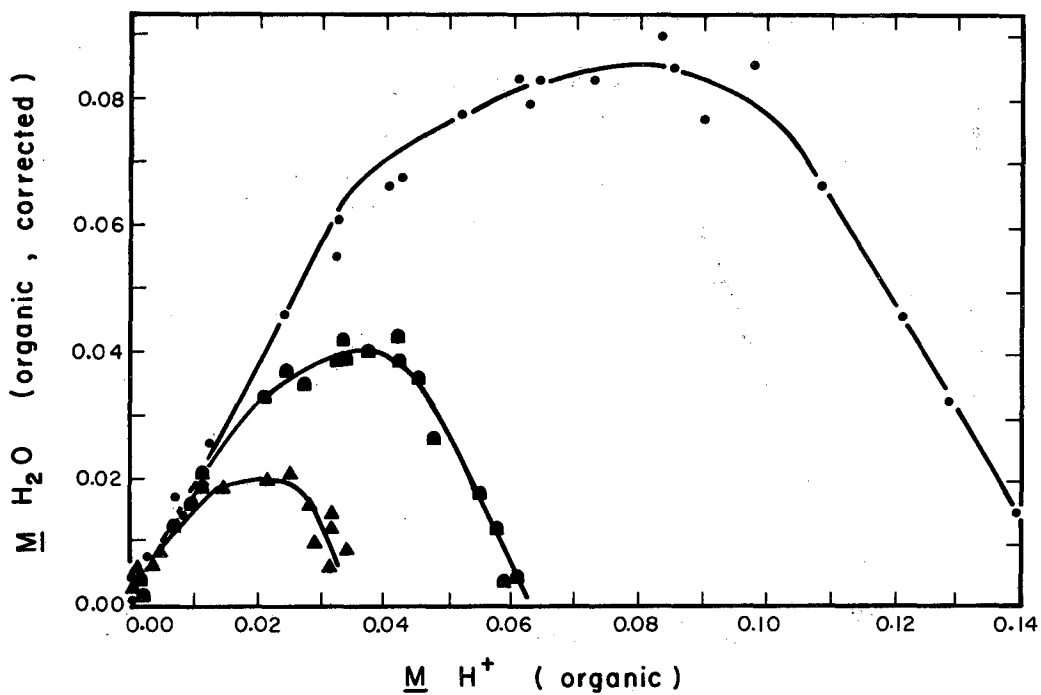
Fig. 6b. Water content vs $HClO_4$ concentration in the organic phase
(as the aqueous $HClO_4$ concentration increases) for total TBP
concentrations: ● 0.128 $\underline{M}$; ● 0.0641 $\underline{M}$; ▲ 0.0384 $\underline{M}$. $\underline{M}$ H_2O
does not include the water dissolved by CCl_4 or complexed as
$TBP \cdot H_2O$.
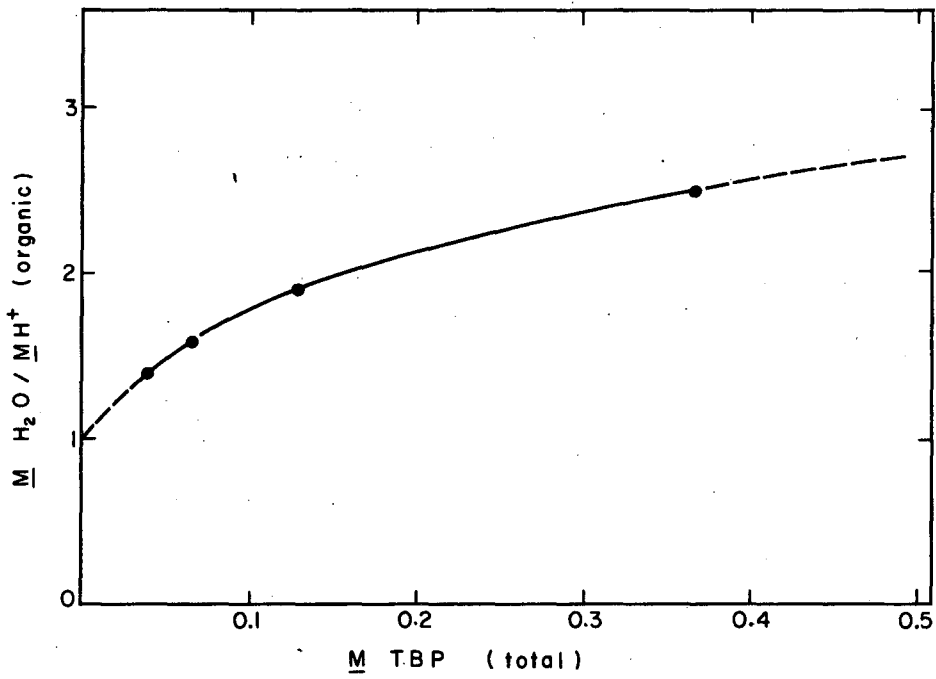
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Fig.7. Variation of H_2O/H^+ ratio in the organic phase with total TBP concentration.
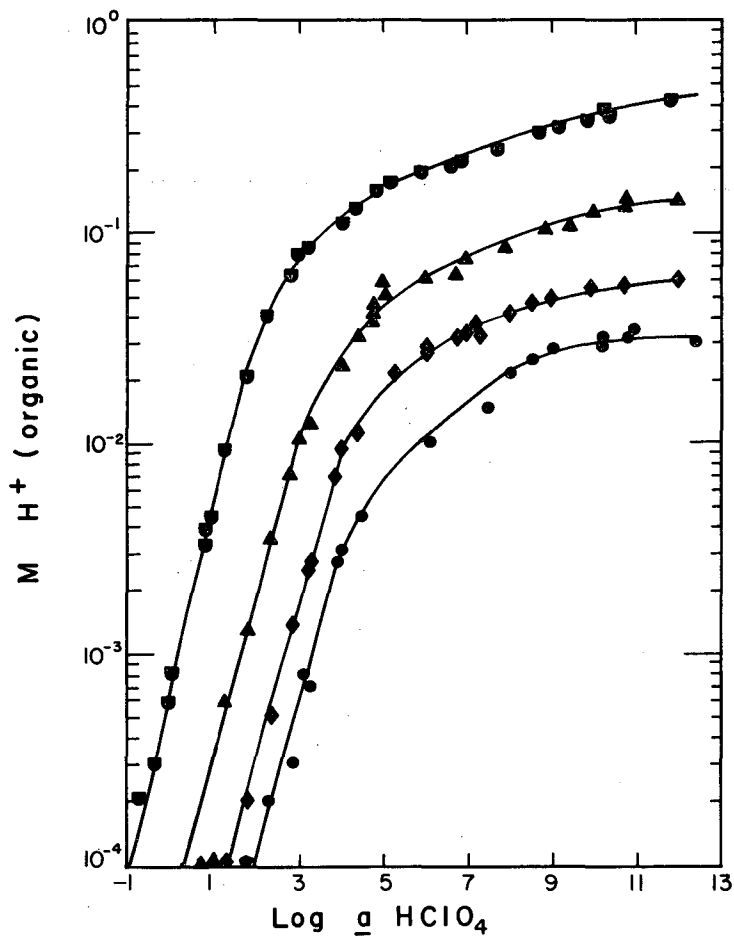
Fig. 8. Variation of acid content of organic phase with aqueous $HClO_4$ activity for total TBP concentrations: ● , 0.0384 $\underline{M}$; ◆ , 0.0641 $\underline{M}$; ▲ , 0.128 $\underline{M}$; and ● , 0.366 $\underline{M}$.
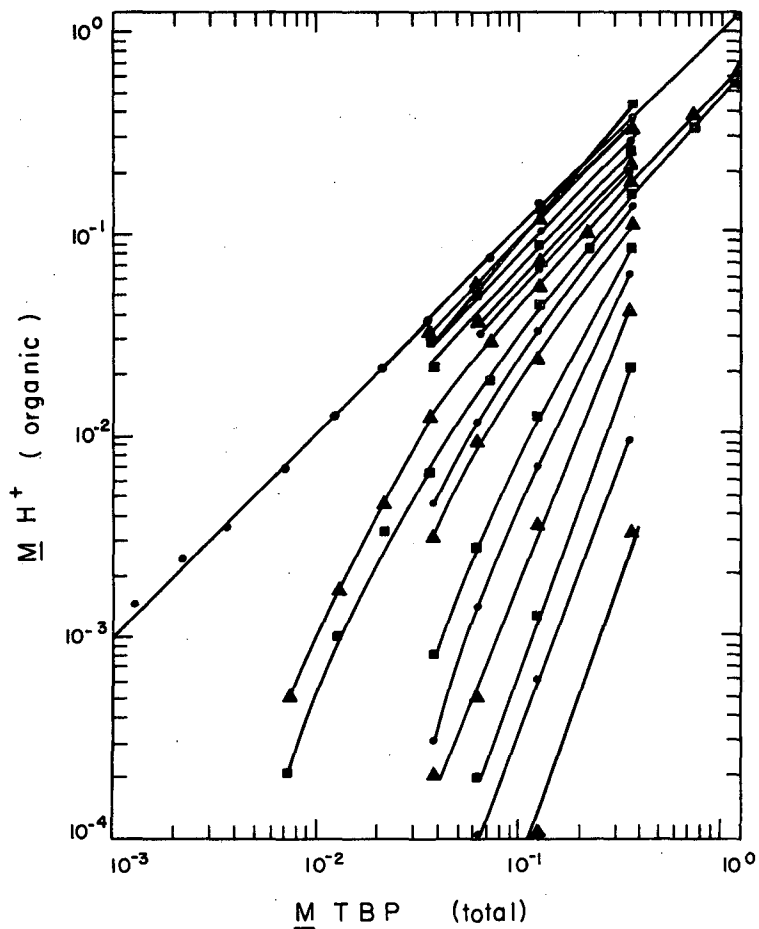
MU-25459

Fig. 9 Variation of acid content of organic phase with total TBP concentration
for increasing aqueous $HClO_4$ activity.