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THE EXTRACTION OF ACIDS BY BASIC ORGANIC SOLVENTS II. TRIBUTYL PHOSPHATE - HBr

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Publication Date

1963-02-01

UCRL-10604

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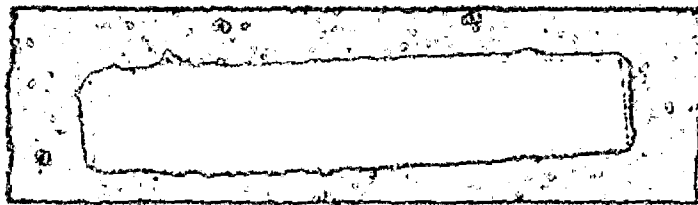
**THE EXTRACTION OF ACIDS
BY BASIC ORGANIC SOLVENTS**

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UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California
Contract No. W-7405-eng-48

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II. Tributyl Phosphate - HBr

D. C. Whitney and R. M. Diamond

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Lawrence Radiation Laboratory
University of California
Berkeley, California

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ABSTRACT

An investigation has been made of the extraction of hydrobromic acid from aqueous solutions into dilute solutions of tributyl phosphate (TBP) in CCl_4 . The principal species which was found to extract over the range 1-10% TBP and 3-8 M aqueous HBr concentration was $\text{H}_3\text{O}^+ \cdot 3\text{TBP} \cdot y\text{H}_2\text{O} \dots \text{Br}^-$, with $0.2 \leq y \leq 1.0$. That is, only the tri-solvated hydronium cation and the bromide anion were observed. This result is interpreted in terms of a proposed general model for such strong acid-basic solvent extraction systems.

THE EXTRACTION OF ACIDS BY BASIC ORGANIC SOLVENTS

II. Tributyl Phosphate - HBr¹D. C. Whitney² and R. M. DiamondLawrence Radiation Laboratory
University of California
Berkeley, California

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INTRODUCTION

The system HBr-H₂O-tributyl phosphate has received but scant attention in the literature. Baldwin et al.³ and Tuck and Diamond⁴ extracted HBr into pure tributyl phosphate (TBP) as part of their studies on acid extraction, and both groups found that the organic phase increased its water content by three molecules for each acid molecule extracted. If a one to one acid-TBP complex is assumed, this indicates four water molecules per acid molecule in the extracted complex. Kertes and Kertes,⁵ by measurement of several physical properties of the system as well as of the amounts of acid and water extracted, studied the distribution of HBr into pure TBP as a function of the aqueous acid concentration, and concluded that the principal extracting species is HBr·2TBP·6H₂O.

-
1. This work was done under the auspices of the U. S. Atomic Energy Commission.
 2. Present address: Chemistry Department, University of California at Davis, Davis, California.
 3. W. H. Baldwin, C. E. Higgins, and B. A. Soldano, J. Phys. Chem. 63, 118 (1959).
 4. D. G. Tuck and R. M. Diamond, J. Phys. Chem. 65, 193 (1961).
 5. A. S. Kertes and V. Kertes, Can. J. Chem. 38, 612 (1960).

The studies all involved HBr extraction into pure TBP. As pointed out by Hesford and McKay,⁶ the organic phases produced in such cases are apt to be far from ideal in their behavior, and because of the complex interactions among the various species involved, caution should be used in the interpretation of the results. In order to avoid the problems inherent in treating such concentrated solutions of ions in an organic phase, it is often desirable to work instead in such dilute solutions that the various species exhibit at least quasi-ideal behavior. Alcock et al.⁷ have shown that the distribution of TBP itself between water and a diluent phase obeys the Nernst partition law for organic phase concentrations up to about 10%, but thereafter shows larger or smaller distribution coefficients, indicating non-ideality in the organic phase. In addition, the present authors have shown that there is a linear relationship between the water extracted by TBP in CCl_4 up to about 10% TBP, but that above 10% TBP a rapidly increasing amount of water extracts.⁸ Both types of experiments suggest that (depending upon the nature of the "inert" diluent) TBP concentrations below about 10% should be employed if simple equilibrium expressions are going to be used, especially if organic phase activity coefficients are going to be neglected, as is usually the case.

6. E. Hesford and H. A. C. McKay, Trans. Faraday Soc. 54, 573 (1958).

7. K. Alcock, S. S. Grimley, T. V. Healy, J. Kennedy and H. A. C. McKay, Trans. Faraday Soc. 52, 39 (1956).

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

Furthermore, if the experimental conditions are chosen so that only a small fraction of the TBP molecules are involved in the extracted acid complex, the organic phase essentially retains the properties of the inert diluent. Changing the concentration of the TBP or of the acid will then have only a slight effect on the activity coefficients of these species in the organic phase, but the resulting variation in the extraction will yield the dependence of the extracting species on the particular component varied (all others held constant) and hence its part in the complex.

This was the procedure employed in the previous paper in this series,⁸ where the authors presented a study of the extraction of HClO_4 and HReO_4 into dilute (< 10% by volume) solutions of TBP in CCl_4 and in iso-octane, and the same techniques will be used in this extension of our investigation of the extraction of strong acids to the HBr-TBP system.

EXPERIMENTAL

Reagents. The preparation of the TBP-CCl₄ solutions has been described previously.⁸ Reagent grade 47% HBr was further purified by saturation with H₂S gas and subsequent distillation. The fraction boiling between 121 and 129°C was collected (constant boiling HBr, b.p. 126°C). All HBr solutions were made from the constant boiling HBr by dilution with conductivity water ($> 7 \times 10^7$ ohm) and were stored in sealed amber-glass bottles to prevent decomposition.

Procedure. The methods used in the equilibrations, water and acid analysis, and infra-red analysis of the acid-TBP solutions have been described.⁸

Owing to the unstable nature of concentrated HBr solutions, the two phases were shaken together for only 15-30 minutes. Equilibrium was assumed to have been achieved by analogy with the HClO₄ extractions, which have been shown to require less than 15 minutes to reach an equilibrium distribution.⁸

Immediately after shaking, the phases were centrifuged and separated. All determinations on the organic phase were completed within 6 hours after separation; no appreciable decomposition or discoloration of the phase was apparent during this time.

All experimental work was done at room temperature, 23±2°C.

RESULTS

Data were obtained on the acid and water content of the organic phase for TBP solutions of 10, 5, 2.5 and 1% by volume TBP in CCl_4 (corresponding to 0.366, 0.183, 0.0915 and 0.0366 M TBP) which were equilibrated with acid solutions ranging from 3 to 8 M in HBr. Insufficient extraction below 3 M HBr fixed the lower limit, and decomposition of the HBr above 8 M set the upper limit. The results of the acid determinations are shown in Fig. 1, where the organic phase acid concentration, $[\text{H}^+]_{(o)}$, is plotted vs the aqueous HBr activity on a log-log scale. Since little activity coefficient data are available for HBr concentrations above 4 molal, it was assumed that $\gamma_{\text{HBr}} \cong \gamma_{\text{HClO}_4}$ for the region between 4 and 12 molal.⁹

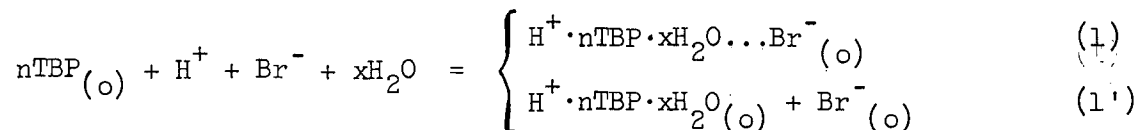
In order to observe the dependence of the extracted species on TBP, the amount of acid extracted as a function of the TBP concentration was determined for several aqueous acid concentrations. The results are shown in Fig. 2 as log-log plots of the organic phase HBr concentration vs the total TBP concentration.

In Fig. 3 is shown a plot of organic phase water concentration vs the organic phase acid concentration. The water content is corrected for the water not associated with the acid-complexed TBP, that is, for the water dissolved in the CCl_4 and for that bound as $\text{TBP}\cdot\text{H}_2\text{O}$. The former quantity is taken as the product of the solubility of water in CCl_4 times the water activity times the mole-fraction of CCl_4 in the organic phase. The latter quantity, usually the larger one, is determined either by infra-red analysis or from the relationship $[\text{TBP}\cdot\text{H}_2\text{O}] = 0.15 [\text{TBP}]$. Both of these methods have been described in the previous paper,⁸ and both give the same results.

9. R. H. Stokes and R. A. Robinson, "Electrolyte Solutions," 2nd Ed. Butterworths, London, 1959), p. 491.

DISCUSSION

The equation for the extraction of HBr by dilute solutions of TBP can be written as



where (o) denotes the organic phase. The resulting organic phase species may be an electrostatic ion pair (1), or dissociated ions (1'), depending upon the conditions, and particularly upon the dielectric constant of the solvent. With the equilibrium TBP concentration and water activity held constant, and replacing the dilute organic solution activities by their concentrations, Eq. (1) leads to a first power dependence of the organic phase acid concentration on the aqueous phase acid activity, while Eq. (1') requires a square root dependence on the aqueous acid activity. The data presented in Fig. 1 permit a decision to be made between these two possibilities if one considers only the lower left side of the figure where the amount of acid extracted has complexed a negligible amount of the original TBP present. A slope of unity is evident. In Fig. 4, the same data has been replotted, but the amount of extracted acid has been corrected to a constant TBP concentration and for the variation in water activity so that the data can be used to decide between Eqs. (1) and (1') more accurately and over a wider range of concentrations. The abscissa in this figure, a'_{HBr} , is defined as $a_{\text{HBr}} a_{\text{H}_2\text{O}}^x$, where the exponent has the range of values $1 \leq x \leq 2$, as shown five paragraphs below, and the water activity of the HBr solutions is taken equal to those

of HClO_4 solutions of the same molality.¹⁰ The correction of the amount of extracted HBr to a constant equilibrium concentration of TBP was done by means of the relationship, $[\text{H}^+]'_{(o)} = [\text{H}^+]_{(o)} [\text{TBP}]^{13} / [\text{TBP}]_{(o)}^{13}$, where the primed quantities refer to the corrected equilibrium concentrations and the unprimed quantities are the actual equilibrium concentrations observed. (The justification for this relationship is given in the third paragraph following where it is shown that three TBP molecules are complexed per HBr molecule extracted.) In Fig. 4, then, is plotted on a log-log scale, the corrected organic phase HBr concentration, $[\text{H}^+]'_{(o)}$, vs a'_{HBr} for four different constant equilibrium TBP concentrations. The straight lines shown are drawn with unit slope, and their agreement with the data indicates that within the range of HBr and TBP concentrations covered in Fig. 4, Eq. (1) holds, and the acid-TBP complex is an ion pair. This is certainly what would be expected for such low dielectric constant media as dilute solutions of TBP in CCl_4 , octane, benzene, etc.

The equilibrium constant can be written then as

$$K_{\text{HBr}} = \frac{(\text{H}^+ \cdot n\text{TBP} \cdot x\text{H}_2\text{O} \dots \text{Br}^-)}{(\text{HBr})(\text{H}_2\text{O})^x (\text{TBP})^n} = \frac{[\text{H}^+ \cdot n\text{TBP} \cdot x\text{H}_2\text{O} \dots \text{Br}^-] \gamma}{(\text{HBr})(\text{H}_2\text{O})^x [\text{TBP}]^n \gamma_{\text{TBP}}} \quad (2)$$

where parentheses denote activity and brackets, concentration.

10. This was done because no data were available for concentrated HBr solutions; the error introduced cannot be very large in this case as the variation in the value of the water activity over the span of the plots in Fig. 4 contributes only a small part of the variation in a'_{HBr} . For example, ignoring the water activity correction completely (a much grosser error than substituting perchloric acid data for hydrobromic acid), would only change the slope by 20% in the worst case in Fig. 4.

By assuming that the ratio of the dilute organic phase activity coefficients, $\gamma/\gamma_{\text{TBP}}^n$, is constant, and by holding the aqueous water and HBr activities constant, expression (2) simplifies to

$$K'_{\text{HBr}} = \frac{[\text{H}^+]_{(o)}}{[\text{TBP}]^n} \quad (3)$$

where $[\text{H}^+]_{(o)}$ is the concentration of the extracting acid species and $[\text{TBP}]$ is the equilibrium TBP concentration.

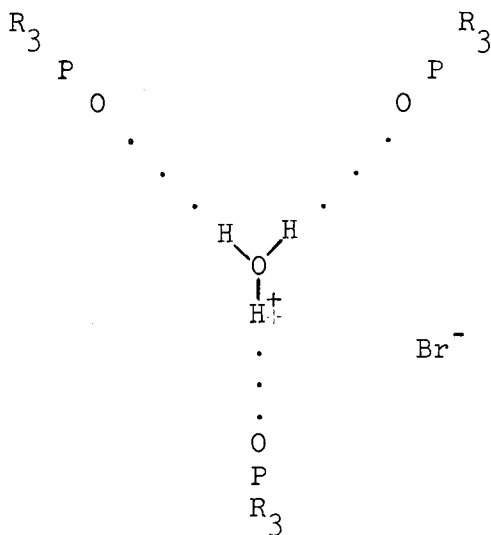
In Fig. 2 are log-log plots of $[\text{H}^+]_{(o)}$ vs the initial total TBP concentration for several aqueous HBr concentrations. Considering the data in the lower right-hand corner where the amount of TBP complexed by extracted acid is very small, slopes of three are obtained, suggesting that three TBP molecules are involved per HBr in the extracted complex. All of the data may then be corrected to equilibrium concentrations of TBP, as required in Eqs. (2) and (3), by subtracting from the total TBP concentration the sum of $3[\text{H}^+]_{(o)}$, to account for the TBP molecules associated with extracted HBr, and $[\text{TBP} \cdot \text{H}_2\text{O}]_{(o)}$, determined as described in the results section. A log-log plot of $[\text{H}^+]_{(o)}$ vs $[\text{TBP}]$ is shown in Fig. 5, and it is seen that up to the point where an appreciable fraction of the TBP is complexed by the acid, a set of lines of slope $n = 3.0$ is obtained for all aqueous HBr concentrations between 3 and 8 M. These results indicate an extracting species with 3 TBP molecules per HBr.¹¹

11. It must be pointed out that this slope is not a result of using a correction factor of 3, since in those cases where the correction is negligible, a slope of 3 already exists. Furthermore, correction factors other than 3, e.g., 4 or 2, do not yield straight lines of slope 4 or 2 respectively.

It is most unlikely that any of these TBP molecules are bonded to the Br^- ion; the basic oxygen of the TBP phosphate group cannot coordinate with another electron rich (basic) species, but only with electron deficient (acidic) ones such as the proton. The existence of the $3 \text{TBP}/\text{H}^+$ complex says that the hydrogen ion is able to bond to three TBP molecules, and this strongly implies that the extracting species is the hydronium ion, H_3O^+ which is indeed capable of three strong hydrogen-bonds to basic molecules. There are good indications now that this is true in aqueous solution; the H_3O^+ ion hydrogen-bonds a first hydration shell of three water molecules much more strongly than the resulting $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$ species bonds further waters or than ordinary water molecules bond to other water molecules. Evidence for this comes from a variety of types of measurements¹²⁻¹⁹ which have been mentioned in earlier papers,^{4,8} and the recent theoretical calculations of Grahn²⁰ illustrate the magnitude of strength possible for the three primary hydrogen bonds of the H_3O^+ ion.

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12. R. M. Diamond and D. G. Tuck, in "Progress in Inorganic Chemistry," F. A. Cotton, ed., Vol. II (Interscience Publishers, Inc., New York, 1960).
 13. a) R. H. Stokes and R. A. Robinson, J. Am. Chem. Soc. 70, 1870 (1948)
b) E. Glueckauf, Trans. Faraday Soc. 51, 1235 (1955).
 14. E. Glueckauf and G. P. Kitt, Proc. Roy. Soc. (London) A228, 922 (1955).
 15. K. N. Bascombe and R. P. Bell, Disc. Faraday Soc. 24, 158 (1957).
 16. P. A. H. Wyatt, ibid. 24, 162 (1957).
 17. E. Wicke, M. Eigen, and T. Ackermann, Z. phys. Chem. (N.F.) 1, 340 (1954).
 18. M. Eigen and L. DeMaeyer, in "The Structure of Electrolyte Solutions," W. J. Hamer, ed., (John Wiley and Sons, Inc., New York, 1959).
 19. H. D. Beckey, Z. Naturforschung 14A, 712 (1959).
 20. R. Grahn, Arkiv. Fysik, 21, 13 (1962).

From Fig. 3, it can be seen that for 10% TBP two water molecules extract per proton, and as the TBP concentration drops, correspondingly less water goes over, i.e., 1.5 H₂O/H⁺ for 5% TBP and 1.2 H₂O/H⁺ for 2.5% TBP. It appears from Fig. 6 that at infinitely dilute TBP concentrations the ratio of H₂O/H⁺ would be 1.0, i.e., H₃O⁺, and the extracting species there would be (R = C₄H₉O)



exactly analogous to the case of HClO₄ extractions.⁸ With increasing TBP concentration, additional water molecules can enter the complex, possibly by forming a hydrogen-bonded bridge between the H₃O⁺ and the TBP molecules, yielding H₃O⁺·3TBP·yH₂O...Br⁻ as the extracting species, again in agreement with the HClO₄ system. Owing to the decomposition of HBr to form Br₂, which will react with the Karl Fischer reagent, the data obtained in the H₂O analyses are subject to relatively greater experimental errors than with the HClO₄ extractions. This fact, coupled with the lower extraction coefficient for HBr (due to the smaller size of the anion),^{12,21,22} may account for the slight differences in the results for the two acids; the agreement, however, is quite good.

21. S. Siekierski and R. Gwoździ, Nukleonika 5, 205 (1960).

22. N. Bjerrum and E. Larsson, Z. phys. Chem. A127, 358 (1927).

The existence of the trisolvated hydronium ion as the extracting cation has now been established for the acids HBr, HReO_4 , and HClO_4 distributing into dilute TBP solutions in CCl_4 or in iso-octane. The extraction process is considered to involve a competition among the basic extractant molecules (TBP), water, and the anions for solvating the proton. With the strong acids being considered, the anion is not basic enough to compete, so only the water and TBP are involved. Water wins, at least to the extent of forming the H_3O^+ ion, and in dilute aqueous solutions water further solvates this ion. But as the aqueous acid concentration is increased, the water activity falls and the TBP is increasingly better able to compete with water for solvating (extracting) the hydronium ion, that is, to provide its first (or second) shell solvation. Most probably, the (hydrated) $\text{H}_3\text{O}^+ \cdot 3\text{TBP}$ ion is the cationic species also in the dilute TBP extraction of HCl and HI, but the experimental difficulties to prove this are considerable. Hydriodic acid oxidizes rather easily while HCl extracts too poorly to be readily determined at these low TBP concentrations. However, Naito and Suzuki²³ have presented evidence of $3 \text{ TBP}/\text{H}^+$ for HCl extractions into dilute TBP solutions, using the very sensitive method of activation analysis. Studies to be published shortly on the complex haloauric acids²⁴ also show $3 \text{ TBP}/\text{H}^+$ for both the chloride and bromide complexes.

23. K. Naito and T. Suzuki, J. Phys. Chem. 66, 983 (1962).

24. M. I. Tocher, D. C. Whitney and R. M. Diamond, "The Extraction of Acids by Basic Organic Solvents. IV. Tributyl Phosphate and Trioctyl Phosphine Oxide - HAuCl_4 and HAuBr_4 ," to be published.

Furthermore, extraction of these acids by the more basic solvent trioctyl phosphine oxide (TOPO) appears promising. It has already been determined that the extracting complex with HClO_4 and HReO_4 is $\text{H}_3\text{O}^+ \cdot 3\text{TOPO} \dots \text{ClO}_4^-$.²⁵

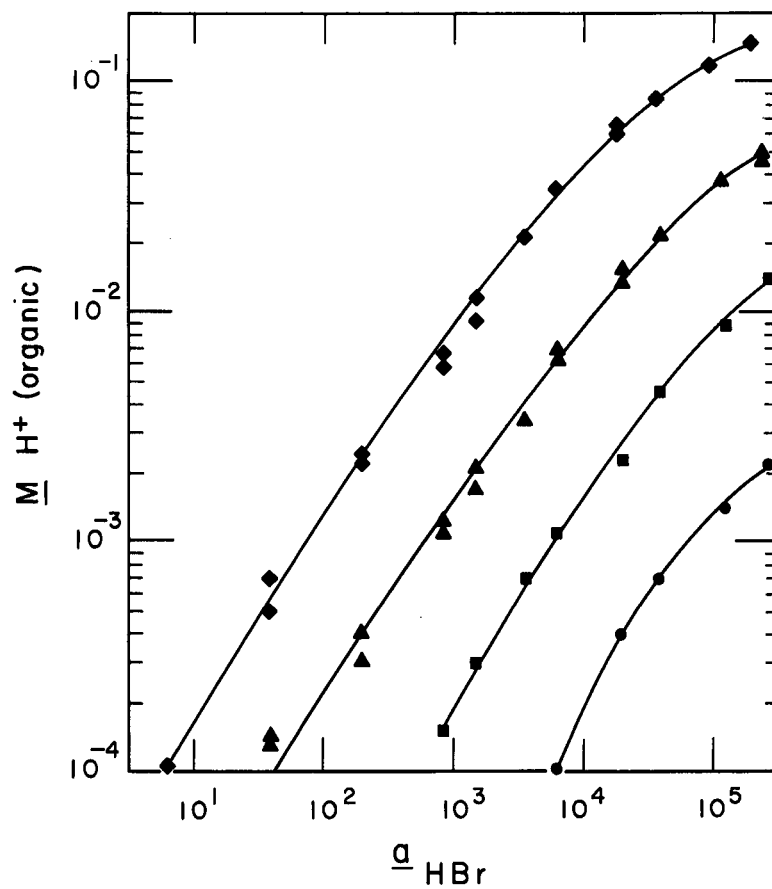
There are two further items of interest to be considered. One is that in Fig. 4 the plots of extracted HBr vs corrected HBr activity appear to rise too steeply when more than about 1/3 of the TBP is complexed as $\text{H}_3\text{O}^+ \cdot 3\text{TBP} \cdot y\text{H}_2\text{O}$. This indicates that another extracted species, of lower TBP content, is making its appearance, and the value of $[\text{H}^+]_{(o)}$ is being over-corrected. It was not possible to characterize the nature of this species in the present work, but quite likely it is a one to one complex of TBP and HBr.

Finally, it should be noted that the conclusions concerning the trisolvation of extracted acids apply only to acids which remain ionized, though not necessarily dissociated, in the organic phase and thus provide H_3O^+ ions. In the case of weaker acids such as HNO_3 ,^{4,26} Cl_3CCOOH ,⁴ and CH_3COOH ,²³ it is well established that a one to one TBP-acid complex is formed. This is due to the extraction of the molecular acid into the organic phase; such a species has only one coordination site, the hydrogen of the molecular acid. Such cases will be considered in Part III of this series.²⁷

25. T. J. Conocchioli, M. I. Tocher and R. M. Diamond, "V. Trioctyl Phosphine Oxide - HClO_4 and HReO_4 ," to be published.

26. D. G. Tuck, J. Chem. Soc. 2783 (1958).

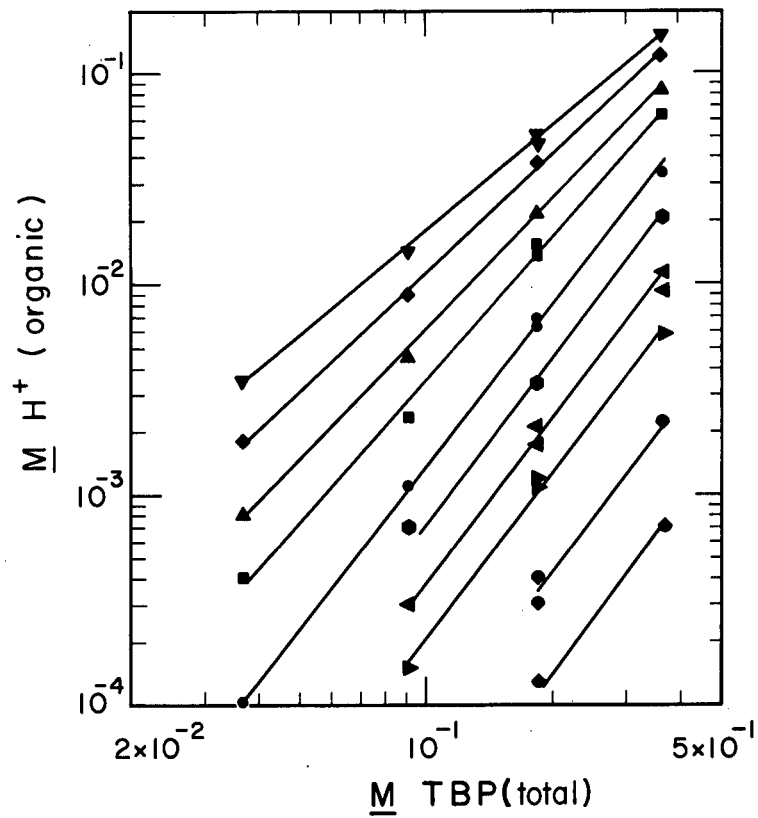
27. D. C. Whitney and R. M. Diamond, "III. Tributyl Phosphate - HNO_3 ," to be published.



MU-28748

Fig. 1. Variation of acid content of organic phase with aqueous HBr activity for total TBP concentrations of:

●, 0.0366 M; ■, 0.0915 M; ▲, 0.183 M; ◆, 0.366 M.



MU-28722

Fig. 2. Variation of acid content of organic phase with total TBP concentration for initial aqueous HBr concentrations of (from bottom to top):

3.21, 4.28, 5.17, 5.57, 6.07, 6.48, 7.12, 7.50, 8.08, and 8.53 M.

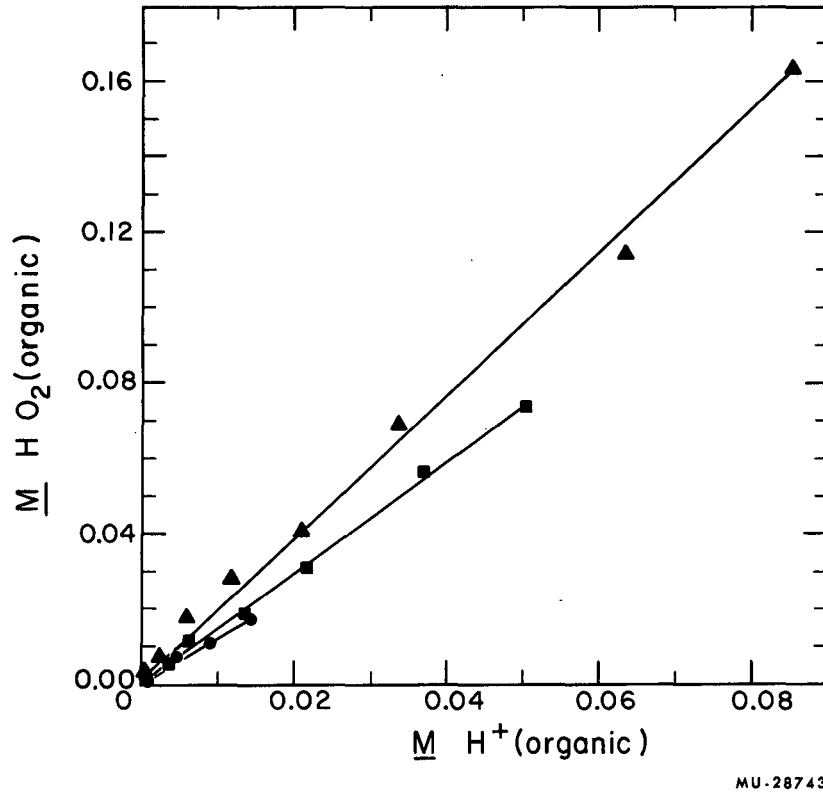
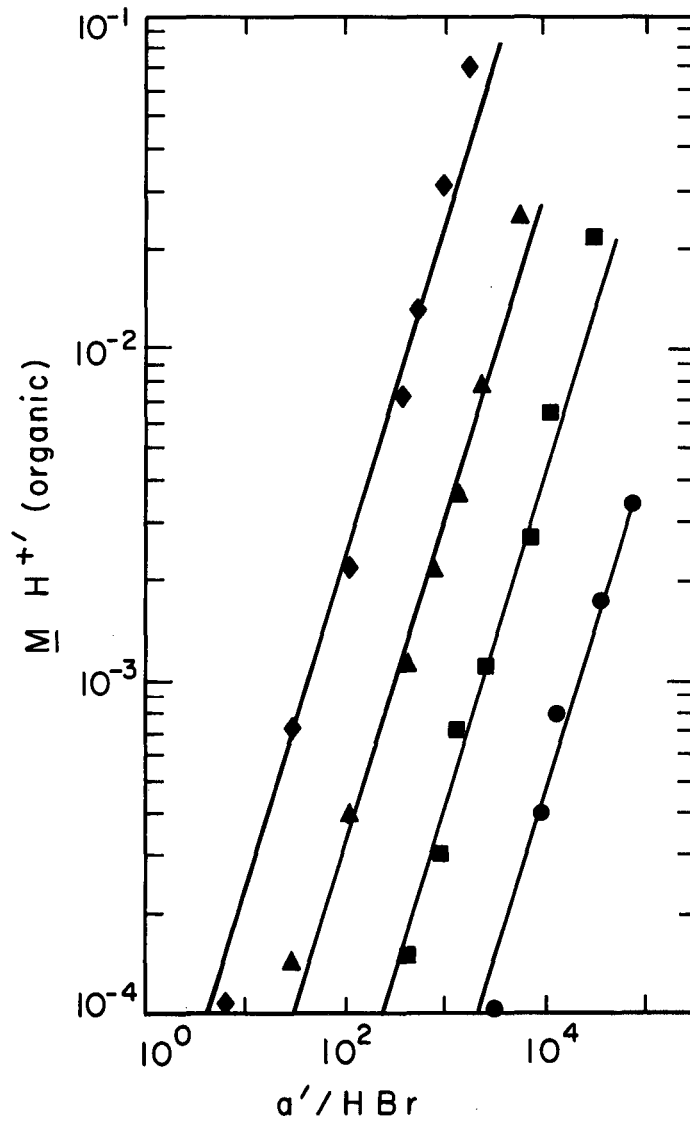


Fig. 3. Variation of water content in the organic phase with organic phase acid concentration, for total TBP concentrations of:

●, 0.0915 M; ■, 0.183 M; ▲, 0.366 M.

The water content does not include the water dissolved by CCl_4 or complexed as $\text{TBP}\cdot\text{H}_2\text{O}$.



MU-30105

Fig. 4. Variation of corrected acid content of organic phase with a'_{HBr} ($a_{HBr} a_{H_2O}^x$) for equilibrium TBP concentrations of:

●, 0.0338 M; ■, 0.0825 M; ▲, 0.164 M; ◆, 0.320 M.

All lines are drawn with a slope of 1.0.

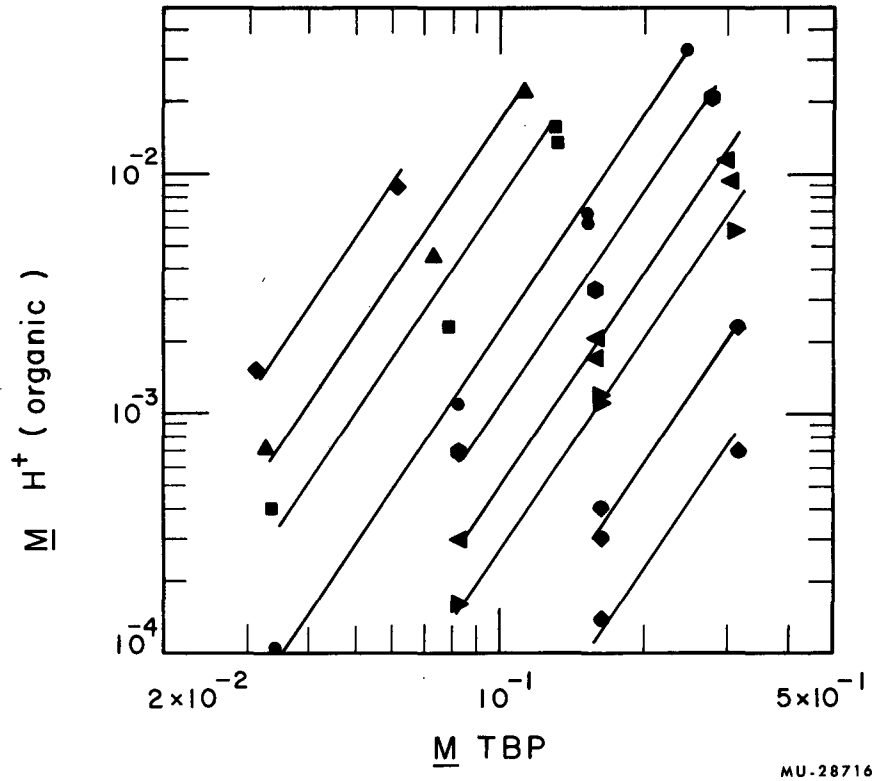
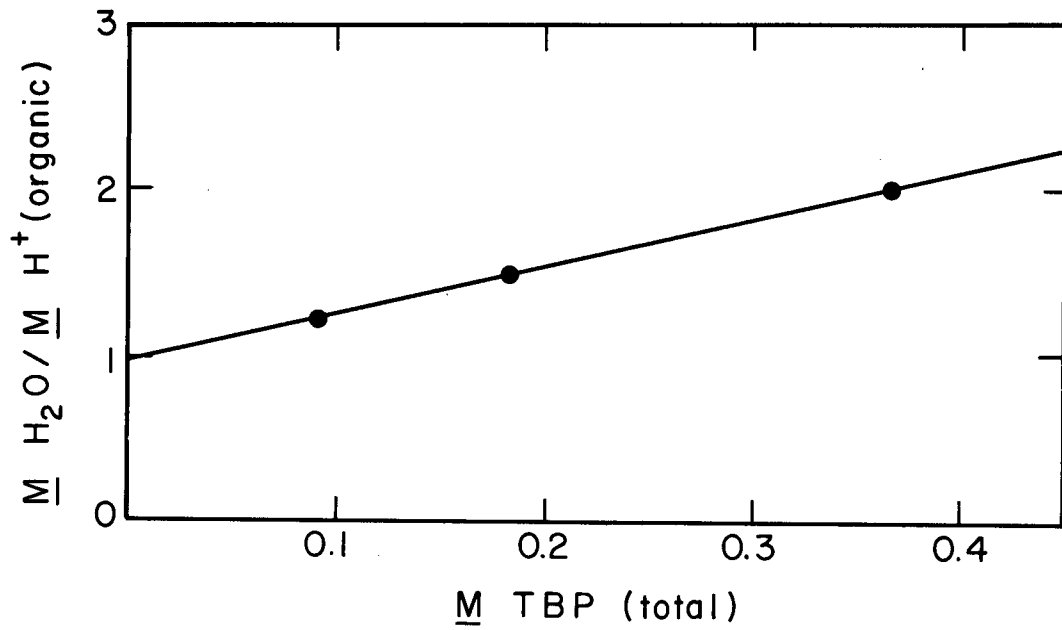


Fig. 5. Variation of acid content of organic phase with equilibrium TBP concentration for initial aqueous HBr concentrations of (from bottom to top):

3.21, 4.28, 5.17, 5.57, 6.07, 6.48, 7.12, 7.50, and 8.08 M.

All lines are drawn with a slope of 3.0.



MU-30104

Fig. 6. Variation of initial H₂O/HBr ratio in the organic phase with total TBP concentration.

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