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A SOLVENT EXTRACTION STUDY OF PROTON SOLVATION

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Contents

Abstract vi

I. Introduction 1

II. Presentation of Problem 4

III. Experimental Methods

A. Reagents 7

B. Procedure 7

1. Organic Phase Analysis 7

2. Tracer Analysis 9

IV. Results

A. TOPO-H_2O 11

B. TOPO-Acid 15

C. TOPO-H_2O-Acid 16

V. Discussion

A. TOPO-H_2O 17

B. TOPO-H_2O-Dilute Acid 19

1. General Discussion 19

2. TOPO-$HClO_4$-CCl_4 22

3. TOPO-HNO_3-CCl_4 33

4. TOPO-$HClO_4$-Nitrobenzene 40

5. TOPO-HNO_3-Nitrobenzene 47

C. TOPO-Concentrated Acid 54

1. TOPO-Concentrated $HClO_4$-CCl_4 54

2. TOPO-Concentrated HNO_3-CCl_4 55

3. TOPO-Concentrated $HClO_4$-Nitrobenzene 57

4. TOPO-Concentrated HNO_3-Nitrobenzene 57

VI. Conclusions 58

Acknowledgments 60

References 61
Appendix A. List of Symbols 64
Appendix B. Tables. 65

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ABSTRACT

The extraction of $HClO_4$ and HNO_3 into dilute solutions of tri-n-octyl phosphine oxide (TOPO) in carbon tetrachloride and nitrobenzene is studied, and the nature of the extracting species is determined. In the extraction of dilute $HClO_4$ (≤ 0.2 M) into dilute TOPO (≤ 0.1 M) in CCl_4, the extracting species are $TOPO \cdot H_2O$ and $H_3O^+ \cdot 3\ TOPO \cdots ClO_4^-$. The predominant species in the extraction of HNO_3 (≤ 0.3 M) is anhydrous and is $TOPO \cdot HNO_3$. In the extraction of both dilute $HClO_4$ and HNO_3 into TOPO in nitrobenzene, the extracting species is $H_3O^+ \cdot 3\ TOPO \cdot yH_2O + X^-$, in which y is probably 0 but may be as large as 3, and in which X^- is the anion. The results of the extraction are interpreted on the basis of the evaluation of the relative basicities of all components in each system and of the dielectric constant of the inert diluent.

I. INTRODUCTION

The process of solvent extraction has long been a useful tool in chemistry. Industrially, the method is used for the separation of metals, e.g., the extraction of uranium. Solvent extraction is also employed as an analytical method for the detection of certain elements. More recently solvent extraction has become a tool in physical chemistry for the study and isolation of certain inorganic species.

This study is limited to the extraction of inorganic acids. In this context, extraction is the process by which an inorganic acid is distributed between an aqueous phase and a water-immiscible organic phase. The organic phase may be either a pure extractant or a solution of an extractant in an inert solvent. The extractant is usally a Lewis base which contains a nitrogen or an oxygen atom with a free electron pair. Specifically, this study is concerned with the solvation of the proton in the organic phase. Further, it is concerned only with those systems in which the extracting species forms actual chemical bonds with the organic extractant, in contrast with those systems in which the extraction of the species does not involve the formation of chemical bonds (in the usual sense). An example of the latter type of system is the one for the extraction of I_2 into CCl_4.[1]

The extraction of the proton (or cations, in general) may be viewed in terms of a competition for solvating the proton (or cation) among water, the extractant, and the anion. The nature of the extracting complex is dependent upon, among other things, the relative basicities of these components in the organic phase. There are, then, three possible conditions under which an inorganic acid can extract: (a) that in which the extractant is the strongest base; (b) that in which water is the strongest base; (c) that in which the anion is the strongest base. Under the first condition, when the extractant is the strongest base, its reaction is directly with the proton to form the anhydrous salt in a typical acid-base reaction. An example is the extraction of acids by amines and the subsequent formation of an ammonium salt. (See for example Ref. 2.)

Under the second condition, water best solvates the proton, and the extracting acid species will probably be a hydronium ion. If the basicity of the extractant is not too different from that of water, the extractant forms the secondary solvation shell about the proton. If the extractant is a very weak base with respect to water, water not only forms the hydronium ion, but also its first solvation shell.[3] The extractant can then solvate the hydronium ion through an intermediary water bridge. An example is the extraction of dilute $HClO_4$ by tributyl phosphate.[4-8] In both cases, it is assumed that the anion is not complexed by the extractant. This assumption seems quite reasonable because the extractant and anion are both bases and no interaction is expected.

Under the third condition, when the anion is the strongest base, it best solvates the proton to form a molecular acid, which is then extracted. A hydrogen bond is formed between the proton of the acid and the basic site on the extractant. An example is the extraction of HNO_3 by tributyl phosphate (TBP), in which the molecular species $TBP \cdot HNO_3$ has been established.[9-18] As the extracting complex is essentially a neutral molecule, molecular-acid extraction involves no charge transfer. This type of extraction can occur easily even in low-dielectric-constant media because no charge separation must be supported; therefore, the distribution ratios in this type of extraction tend to be high.

A further consideration is the activity of each component in the extraction system. Consider the activity of water in the aqueous phase. If the water activity is low, the water molecules cannot compete as well for the proton as when the activity is 1 or approximately equal to 1. If the activity of the extractant is high, compared with that of water, the extractant may solvate the proton in preference to the other bases present, and the extent of extraction will increase. Similarly, if the activity of the extractant is reduced, there is a corresponding decrease in extraction.

There are several methods for the determination of the extracting complex. One method is to measure the stoichiometric concentrations of the different components in the organic phase. This method, however, is not completely reliable because the experimental conditions are limited to one concentration of, or to a concentrated solution of, the extractant. Such single determinations are not always valid in indicating the general nature of the extracting complex.

A better method for examining the complex has been suggested by Hesford et al.[19-21] If the activity of only one component in the system is varied while all others are held constant, the resulting variation in the extraction of the complex will show the dependence of the extracting species on that particular component; thus, its part in the complex will be determined. Such variations in activity may involve changes in activity coefficients, but concentrations are what are usually measured. Because very little is known about activity coefficients in an organic phase, the problem may best be solved by limiting the concentration of the extractant to less than a few tenths molar in some inert solvent, and choosing the experimental conditions such that only a few percent of the extractant molecules are involved in the extraction complex. The organic phase thus retains the properties of the inert diluent. Changes in concentration of the extractant, acid, or water in that phase will have only a slight effect on their activity coefficients. After the nature of the extracting species in the dilute extractant is established, studies may be extended to more concentrated solutions to see if, in fact, more complex interactions are occurring in the organic phase.

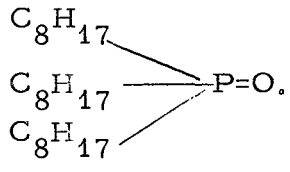
II. PRESENTATION OF PROBLEM

Of the many organic bases, the most typical classes of compounds used for acid-base extraction are the trialkylamines, trialkyl phosphine oxides, trialkyl phosphates, ketones, and ethers, listed in order of decreasing base strength. Extensive studies have been made on many of these compounds and their extraction of acids in various solvents.

Considerable work has been published on the extraction properties of tributyl phosphate (TBP), a relatively weak base, with strong acids. Some studies in dilute solutions of TBP suggest that the extracting acid species is trisolvated by the TBP.[7,9,22,23] In pure TBP, it has been suggested that the acid species is the trihydrated hydronium ion, $H_9O_4^+$.[4,5] More recently, a model for the general extraction of dilute strong acids by TBP has been proposed, i.e., $H_3O\ 3\,TBP \cdot yH_2O \cdots X^-$, where $0 \leq y \leq 3$ and X^- is the anion.[8] The extraction complex for TBP-dilute strong acids always seems to contain water; in other words, water is a better base than is TBP.

As stated earlier, the trialkylamines are very strong bases and have been shown to displace all water molecules from around the proton forming an ammonium ion; thus, such extractions are anhydrous. (See for example Ref. 2.)

The extractant used in this work was tri-n-octyl phosphine oxide (TOPO), which is a base intermediate between TBP and the amines. The structure of TOPO is



The choice of TOPO as an extractant was also influenced by the fact that the molecule has only one basic site—the oxygen. The use of TOPO, then, eliminated the three ester oxygens present in TBP, thereby excluding any possible reaction at these sites.

Some studies have been conducted on the extraction of mineral and complex acids by TOPO. White and Ross[24] have done extensive work on the extraction of $HClO_4$, HNO_3, HCl, H_2SO_4, and H_3PO_4. Their only suggestion for an extraction adduct was TOPO-HNO_3 where a first power dependence on TOPO was found. They neglected the presence of water in any extraction complex. This study will show that a study of the TOPO-H_2O system and the water content must be included to satisfactorily explain the extraction mechanism of the strong mineral acids. Zingaro and White[25] and Martin et al.[26] also suggest a TOPO · HNO_3 complex for HNO_3. For the extraction of Fe out of HCl, Ross and White[27] have determined that $HFeCl_4$ is present in the organic phase, and as an extraction adduct suggest 2 TOPO·$HFeCl_4$ at very high Fe concentrations. Boyd and Larson[28] indicate that $HTcO_4$ is the extracting species for Tc and acid solutions. They suggest the complex 2 TOPO· $HTcO_4$. Whitney et al.[23] have extracted Au out of HCl solutions; they concluded that gold extracts as $HAuCl_4$ with a third-power dependence on TOPO. They extracted $HReO_4$ and also found a third-power dependence.

The acids chosen for this investigation were $HClO_4$ and HNO_3. $HClO_4$ was chosen because ClO_4^- forms a very weak base and HNO_3 was chosen because NO_3^- forms a relatively strong base. In addition, $HReO_4$ was used in conjunction with the studies on $HClO_4$. $HReO_4$ has about the same acid strength as $HClO_4$ and has similar ionic size, but Re has a convenient radioisotope Re^{186} ($t_{\frac{1}{2}}$ = 90 h),[29] which made possible a method for extending studies into the very dilute region.

The solvents used were CCl_4 and nitrobenzene. CCl_4 has a very low dielectric constant; it cannot support a charge separation of moderately sized ions. In such a low-dielectric-constant medium, the attraction between the proton and the anion is increased over the value in water. The extracting complex is usually in the form of ion-pairs or molecules. Nitrobenzene, on the other hand, is a high-dielectric-constant medium and can support a charge separation. In a higher dielectric-constant medium, ionization and dissociation are promoted and the competition among

all bases present in the organic phase is not hindered by the formation of ion-pairs or molecules.

The present study, then, involved the determination of acid and water in the organic phase and the number of TOPO molecules associated with each proton, i.e., the determination of the extracting complex.

III. EXPERIMENTAL METHODS

A. Reagents

The TOPO used was Eastman White Label product. Purification by equilibration with mild base and recrystallization gave a product with a behavior identical to that of the original product; therefore, the product was used as obtained. Solutions of TOPO were prepared in CCl_4 (Baker and Adamson reagent grade) or nitrobenzene (Eastman White Label) and stored over molecular sieves (Linde Co., 1/16-in. diam pellets) in order to remove water from and prevent hydrolysis of the solutions. All dilutions of TOPO were made in volumetric glassware from a stock 0.1 M solution. At the time of each usage, solutions were filtered under mild vacuum conditions in order to remove suspended particles of molecular sieves.

The $HClO_4$ solutions were prepared from G. F. Smith reagent-grade $HClO_4$(70-72%) with distilled water. The HNO_3 solutions were prepared from Merck reagent grade HNO_3(70-71%).

Determinations of aqueous acid concentrations were made by standard analytical methods, i.e., titration with standard base to the red end point of phenol red (pH = 7). The radioactive $Re^{186}O_4^-$ tracer was prepared by irradiating $KReO_4$ with neutrons in the Livermore pool-type reactor. The product was dissolved in distilled water to give approximately 10^{-3} M $KReO_4$.

Matheson, Coleman, and Bell stabilized and premixed single-solution Karl Fischer reagent was used. Methanol used in the Karl Fischer analysis blank was Baker and Adamson Electronic grade ($\leq$ 0.1% H_2O). Pyridine used in the same blank was Baker and Adamson reagent grade (0.1% H_2O).

B. Procedure

1. Organic Phase Analysis

Equal volumes of acid and TOPO solutions were equilibrated in glass stoppered bottles. Samples were normally shaken from 1 to 3 hours with a wrist action shaker. Some samples were shaken as much

as 6 hours with no detectable difference in extraction. Previous work in this laboratory indicated that equilibrium is attained in similar systems in less than 1 hour.

After equilibration, samples were transferred to centrifuge cones and centrifuged for 1 to 3 minutes. The organic phase was the bottom phase in all cases except those in which TOPO solutions equilibrated with greater than 6 M $HClO_4$. In order to insure that contamination by the aqueous phase was minimal, the organic phase was removed by the following technique: A stream of air was passed through a transfer pipette as it traveled through the aqueous phase; the organic phase was withdrawn; and droplets of the phase were allowed to bubble through the aqueous phase as the pipette was removed. The tip of the pipette was wiped with an absorbent tissue to remove adhering drops of the aqueous phase.

The acid content of the organic phase was determined by direct two-phase titrations. One to two milliliters of water were added to an aliquot of the organic phase and the two phases were agitated by a magnetic stirrer for approximately 1 minute. The aqueous phase was then titrated with 0.0100 M or 0.1000 M NaOH, with the stirring being continued throughout the titration. Phenol red (pH = 7) was used as the indicator and determinations were made to its red end point. A blank was run using water-saturated TOPO solutions; the amount of NaOH used for the blank was subtracted from that used for the sample. In some cases, particularly with nitrobenzene, the acid was found to have an appreciable extraction into the inert solvent even when no extractant was present. This amount was considered a correction factor and was subtracted from the organic acid concentration with extractant present in order to obtain the true amount of acid extracted by the organic base.

The water content of the organic phase was determined by the Karl Fischer method, using a direct visual end point.[30] A blank containing 2 to 3 ml of dried methanol and 0.1 to 1.0 ml of pyridine was first titrated to the wine-red end point. An aliquot of the organic phase was then added and titrated. The difference between the two end points

was the amount of water present in the sample. Titrations were done in 25 ml volumetric flasks. Each time a few drops of Karl Fischer reagent were added to the sample, the glass stopper was replaced, to insure that no water from the air was introduced while mixing the sample and reagent. The Karl Fischer reagent was standardized by the same method, with samples of methanol with known water content.

A Beckman IR-5 double-beam recording spectrophotometer was used for the infrared analysis of the water content in the organic phase. Dry CCl_4, water-saturated nitrobenzene, or a dry TOPO solution in CCl_4 of the same concentration as the sample was used as a reference. Sample solutions and reference were contained in matched 2.0 or 0.2 mm cells with CaF_2 windows or 0.5 mm cells with AgCl windows. When dry CCl_4 was used as the reference, absorption values of water in CCl_4 were determined in order to correct the total absorption in the sample and to ascertain the amount of TOPO-bonded water alone. Quantitative correlation was made between water peak-absorption values and water values obtained by the Karl Fischer method.

2. Tracer Analysis

In the tracer studies between 10 and 40 μl of $KReO_4$ tracer were injected by a micro-pipette into equal volumes of acid and extractant phase in 60ml glass-stoppered bottles. Samples were shaken from 30 to 60 minutes, transferred to centrifuge cones, and centrifuged for from 1 to 3 minutes. The organic phase was removed in 2.00 ml aliquots by the same technique described above, and placed in 1-dram screw-cap vials for counting; 2 ml aliquots of the aqueous phase were also removed and placed in vials. Gamma counting was done on each phase with a well-type Na(Tl)I scintillation crystal and a single-channel analyzer. Samples were counted for 10^4 counts or 10 minutes, whichever occurred first. At no time was the counting time less than one minute. The total number of counts/min in both phases (corrected for background) was equated to the macro $HClO_4$ concentration. Then the fraction of the total counts found in each phase was multiplied times the original $HClO_4$ concentration in order to show the amount of acid in that phase.

All experimental work was done at room temperature, 23° ± 2° C, with no detectable changes in extraction over this range.

IV. RESULTS

A. TOPO-H_2O

Investigation was first made of the TOPO-H_2O system. Solutions of 0.001 to 0.5 M TOPO in CCl_4 and 0.01 to 0.2 M TOPO in nitrobenzene were equilibrated with water, and the water content in the organic phase was determined by the Karl Fischer method. Figures 1 and 2 show a plot of log organic-phase water vs log total TOPO. The values shown are corrected for the amount of water dissolved in CCl_4 or nitrobenzene alone. This correction term is merely the solubility of H_2O in the solvent times the solvent's volume fraction (Tables I and II).

Figure 1 also shows the results of the infrared spectral analyses made of the water content in TOPO-CCl_4 solutions. The fundamental vibrational stretching modes of water are found at absorption peaks of 2.70 μ and 2.75 μ, where 2.70 μ is the antisymmetric stretch and 2.75 μ is the symmetric stretch. The positions and relative magnitudes of these peaks are nearly identical for both gaseous H_2O and for H_2O dissolved in CCl_4, indicating that there is no hydrogen bonding present. When no hydrogen bonding is present, the shorter wavelength peak shows the greater absorption. On the other hand, when water is hydrogen bonded, the ratio of peak heights changes. If the bonding is sufficiently strong, the longer wavelength peak will have the greater absorption.[31]

Spectra of dried TOPO solutions showed no absorption peaks in the region from 2.3 μ to 3.0 μ. However, when water was extracted into dilute TOPO ($\leq$ 0.1 M) solutions, the two water peaks appeared at a longer wavelength, or lower energy (2.75 μ and 3.0 μ, respectively), than for monomeric H_2O or for TBP·H_2O,[8] and the 3.0 μ peak showed the greater absorption. These changes indicate the hydrogen bonding of water to the TOPO and a corresponding weakening of both O-H bonds.

Other absorption peaks for water are present in the infrared spectrum from 2 μ to 16 μ. These are the H-O-H bending mode peak at 6.17 μ and its first harmonic at 3.17 μ. Quantitative correlations, however, between concentrations of extractants and peak heights could be made only

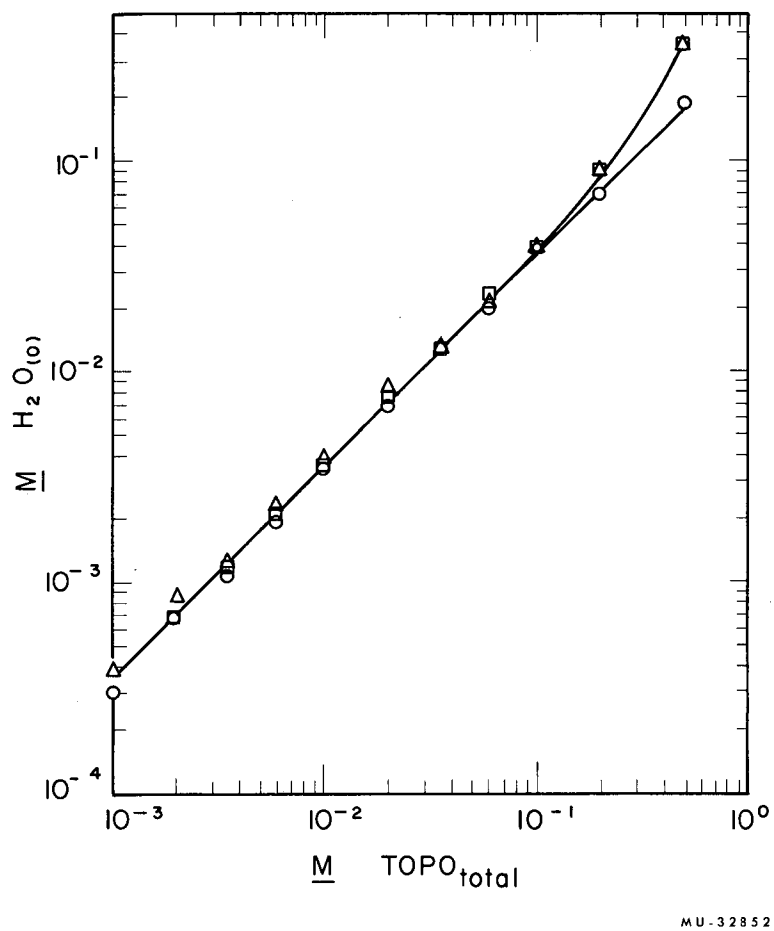


Fig. 1. Variation of water content of organic phase (CCl_4 diluent) with TOPO concentration, corrected for solubility of H_2O in CCl_4: ■ Karl Fischer; ● 2.75 μ peak; ▲ 3.0 μ peak.

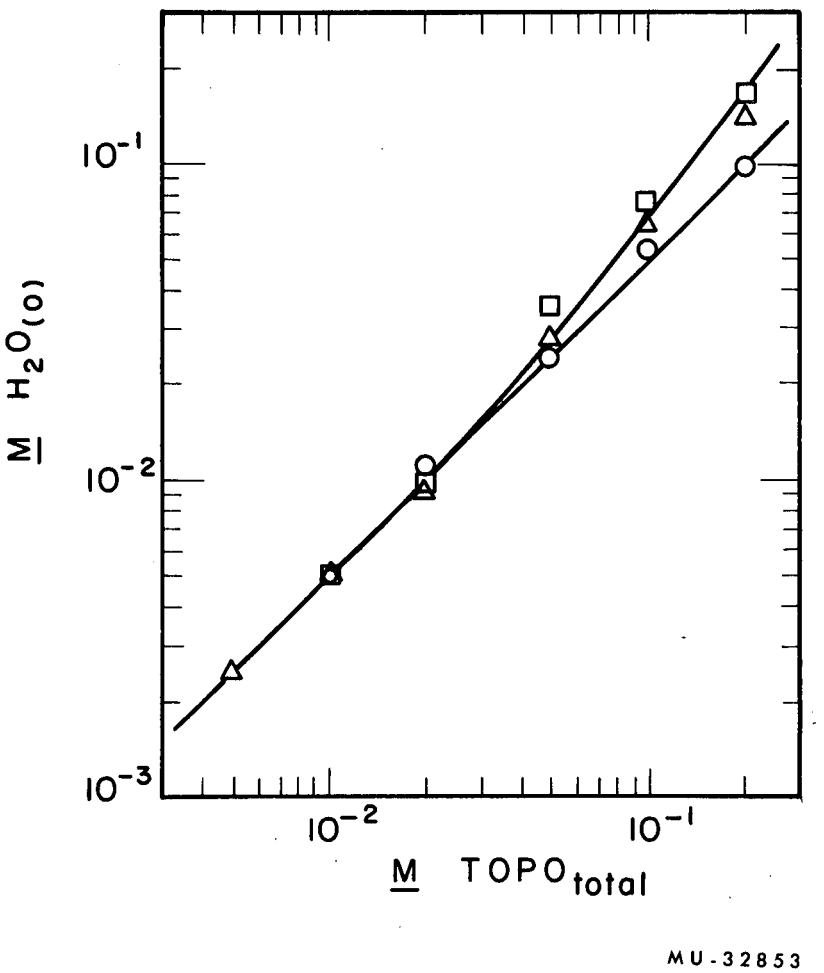


Fig. 2. Variation of water content of organic phase (nitrobenzene diluent) with TOPO concentration, corrected for solubility of H_2O in nitrobenzene: ■ Karl Fischer; ● 2.75 μ peak; ▲ 3.0 μ peak.

for the 2.75 μ and 3.0 μ peaks, owing to interference from other components in the solutions.

The conclusion that hydrogen bonding occurs between water and TOPO was also substantiated by a shift in the P = O peak to a higher wavelength. A solution of dry TOPO in CCl_4 showed this peak at 8.5 μ. A spectrum of water-saturated TOPO solutions showed, however, that the peak had shifted to 8.7 μ. Since the P = O bond would be weakened by hydrogen bonding, it again seemed reasonable to assign the 8.7 μ peak to the bonded P=O stretch. No quantitative use was made of this peak as it was subject to interference from increased acid content in the organic phase.

Spectra were taken of water-saturated TOPO solutions from 0.001 to 0.5 M TOPO. Calibration curves relating the absorption peak height of the 2.75 μ and 3.0 μ peaks to the water content were normalized to Karl Fischer titration values in the region of 0.06 to 0.1 M TOPO; here the water concentrations were sufficiently high and subject to the least experimental error. A plot of log organic-phase water vs log total TOPO determined by either peaks gave results in excellent agreement with Karl Fischer values as high as 0.1 M TOPO. At this point the plots of the two peak heights diverged and the plot of the 3.0 μ peak followed the Karl Fischer values, while that of the 2.75 μ peak remained linear. It was concluded that the 3.0 μ peak was a measure of the total water (see Fig. 1).

Infrared spectra were also taken of the TOPO-H_2O-nitrobenzene system. Spectra of water-saturated nitrobenzene showed absorption peaks at 2.77 μ and 2.83 μ. In order to ascertain that these peaks were actually water peaks, spectra of partially-dried and dried nitrobenzene were recorded; the 2.77 μ and 2.83 μ peak heights decreased while other characteristic nitrobenzene peaks remained constant. Spectra of water-saturated nitrobenzene solutions of TOPO from 0.005 to 0.2 M in TOPO showed water absorption peaks at 2.77 μ and 3.0 μ. Both peak heights increased linearly with increased TOPO concentrations as high as 0.03 M TOPO. At this point the plots of the two peak heights diverged, with the values of the 2.77 μ peak remaining linear and those of the 3.0 μ following the Karl Fischer values which also begin to deviate from linearity and

rise more steeply. Because this behavior was the same as in the CCl_4 case it seemed reasonable to assign these peaks also as water peaks in the TOPO-H_2O system. The infrared peak absorbances were superimposed to the Karl Fischer values for the best fit. The results of both determinations are shown in Fig. 2.

B. TOPO-Acid

Concentrations of acid from 0.01 to 11 M $HClO_4$ and 0.01 to 16 M HNO_3 were equilibrated with dilute solutions of TOPO in CCl_4 and nitrobenzene from 0.01 to 0.1 M. The organic acid content was determined at each external (aqueous) acid concentration. The $Re^{186}O_4^-$ tracer extended the $HClO_4$ data to 0.001 M in aqueous acid for the system in CCl_4, and to 0.0001 M for the system in nitrobenzene. Figures 3, 5, 11, 16, and 19 show plots of log organic-phase acid vs log aqueous acid (see also Tables III to VIII).

The aqueous acid concentrations shown in Figs. 3, 5, 11, 16, and 19 are equilibrium acid concentrations, i.e., the initial aqueous acid molarity has been corrected for the amount of H^+ extracted into the organic phase. The experimental organic acid concentrations have also been corrected for the amount of acid which extracts into the solvent without TOPO present. The extraction of $HClO_4$ into CCl_4 was found to be negligible. No appreciable HNO_3 extracted into CCl_4 up to 6 M HNO_3, but beyond this point the extraction was sufficiently high to require correction of the experimental organic acid content.

In nitrobenzene the extraction of $HClO_4$ and HNO_3 appeared appreciable over the entire range covered. Available data for the extraction of these acids into pure nitrobenzene, however, covered only the region from 0.001 to 10 M $HClO_4$ and from 0.1 to 10 M HNO_3;[32] therefore, corrections for the very dilute region had to be obtained by extrapolation. In the case of $HClO_4$, the extraction curve (log initial acid concentration vs log extracted acid) was linear from 0.001 to 0.1 M initial $HClO_4$; thus, the line was extended to 0.0001 M $HClO_4$ and corrections were read from this curve. The extraction curve of HNO_3 was

linear from 0.1 to 0.3 M on a log-log plot. This line was also extended to 0.01 M HNO_3 and corrections were made from this extrapolation. It might be added the corrections in this extrapolated region were not very important in the analysis.

Figures 7, 13, 18, and 22 show plots of log organic-phase acid vs log initial TOPO. The organic-phase acid concentrations have again been corrected for extraction into the pure solvent.

C. TOPO-H_2O-Acid

Determinations were also made of the amount of H_2O extracting with acid or, more specifically, the H_2O/H^+ ratio for the extractions by TOPO in CCl_4 only. Solutions of 0.01, 0.05, and 0.1 M TOPO were equilibrated with aqueous solutions of acid from 0.01 to 12 or 16 M, depending upon the specific acid used, and the amount of H_2O and H^+ in the organic phase was measured.

The total amount of water in the organic phase was determined by the Karl Fischer method. This experimental value, however, included water dissolved in CCl_4 alone, which may be calculated as the product of the solubility of pure water in CCl_4, the aqueous water activity, and the volume fraction of CCl_4. These corrected results are shown in Figs. 9 and 15 (see also Tables III and V).

Infrared spectra were also recorded for 0.1 M TOPO solutions equilibrated with acid. Because a dry TOPO solution was used as a reference, the water absorption peaks (after correction for H_2O in CCl_4 above) were a measure of TOPO $\cdot$ H_2O.

V. DISCUSSION

A. TOPO-H_2O

It was assumed that the TOPO-water system was maintained independently of any TOPO-acid system. TOPO molecules bonded to water are not readily available for acid extraction. Therefore, the initial investigation was of the extraction of pure water by TOPO. The equation for the extraction of water may be written

$$nTOPO_{(o)} + H_2O = H_2O \cdot nTOPO_{(o)} \qquad (1)$$

where (o) indicates the organic phase. The corresponding equilibrium constant is

$$K_{H_2O} = \frac{(H_2O \cdot nTOPO)}{(TOPO)^n (H_2O)} = \frac{[H_2O \cdot nTOPO]\, \gamma_{H_2O \cdot nTOPO}}{[TOPO]^n \gamma^n_{TOPO}\, (H_2O)} \; ; \qquad (2)$$

( ) signify activities and [ ] concentrations, and γ represents the activity coefficient. [TOPO] always means the equilibrium TOPO concentration. Initial or total TOPO concentration will be specifically indicated.

Although very little is known about activity coefficients in organic solutions, the assumption was made that the ratio of activity coefficients $\gamma_{H_2O \cdot nTOPO} / \gamma^n_{TOPO}$ is unity; thus, organic-phase concentrations were used instead of thermodynamic activities. This assumption seems reasonable as the solutions of TOPO were kept in a very dilute region; therefore, the properties of the inert diluent were retained. As will be seen later, the results of extraction also substantiate this assumption. It was also assumed that the water activity is approximately equal to 1, since the solubility of TOPO in water is negligibly small. The equation may then be written

$$K''_{H_2O} = \frac{[H_2O \cdot nTOPO]}{[TOPO]^n} \; . \qquad (3)$$

Taking logarithms and rearranging yields

$$\log[H_2O \cdot n\,TOPO] = n \log[TOPO] + \log K''_{H_2O} \cdot \qquad (3a)$$

If a plot of $\log[H_2O \cdot n\,TOPO]$ vs $\log[TOPO]$ is made, the slope will determine n, the number of TOPO molecules per water molecule. The equilibrium TOPO is the amount of free TOPO and may be calculated as $[TOPO] = [TOPO]_{total} - n[nTOPO \cdot H_2O]$, in which [TOPO] total is the initial TOPO concentration and $n[H_2O \cdot nTOPO]$ is n times the water dissolved in the organic phase.

Figures 1 and 2 show such plots for log organic-phase water vs log initial TOPO in CCl_4 and nitrobenzene, respectively. In the case of TOPO solutions in CCl_4, the curve is linear from 0.001 to 0.1 M TOPO. Correction to equilibrium TOPO in the above expression yields a value of n = 1 and $K''_{H_2O} = 0.563$, which means that only 36% of the total TOPO is bonded to H_2O.

Above 0.1 M TOPO, the slope rises more steeply than one. This rise indicates either the introduction of a new TOPO-H_2O complex or the breakdown of the assumptions made for dilute solutions. The linear portion of the curve, however, supports the assumption of a constant-activity coefficient ratio for TOPO species in the organic phase in solutions of less than 0.1 M TOPO in CCl_4.

The water content of TOPO solutions in nitrobenzene provides a more complicated situation. Experimental determinations of water are made difficult since the solubility of H_2O in nitrobenzene is considerably greater (M H_2O = 0.14) than in CCl_4 (M H_2O = 0.0101), and the TOPO-H_2O values are small differences between relatively large numbers. As seen in Fig. 2, the log-log plot of water vs total TOPO is linear with slope equal to unity from 0.005 to approximately 0.03 M TOPO, and with about 50% of the TOPO bonded to water; thus, K'' H_2O = 1. Above 0.03 M, the slope of the curve rises more steeply.

B. TOPO-H_2O-Dilute Acid

1. General Discussion

The reaction for the extraction of dilute acids by dilute solutions of TOPO may be written

$$HX + yH_2O + nTOPO_{(o)} = HX \cdot nTOPO \cdot yH_2O_{(o)} \qquad (4a)$$

if the extracting species is molecular; if ion-paired, the equation is written as

$$HX + yH_2O + nTOPO_{(o)} = H^+ \cdot nTOPO \cdot yH_2O \cdots X^-_{(o)}; \qquad (4b)$$

and if the species is dissociated as

$$HX + yH_2O + nTOPO_{(o)} = H^+ \cdot nTOPO \cdot yH_2O_{(o)} + X^-_{(o)} \qquad (4c)$$

where y is the number of water molecules extracted per proton and n is the number of TOPO molecules associated with each proton. Again the assumption is made that the anion in Eqs. (4b) and (4c) is chosen to be one that is not hydrated nor complexed with the extractant in the organic phase, and also that corrections have been made for the extraction of water and acid into the pure solvent.

The corresponding equilibrium constants for Eqs. (4a), (4b), and (4c) respectively are

$$K_{HX} = \frac{(HX \cdot nTOPO \cdot yH_2O)}{(TOPO)^n (H_2O)^y (HX)} = \frac{[HX \cdot nTOPO \cdot yH_2O]\,\gamma}{[TOPO]^n \gamma^n_{TOPO} (H_2O)^y (HX)} \qquad (5a)$$

$$K_{HX} = \frac{(H^+ \cdot nTOPO \cdot yH_2O \cdots X^-)}{(TOPO)^n (HX)(H_2O)^y} = \frac{[H^+ \cdot nTOPO \cdot yH_2O \cdots X^-]\,\gamma}{[TOPO]^n \gamma^n_{TOPO} (HX)(H_2O)^y} \qquad (5b)$$

$$K_{HX} = \frac{(H^+ \ nTOPO \ yH_2O)(X^-)}{(TOPO)^n(HX)(H_2O)^y} = \frac{[H^+ \cdot nTOPO \ yH_2O]\gamma_+[X^-]\gamma_-}{[TOPO]^n\gamma^n_{TOPO}(HX)(H_2O)^y} . \quad (5c)$$

The assumption is again made that the ratio γ/γ^n_{TOPO} or $\gamma_+\gamma_-/\gamma^n TOPO$ is unity, as the TOPO solutions are in a dilute, near-ideal region. Because there are the same number of organic species containing X^- and H^+, the amount of H^+ ion in the organic phase [Eqs. (5a), (5b), and (5c)] may be simplified by the following substitutions:

$$[HX \cdot nTOPO \cdot yH_2O] = [H^+]_{(o)}$$

$$[H^+ \cdot nTOPO \cdot yH_2O \cdots X^-] = [H^+]_{(o)}$$

$$[H^+ \cdot nTOPO \cdot yH_2O][X^-] = [H^+]^2_{(o)} .$$

Since the power of H^+ is either 1 or 2, let the general expression be $[H^+]^m_{(o)}$, for which $m = 1$ for a molecular or ion-paired species and $m = 2$ for dissociated ions.

Because the range of validity for the above expressions is for dilute acid solutions of concentrations less than 0.2 M (as will be shown), the activity of water remains approximately equal to 1. Therefore, the equilibrium constant may be rewritten

$$K'_{HX} = \frac{[H^+]^m_{(o)}}{(HX)[TOPO]^n_{(o)}} ; \quad (6)$$

taking logarithms and rearranging yields

$$m \log[H^+]_{(o)} = \log(HX) + n \log[TOPO] + \log K'_{HX} . \quad (7)$$

If the equilibrium TOPO concentration is kept constant, the slope of the plot of $\log[H^+]_{(o)}$ vs $\log(HX)$ will determine $1/m$. As the amount of extracted acid increases, however, the amount of TOPO tied up in the

complex also increases. Therefore, the raw data must be corrected to a fixed equilibrium TOPO concentration. The following expression may be used:

$$[H^+]'_{(o)} = [H^+]_{(o)} \times \frac{[TOPO]^n_{total}}{[TOPO]^n}. \tag{8}$$

$[H^+]'_{(o)}$ is the corrected organic-phase acid concentration and $[H^+]_{(o)}$ is the measured value. The expression [TOPO] total represents the initial TOPO concentration to which the data are being corrected, and [TOPO] is the actual concentration of unbonded TOPO. The latter does not include $TOPO \cdot H_2O$ nor TOPO bound to the proton; thus, these corrections must be evaluated. The TOPO used in the acid complex will be $n \times [H^+]_{(o)}$, and the equilibrium TOPO concentration may be calculated from the following expression:

$$[TOPO] = [TOPO]_{total} - [TOPO \cdot H_2O] - n[H^+]_{(o)}. \tag{9}$$

Substitution of the value of $[TOPO \cdot H_2O]$ from Eq. (2) (including the water-activity term as the water activity decreases with increasing acid concentration) yields

$$[TOPO] = \frac{[TOPO]_{total} - n[H^+]_{(o)}}{1 + K'_{H_2O}(H_2O)}. \tag{10}$$

From Eq. (7) it can be seen that if the activity of HX is kept constant, a plot of $\log [H^+]_{(o)}$ vs $\log [TOPO]$ will yield a curve, the slope of which is n/m. For a molecular or ion-paired complex, $m = 1$ and the slope equals n. For the case of dissociated ions, $m = 2$ and n/m equals $n/2$; thus, n is determined by this method. Again, the initial TOPO concentration must be corrected to the equilibrium concentration. The calculation is given above in Eq. (10).

The number of water molecules per proton, y, remains undetermined. As previously described, the water content of the organic phase (for only those systems done in CCl_4) was determined by the Karl Fischer method and by analysis of infrared spectra. The Karl Fischer method gave an experimental value for the total amount of water present.

This value had to be corrected for the solubility of water in CCl_4 and for the amount of water involved in the $TOPO \cdot H_2O$ complex. The former term is calculated in the way previously described for the case of $TOPO \cdot H_2O$, except that in the acid extraction the decreasing activity of H_2O in the aqueous phase must be taken into account by the equation $[H_2O_{CCl_4}] = 0.0101 \times V_{CCl_4} \times (H_2O)$, where V_{CCl_4} is the volume fraction of CCl_4. The latter term may be calculated from Eq. 2'.

$$[TOPO \cdot H_2O] = [TOPO]\,(H_2O)\,K'_{H_2O}, \qquad (2')$$

in which K'_{H_2O} represents the equilibrium constant including (H_2O), and from the assumption that the $TOPO-H_2O$ system is maintained independently of the $TOPO-acid-H_2O$ system. The validity of the calculation was confirmed by the fact that both the 2.75μ and 3.0 μ peaks in the infrared spectra disappeared at the same point where the calculated value of $TOPO \cdot H_2O$ equaled zero. Thus, the water bound in the acid complex, $[H_2O]_{acid}$, may be expressed:

$$[H_2O]_{acid} = [H_2O]_{(o)} - [TOPO \cdot H_2O] - [H_2O_{CCl_4}]. \qquad (11)$$

2. <u>$TOPO-HClO_4-CCl_4$</u>

Figure 3 shows the results of the extraction of $HClO_4$ into $TOPO-CCl_4$ solutions. The slopes of the experimental log-log curves up to an aqueous $HClO_4$ concentration of 0.2 M is approximately equal to 1. For $HClO_4-TOPO-CCl_4$ the correction factor to a constant equilibrium TOPO concentration equal to the initial value is

$$[H^+]'_{(o)} = [H^+]_{(o)} \frac{[TOPO]^3_{total}}{[TOPO]^3}.$$

The justification for this term will be given below. Figure 4 shows that application of this correction factor yielded a slope, 1/m, of 1. Therefore m = 1. The species is either molecular or ion-paired. This conclusion agrees with conductivity measurements made by Hesford and McKay for $TBP-HClO_4$-benzene, in which the conductivity was negligibly small at concentrations similar to those used in this study.[33]

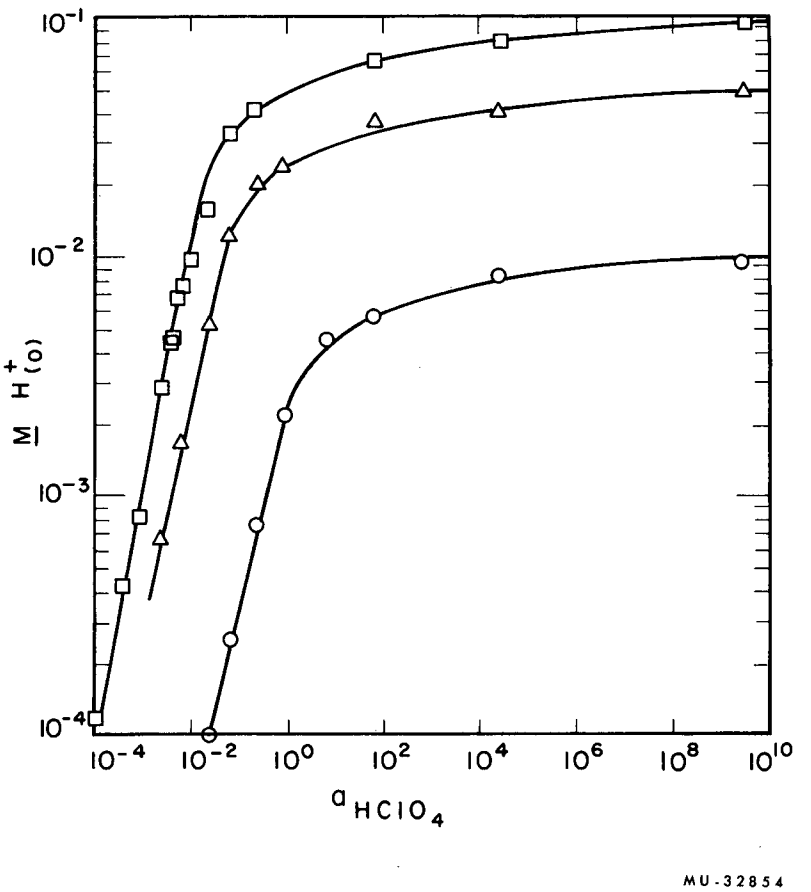


Fig. 3. Variation of organic-phase acid content (CCl_4 diluent) with aqueous $HClO_4$ activity for total TOPO concentrations of ■ 0.1 M; ▲ 0.05 M; ● 0.01 M.

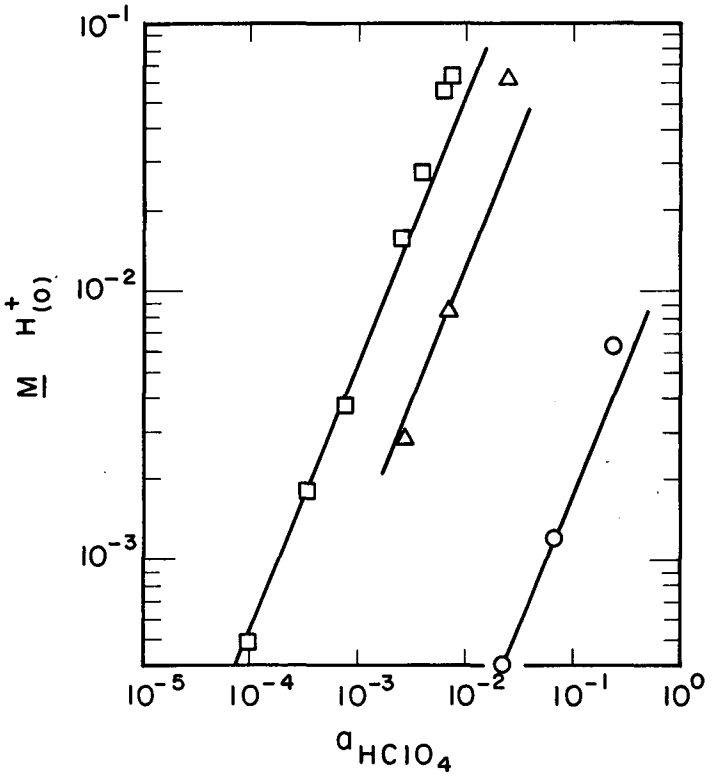


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Fig. 4. Variation of organic-phase acid content (CCl_4 diluent) with aqueous $HClO_4$ activity for fixed TOPO concentrations of ■ 0.1 M; ▲ 0.05 M; ● 0.01 M. All lines drawn with slopes 1.0.

Figure 5 shows the same plot of log $[H^+]_{(o)}$ vs log aqueous acid for $HReO_4$. Because microtitrations of $HClO_4$ were reliable only to 10^{-4} M H^+ in the organic phase, $Re^{186}O_4^-$ tracer was used to extend the curves to more dilute solutions. The linear portion of the experimental curve has a slope approximately equal to 1. The correction factor used for $HClO_4$ was also used for $HReO_4$, and Fig. 6 shows the corrected values again yielding $1/m = 1$. It must be noted, however, that the extraction of $HReO_4$ tracer acid in $HClO_4$ differs somewhat from that of $HClO_4$ itself. The extraction measured is actually the extraction of trace $HReO_4$ out of $HClO_4$ solutions. The conclusions that can be drawn, however, are not affected.

The experimental plot of log $[H^+]_{(o)}$ vs log $[TOPO]_{total}$ is given in Fig. 7 for $HClO_4$ ($HReO_4$). However, in using Eq. (7) to determine n (the number of TOPO molecules per proton in the complex) log $[H^+]_{(o)}$ must be plotted against log [TOPO], not log $[TOPO]_{total}$. A lower limit on n can, however, be obtained from Fig. 7. A value of n somewhat less than 3 is found. The value of $n = 3$ was used and the equilibrium TOPO was calculated from Eq. (10). The resulting curve for log $[H^+]_{(o)}$ vs log [TOPO] yielded a slope of 3 until at least 40% of the total TOPO was complexed by acid. Corrections using $n = 2$ and $n = 4$ did not yield the corresponding slopes. Therefore, n is, in fact equal to 3 (Fig. 8).

The water content in samples extracted with $HClO_4$ was determined (Fig. 9). The concentration of $TOPO \cdot H_2O$ was calculated from Eq. (2') and from the infrared water-absorption peaks. The values from these two methods agreed within 2 to 5%. The amount of water in the acid complex, $[H_2O]_{acid}$, was then calculated from Eq. (11). A plot of $[H_2O]_{acid}$ vs $[H^+]_{(o)}$ is shown in Fig. 10. It can be seen that the curve passes thru the origin and its slope is 1 initially; the H_2O/H^+ ratio equals 1. In summation, if the stoichiometric ratio of $TOPO/H^+$ is greater than 3, the corresponding ratio of $TOPO/H^+$ in $HClO_4$ extractions is 3 and H_2O/H^+ equals 1. Since the acid species which extracts into TOPO is trisolvated, the indication seems strong that the hydronium ion is the species about which the three TOPO molecules are

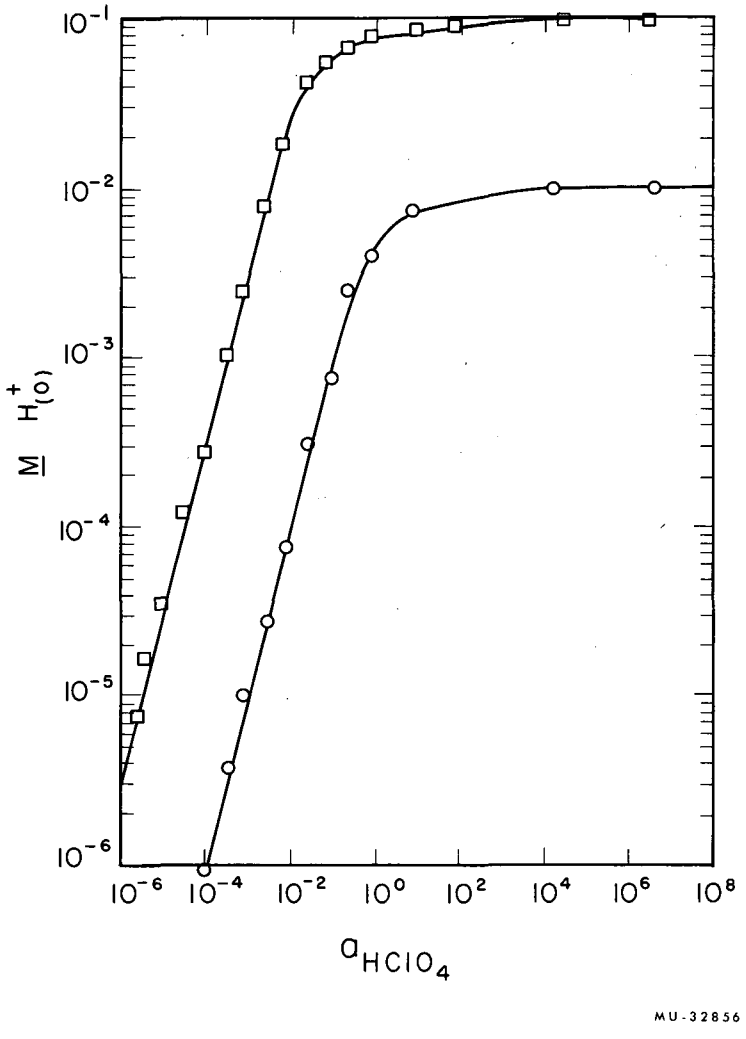


Fig. 5. Variation of organic-phase acid content (measured by $HReO_4$ tracer, CCl_4 diluent) with aqueous $HClO_4$ activity for total TOPO concentrations of ■ 0.1 $\underline{M}$; ● 0.01 $\underline{M}$.

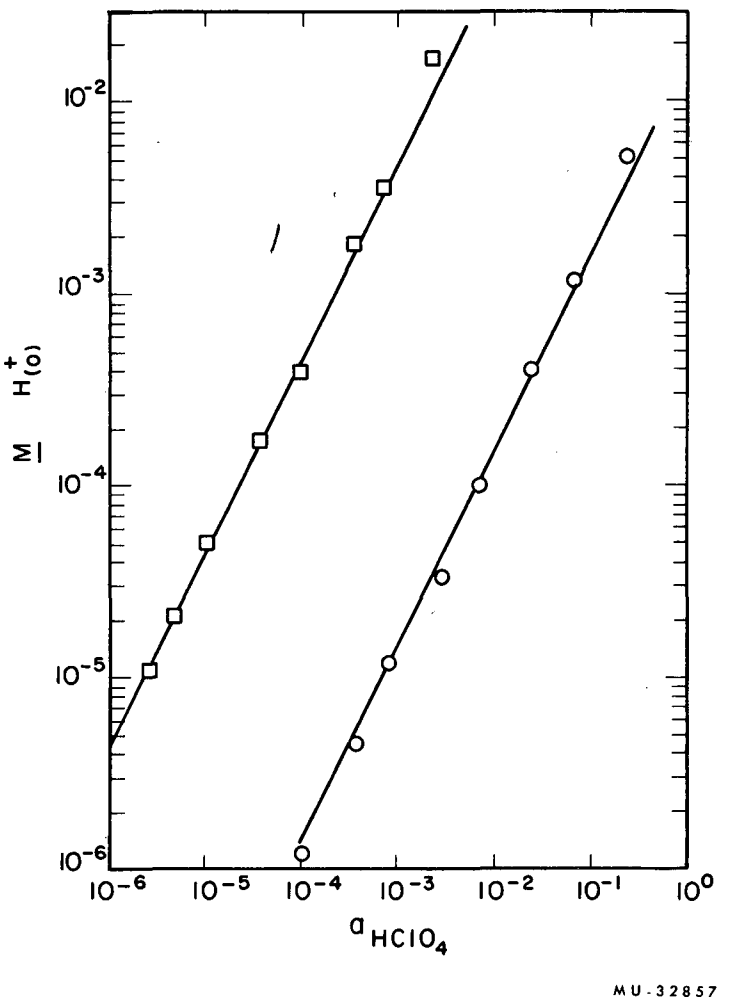


Fig. 6. Variation of organic-phase acid content (measured by $HReO_4$ tracer, CCl_4 diluent) with aqueous $HClO_4$ activity for fixed TOPO concentrations of ■ 0.1 M; ● 0.01 M. All lines drawn with slopes 1.0.

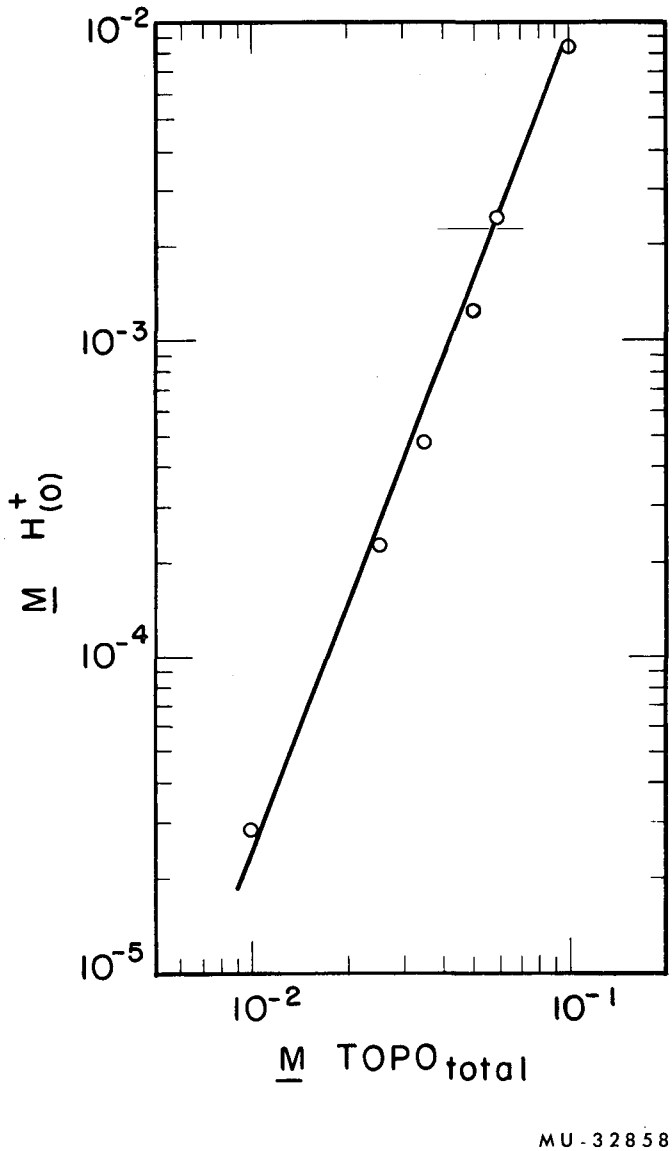


Fig. 7. Variation of organic-phase acid content (measured by $HReO_4$ tracer, CCl_4 diluent) with initial TOPO concentration for aqueous $HClO_4$ activity of 2.8×10^{-3}.

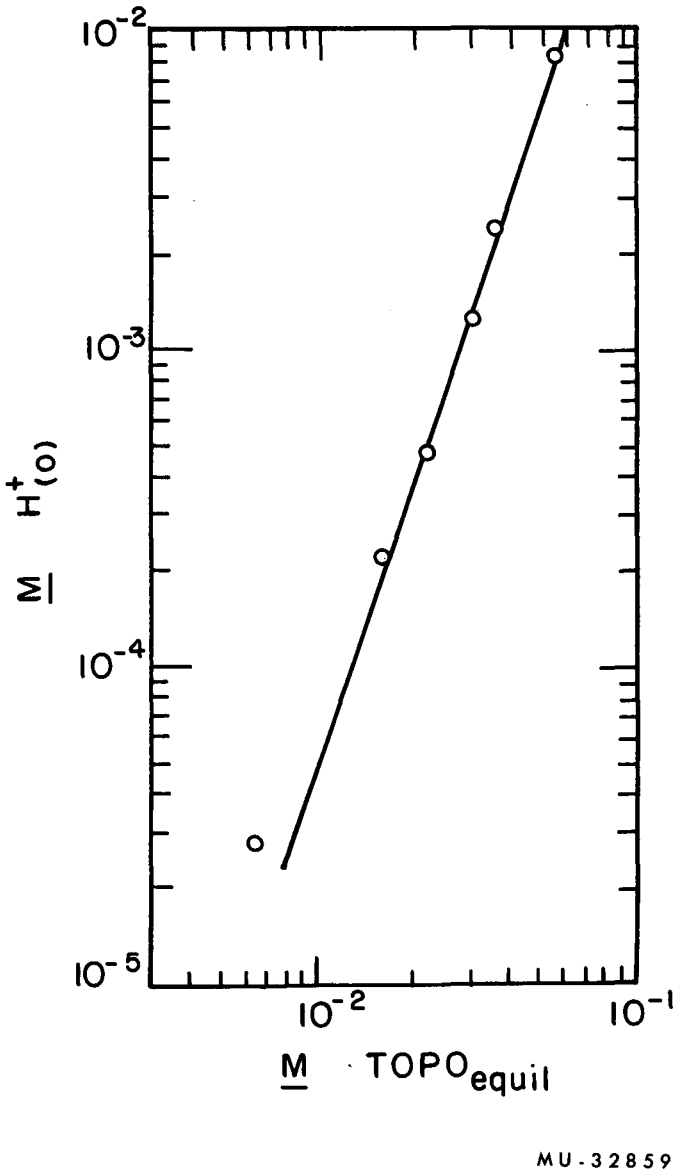


Fig. 8. Variation of organic-phase acid content (measured by $HReO_4$ tracer, CCl_4 diluent) with equilibrium TOPO concentrations for aqueous $HClO_4$ activity of 2.8×10^{-3}. Line drawn with slope 3.0.

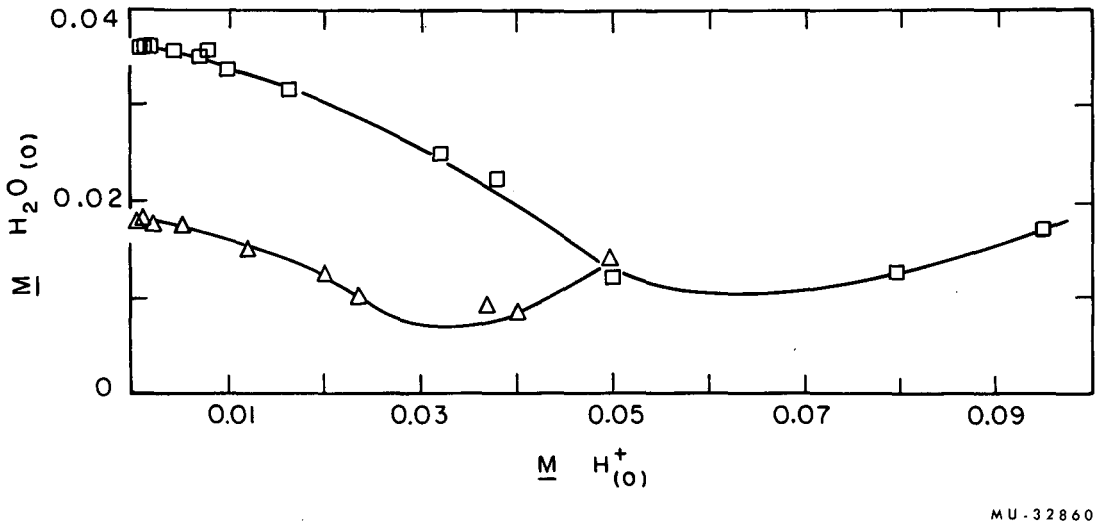


Fig. 9. Variation of organic-phase water content (CCl_4 diluent, corrected only for solubility of H_2O in CCl_4) with organic-phase $HClO_4$ acid content: ■ 0.1 M TOPO; ▲ 0.05 M TOPO.

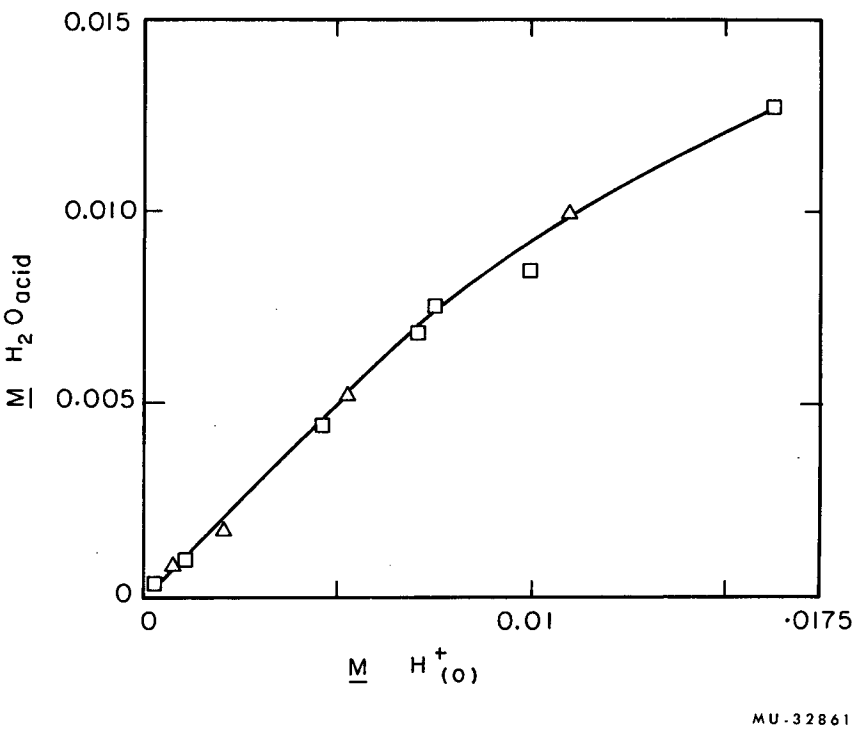
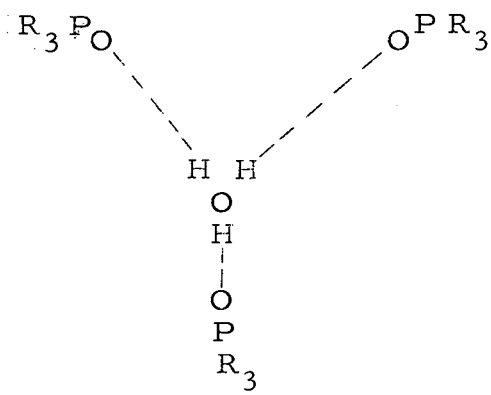


Fig. 10. Variation of organic-phase water content (CCl_4 diluent; M H_2O acid does not include H_2O dissolved in CCl_4 nor complexed in TOPO · H_2O) with organic-phase $HClO_4$ acid content: ■ 0.1 M TOPO; ▲ 0.05 M TOPO.

coordinated. The hydronium ion readily lends itself to trisolvation because each of the three hydrogens are possible bonding sites. The H_2O/H^+ ratio has been determined for systems similar to the present one, i.e., the use of dilute solutions of basic extractants with strong acids.[8,34] These ratios vary from 1 to 4, depending on the system; thus, the hydronium ion may be further hydrated. Because TOPO is a stronger base than TBP, it should be better able to displace the water from around H_3O^+ and thus extract the hydronium ion over a wide range of TOPO and acid concentrations.

In addition, the species is expected to be an ion-pair because (a) it seems unlikely that a molecular acid could coordinate three TOPO molecules plus a water molecule about itself; (b) the dielectric constant of CCl_4 ($\epsilon = 2.2$)[35] is very low, so that it cannot support a charge separation of moderate-sized ions; and (c) the ClO_4^- ion is a very weak base and extraction of molecular $HClO_4$ into dilute solution would not be expected.

On the basis of the foregoing considerations it may be stated that in CCl_4 solutions up to 0.1 M TOPO and aqueous acid up to 0.2 M $HClO_4$ (a) there are three TOPO molecules per proton in the extracting complex; (b) there is one water molecule per proton; (c) the extracting species is an ion pair. The most likely structure for the extracting complex in the TOPO-dilute $HClO_4$-H_2O system is



where R is the n-octyl group, C_8H_{17}. The oxygens on each TOPO molecule are hydrogen bonded to each of the hydrogens on the hydronium

ion. The species may be written $H_3O^+ \cdot TOPO \cdots ClO_4^-$.

3. TOPO-HNO_3-CCl_4

In the case of the extraction of HNO_3, experimental $\log[H^+]_{(o)}$ vs $\log(HNO_3)$ plots yielded slopes of approximately 1 (Fig. 11). The application of the following expression (justified later) for the correction to a constant TOPO concentration gave slopes of exactly 1 for dilute (≤ 0.3 M) HNO_3:

$$[H^+]'_{(o)} = [H^+]_{(o)} \frac{[TOPO]_{total}}{[TOPO]} .$$

The corrected results are shown in Fig. 12. The fact that m = 1 establishes the extracting complex as either molecular or ion-paired.

Figure 13 gives the results of a plot of $\log[H^+]_{(o)}$ vs $\log[TOPO]$ total. The slope here is approximately equal to 1. Taking n as equal to 1, the equilibrium TOPO concentrations were calculated from Eq. (10). The corrected curves are shown in Fig. 14 where the slope $n/m = n/1 = 1$; thus there is only one TOPO molecule per proton in the region where the stoichiometric $TOPO/H^+$ ratio is equal to or greater than 1.

Determinations of the water content for HNO_3 extraction showed that the H_2O/H^+ ratio was always ≤ 0.13, indicating that a negligible amount of water was involved in the extracting complex. If the predominant extracting species contains no water molecules and only one TOPO molecule per proton, then the organic-phase water concentration should fall to zero when the organic-phase acid concentration equals the total TOPO concentration. As seen in Fig. 15, the H_2O concentration never goes to zero. If, however, the initial slope of the $[H_2O]_{(o)}$ vs $[H^+]_{(o)}$ curve is extrapolated to $[H_2O]_{(o)} = 0$, the line intersects exactly the $[H^+]_{(o)}$ concentration which is equal to [TOPO] total. Certainly, up to the point where the stoichiometric $TOPO/H^+ \leq 1.67$, the predominant extracting species contains no water molecules. But as the organic-phase acid concentration increases, there is a minimum in the water curve and then the H_2O concentration begins to rise. These results will be discussed in a later section.

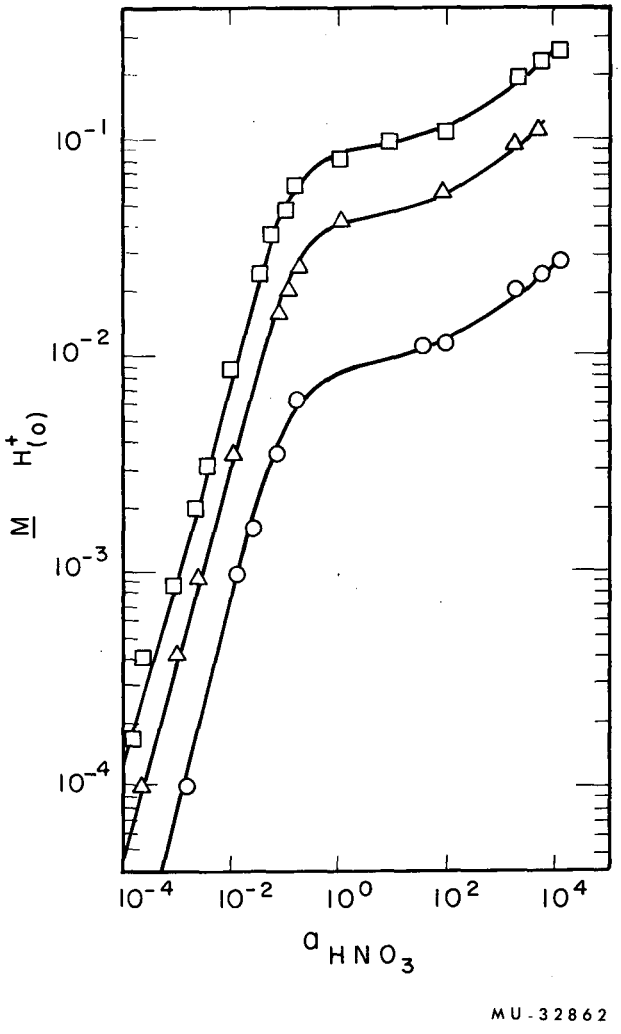


Fig. 11. Variation of organic-phase acid content (CCl_4 diluent, corrected for solubility of HNO_3 in CCl_4) with aqueous HNO_3 activity for total TOPO concentrations of: ■ 0.1 M; ▲ 0.05 M; ● 0.01 M.

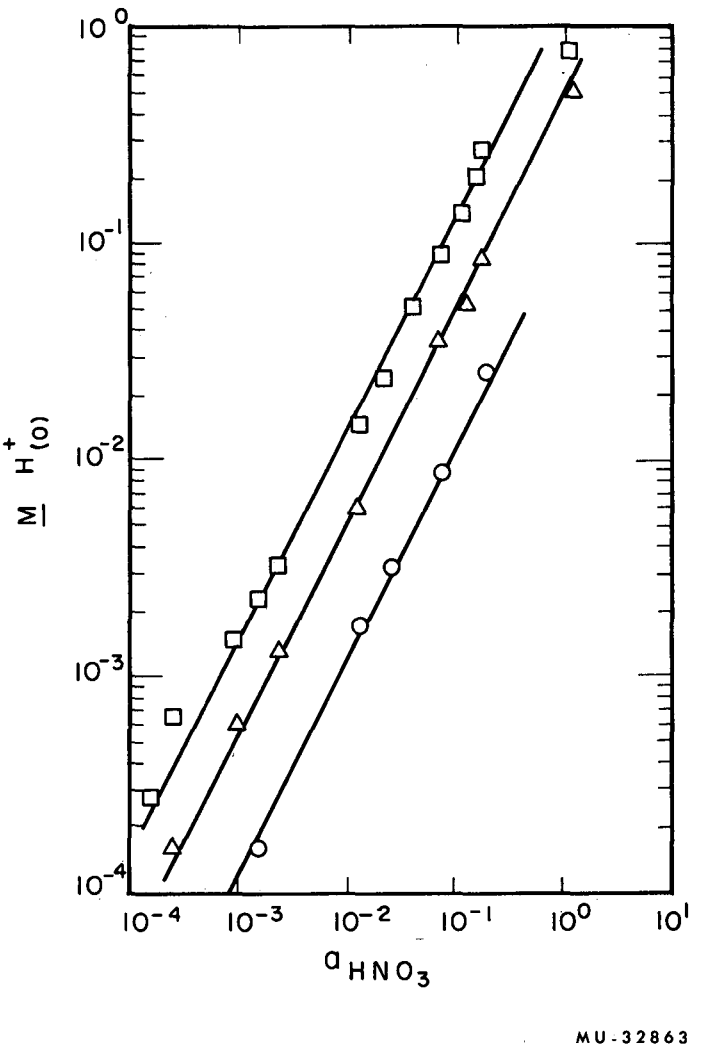


Fig. 12. Variation of organic-phase acid content (CCl_4 diluent, corrected for solubility of HNO_3 in CCl_4) with aqueous HNO_3 activity of fixed TOPO concentrations of: ■ 0.1 M; ▲ 0.05 M; ● 0.01 M. All lines drawn with slopes 1.0.

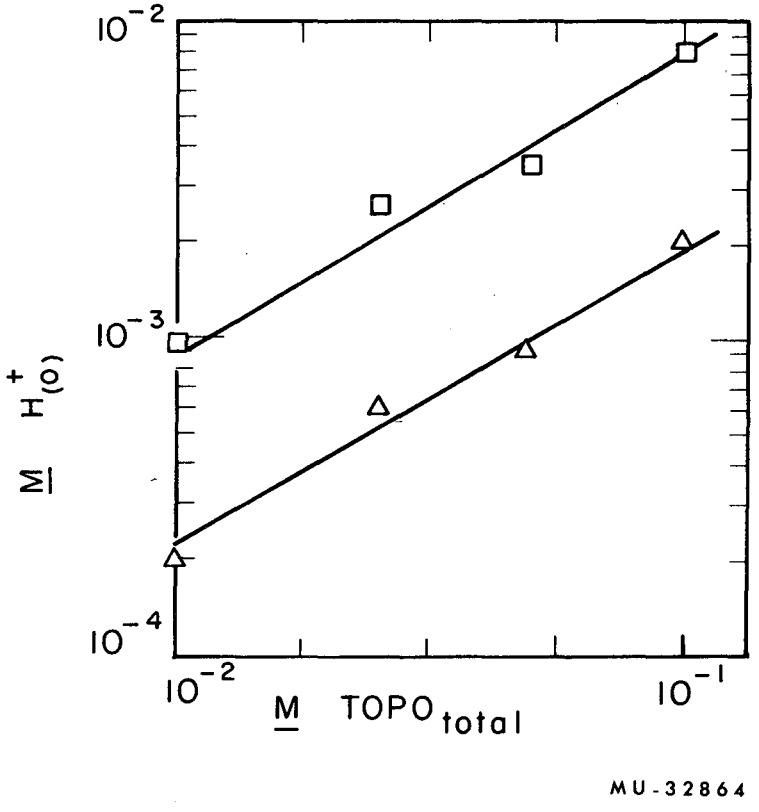


Fig. 13. Variation of organic-phase acid content (CCl_4 diluent) with total TOPO concentrations for aqueous HNO_4 activity of ■ 2.5×10^{-3}; ▲ 1.3×10^{-2}.

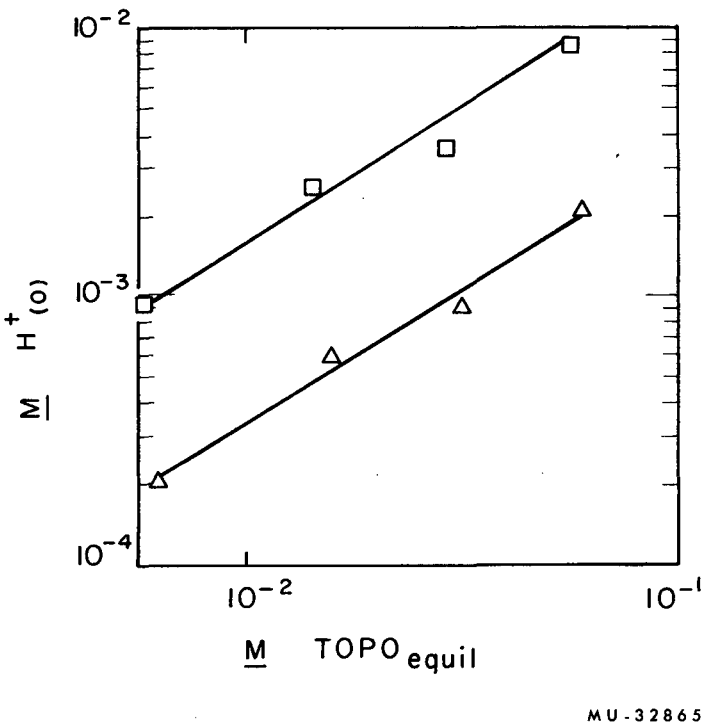


Fig. 14. Variation of organic-phase acid content (CCl_4 diluent) with equilibrium TOPO concentrations for aqueous HNO_3 activity of ■ 2.5×10^{-3}; ▲ 1.3×10^{-2}.

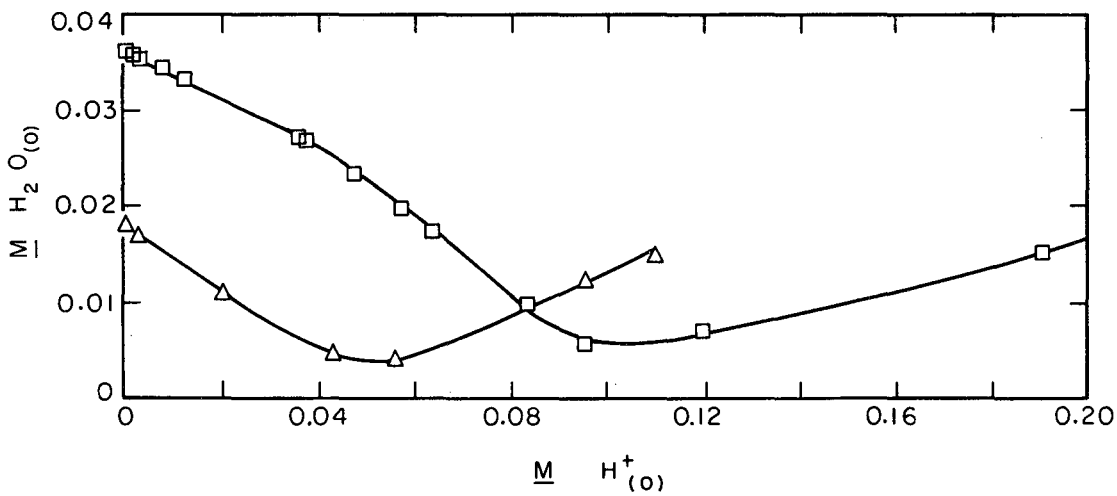


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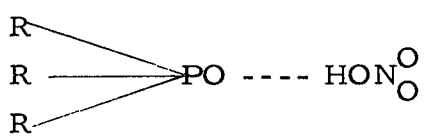
Fig. 15. Variation of organic-phase water content (CCl_4 diluent, corrected only for solubility of H_2O in CCl_4) with organic-phase acid content: ■ 0.1 M TOPO; ▲ 0.05 M TOPO.

Infrared analyses were also made of the water content. As dry TOPO solutions again were used as reference samples, the 2.75 μ and 3.0 μ peak heights were a measure of the $TOPO \cdot H_2O$ concentration in the acid extractions after correction for $[H_2O_{CCl_4}]$. Both the 2.75 μ and 3.0 μ peaks disappeared at about the acid concentration corresponding to the calculated $TOPO \cdot H_2O$ value of zero. The infrared water values, however, were ≈ 0.01 M lower than the Karl Fischer values. Högfeldt has more recently suggested that NO_3^- interferes with the Karl Fischer titrations, yielding results which are greater than the true water value.[36] This may explain this difference. In any case, both results were in agreement in that essentially no water molecules extract with the TOPO-acid complex.

As (a) one TOPO molecule is associated with each proton, (b) essentially no water is extracted, and (c) NO_3^- is a relatively strong base, the structure of the species may therefore be written as



where the oxygen of the TOPO is hydrogen bonded to the hydrogen of the HNO_3.

Zingaro and White,[25] and White and Ross,[24] have also studied the extraction of HNO_3 by TOPO into cyclohexane. They have suggested the species is $TOPO \cdot HNO_3$. Similar results were found by Whitney for TBP extraction of HNO_3 in CCl_4.[17] As previously discussed, the consideration of a hydrated form of the proton as the extracting species need not be weighed heavily when the anion of the acid is a strong base. In this case, the NO_3^- ion is a better competitor for the proton than is H_2O or TOPO, and the latter can coordinate only with the resulting molecular acid.

4. TOPO-$HClO_4$-Nitrobenzene

Because the dielectric constant of CCl_4 is very low ($\epsilon = 2.2$),[36] a study was made of the extraction of $HClO_4$ by TOPO into nitrobenzene, a solvent with a considerably higher dielectric constant ($\epsilon = 35$).[36] Nitrobenzene, having a higher dielectric constant, can better accept a charge separation in the extracting complex than can CCl_4, and the ion-pair observed in extraction into TOPO-CCl_4 may dissociate. The experimental log-log plot of organic-phase acid vs aqueous $HClO_4$ is given in Fig. 16. Figure 17 shows that for the extraction of dilute $HClO_4$(≤ 0.06 M), the slope of $\log[H^+]_{(o)}$ vs $\log(HClO_4)$ equals 1/2 when the TOPO concentration is corrected (as previously discussed in V.B. 2). As $1/m = 1/2$, $m = 2$. The value of 2 indicates that the extracting complex is in the form of dissociated ions. Activity coefficients of the acid species have been neglected. These activity coefficients, as calculated from an extended Debye-Hückel expression, do not affect the slopes significantly.

The results of a plot of $\log[H^+]_{(o)}$ vs $\log[TOPO]_{total}$ are given in Fig. 18. The slope of the curve is approximately equal to 1.25. In order to obtain the power dependence on TOPO, the plot must be made for equilibrium TOPO. Because $m = 2$, the slope of the experimental plot is equal to $n/2$ or $n = 2.5$. A value of $n = 2$ or $n = 3$ may be used to determine the amount of TOPO tied up with acid (namely $n[H^+]_{(o)}$). The value $n = 3$ was chosen since this value was consistent with the model already presented in the CCl_4 case, and the correction to be applied will increase the slope a little. The initial TOPO concentrations were corrected to $[TOPO]_{total} - 3[H^+]_{(o)}$ and the results are plotted in Fig. 19A. But the TOPO concentration must be further corrected for the amount bound to water.

For those concentrations of $[TOPO]_{total}-3[H^+]_{(o)}$ up to approximately 0.02 M (that is where the slope of the curve in Fig. 2 is unity), the amount of $TOPO \cdot H_2O$ may be read directly from the curve in Fig. 2. For those TOPO concentrations greater than 0.03 M one no longer knows that the only water-TOPO species is the one-to-one species TOPO-H_2O, but the curve determined by the Karl Fischer titrations provides a limit for the TOPO bound to water. The results of this correction

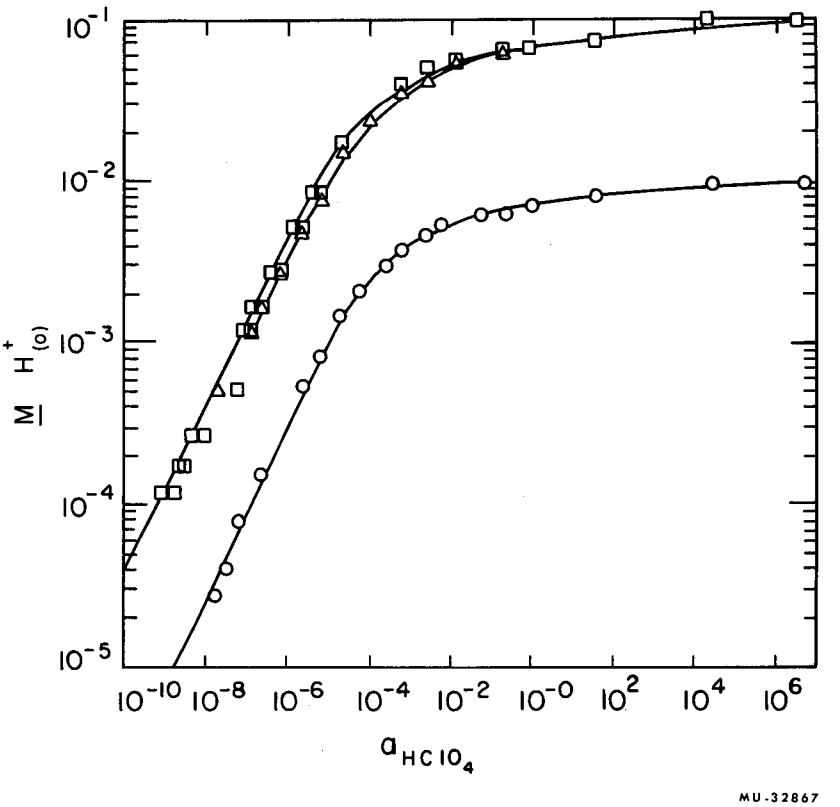


Fig. 16. Variation of organic-phase acid content (nitrobenzene diluent, corrected for solubility of $HClO_4$ in nitrobenzene) with aqueous $HClO_4$ activity for total TOPO concentrations of: ■ 0.1 M TOPO (measured by $HReO_4$ tracer); ▲ 0.1 M TOPO; ● 0.01 M TOPO (measured by $HReO_4$ tracer).

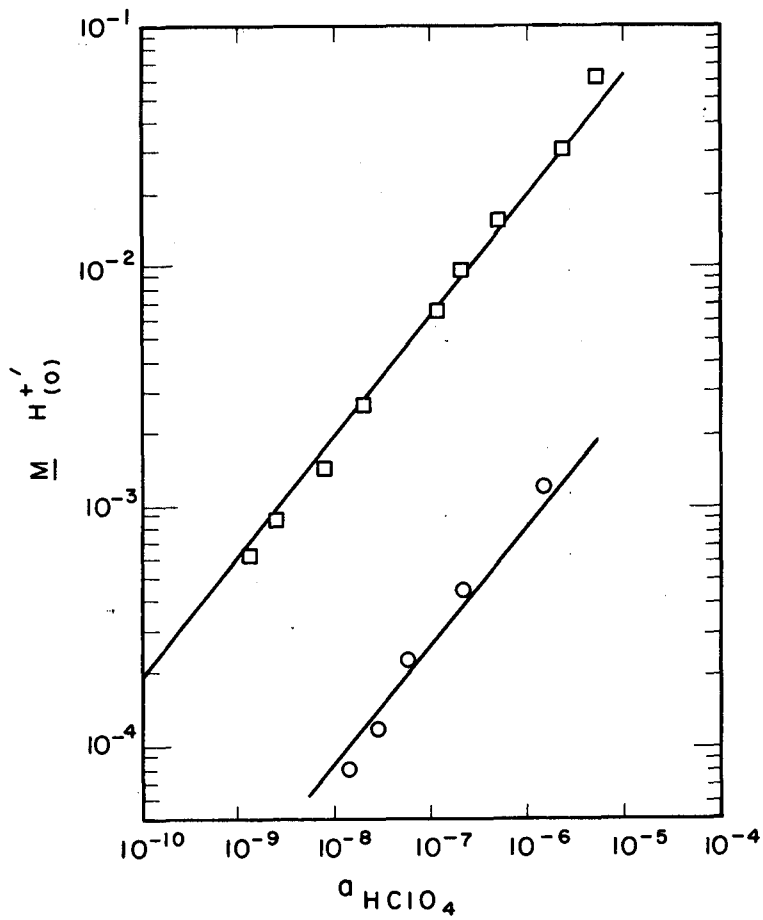


Fig. 17. Variation of organic-phase acid content (nitrobenzene diluent, corrected for solubility of $HClO_4$ in nitrobenzene, measured by $HReO_4$ tracer) with aqueous $HClO_4$ activity for fixed TOPO concentrations of: ■ 0.1 M; ● 0.01 M. Lines drawn with slopes 1/2.

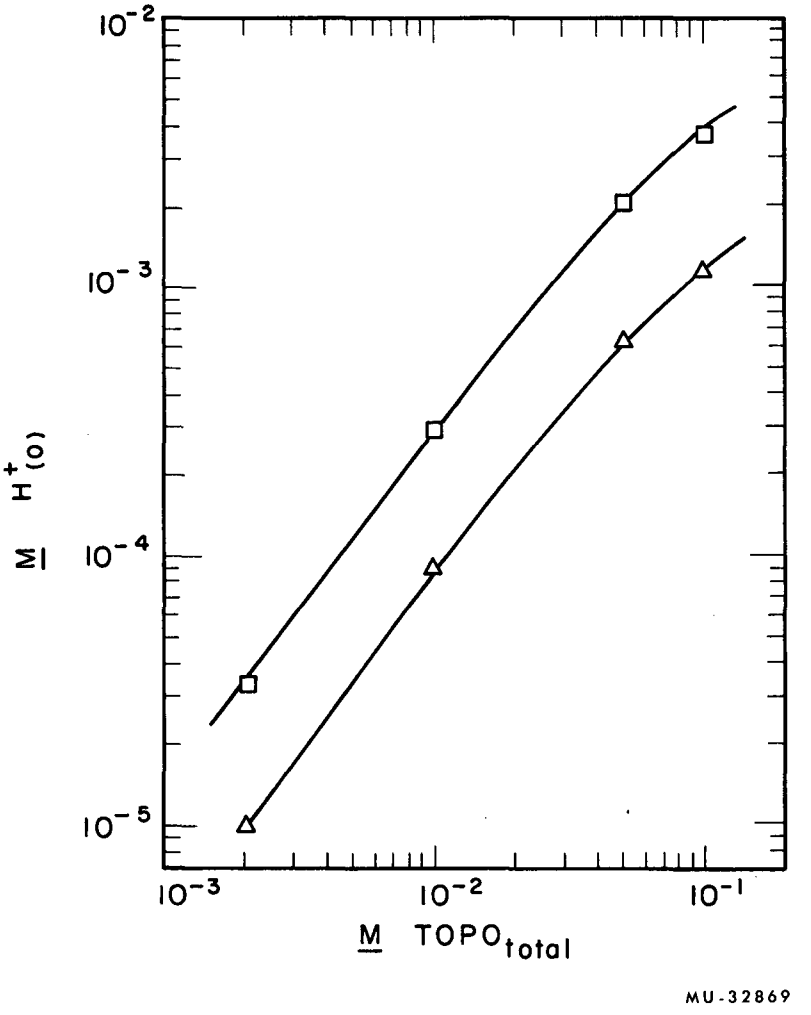


Fig. 18. Variation of organic-phase acid content (nitrobenzene diluent) with total TOPO concentrations for aqueous $HClO_4$ activity of: ■ 1.0×10^{-6}; ▲ 1.0×10^{-7}.

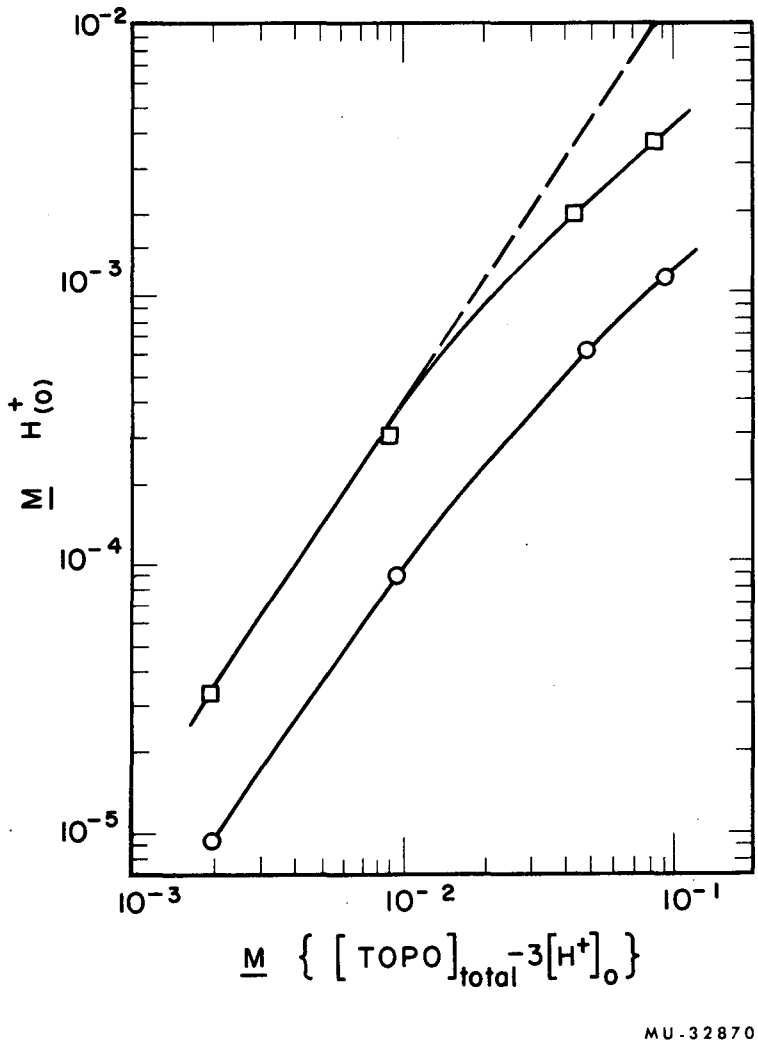


Fig. 19A. Variation of organic-phase acid content (nitrobenzene diluent) with concentrations of TOPO not tied up with acid for aqueous $HClO_4$ activity of 1.0×10^{-6}.

are shown in Fig. 19B. It can be seen that the slope is approximately 3/2, i.e., n = 3.0. Use of the value of n = 2 did not yield a slope of 1 appropriate to such a value of n.

No attempt was made to determine the total amount of water present in acid extraction. The difficulty in this determination is that the water extracting into pure nitrobenzene is appreciable, and the extraction of $HClO_4$ by nitrobenzene is also appreciable and may be accompanied by excess water. Some conclusions, however, can be drawn concerning the extracting species on the basis of the foregoing data and the results of the TOPO-$HClO_4$-CCl_4 system.

In the region where the stoichiometric TOPO/H^+ ratio is greater than 3, the value of n = 3 was found for the complex so that there are three TOPO molecules per proton and the species is dissociated. Again, one is forced to conclude that the TOPO molecules are coordinated to an acidic species with three bonding sites. By analogy with the $HClO_4$-TOPO-CCl_4 data, this species is most probably a hydronium ion. If TOPO acts as a weaker base in nitrobenzene than in the CCl_4, the hydronium ion is possibly further hydrated. Consequently, the species may be written $H_3O^+ \cdot 3TOPO \cdot yH_2O + ClO_4^-$, where the value of y is probably zero but could range from 0 to 3.[9]

This $HClO_4$ extraction also points out that the nature of the extracting species is not only dependent upon the outcome of the competition for the solvation of the proton, but also upon the dielectric constant of the diluent. Nitrobenzene's ability to support a charge separation better than CCl_4 is evidenced by the dissociation of the complex. Also, the extent of extraction of $HClO_4$ into TOPO-nitrobenzene is increased to 100 times the value obtained for $HClO_4$ into TOPO-CCl_4. There is a smaller increase in the electrostatic free energy in transferring ions from water to a high-dielectric-constant medium, such as nitrobenzene, than to a low-dielectric-constant medium, such as CCl_4. This energy change may be seen from the Born equation.

$$\Delta F = -\left(\frac{Z_1^2 e^2}{2r_i} + \frac{Z_2 e^2}{2r_2}\right)\left(\frac{1}{\epsilon_w} - \frac{1}{\epsilon_o}\right).$$

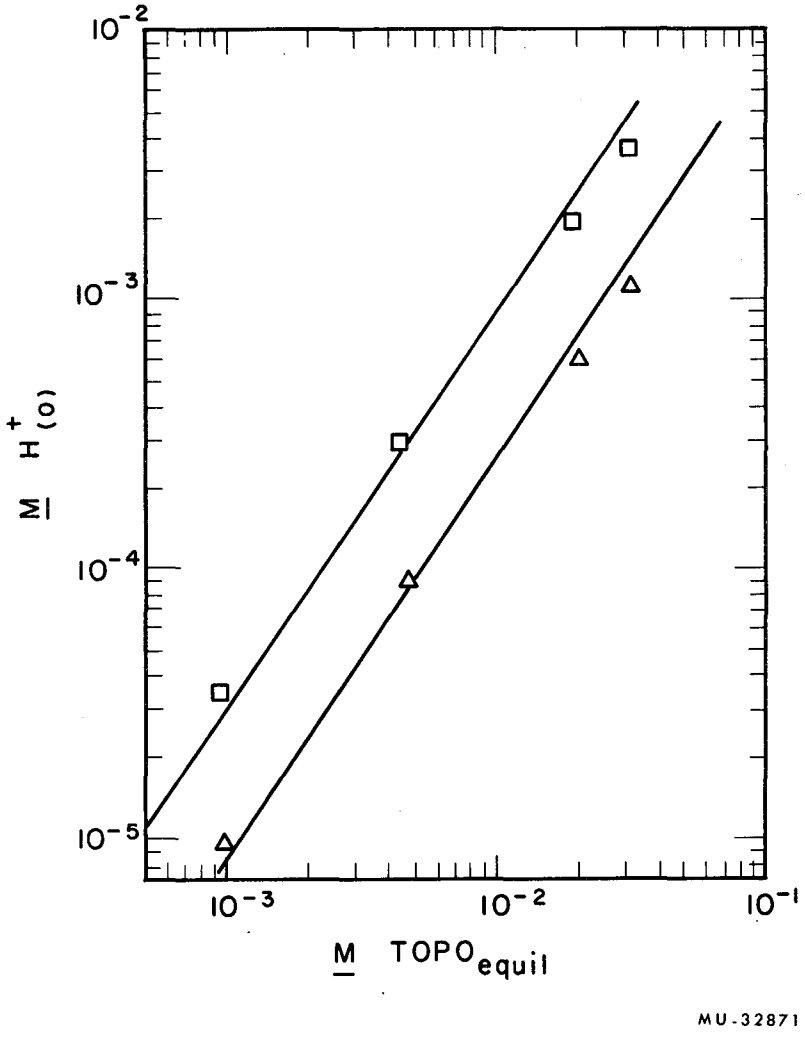


Fig. 19B. Variation of organic-phase acid content (nitrobenzene diluent) with equilibrium TOPO concentrations for aqueous $HClO_4$ activity of: ■ 1.0×10^{-6}; ▲ 1.0×10^{-7}. Lines drawn with slopes 3/2.

It must be noted that such a classical equation assumes a continuous medium and is not a true representation of the system; nevertheless, the effect remains. Therefore, a high-dielectric-constant medium will extract ionic species far better than low-dielectric-constant media. Ion-pair formation in the low-dielectric-constant medium does give back some Coulombic energy. Ion-pairing, however, is not a prerequisite to extraction, as is sometimes said, but is rather the result of using low dielectric-constant media.

5. TOPO-HNO_3-Nitrobenzene

Figure 20 shows the results of the plot of the uncorrected $\log[H^+]_{(o)}$ vs $\log(HNO_3)$ with a slope of approximately 1/2. The expression

$$[H^+]'_{(o)} = [H^+]_{(o)} \frac{[TOPO]^{3/2}_{total}}{[TOPO]^{3/2}}$$

was used to correct the experimental organic-phase acid concentration to a constant equilibrium TOPO concentration. The results are shown in Fig. 21 in which the slope of the curve $1/m = 1/2$; thus $m = 2$. As in the case of $HClO_4$ extraction by TOPO into nitrobenzene, the species is ionized and dissociated. This is in great contrast to the molecular extraction of HNO_3 by TOPO into CCl_4.

Figure 22 shows a plot of $\log[H^+]_{(o)}$ vs $\log[TOPO]_{total}$ with the slope of the curve approximately equal to 1.2 or $n = 2.4$. From the CCl_4 case, one might expect $n = 1$. A value of $n = 2$ or $n = 3$ may be used to correct to equilibrium TOPO concentrations. The value $n = 3$ was chosen as it seemed to fit the models previously presented. The equilibrium TOPO concentration were calculated from Eq. (9) and from Fig. 2, as discussed in Section V. B. 4. The slope of the corrected curve shown in Fig. 23A and B, equals $n/m = 3/2$, but the data are not very good. Most likely, though, there are three TOPO molecules per proton. Determination of the water content in the acid extraction was not attempted for reasons given in Section V. B. 4.

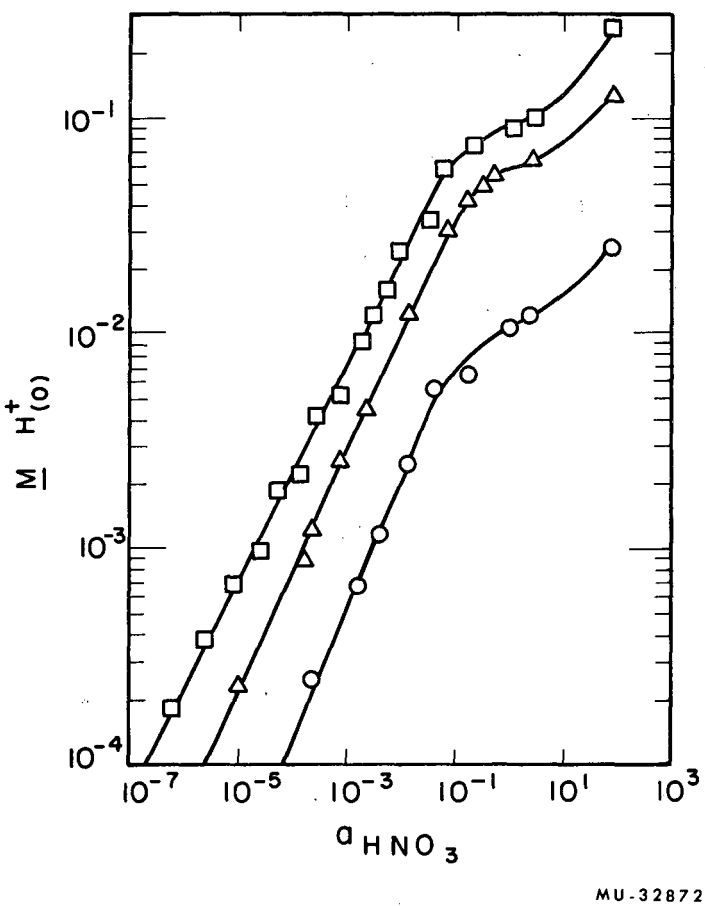


Fig. 20. Variation of organic-phase acid content (nitrobenzene diluent, corrected for solubility of HNO_3 in nitrobenzene) with aqueous HNO_3 activity for total TOPO concentrations: ■ 0.1 $\underline{M}$; ▲ 0.05 $\underline{M}$; ● 0.01 $\underline{M}$.

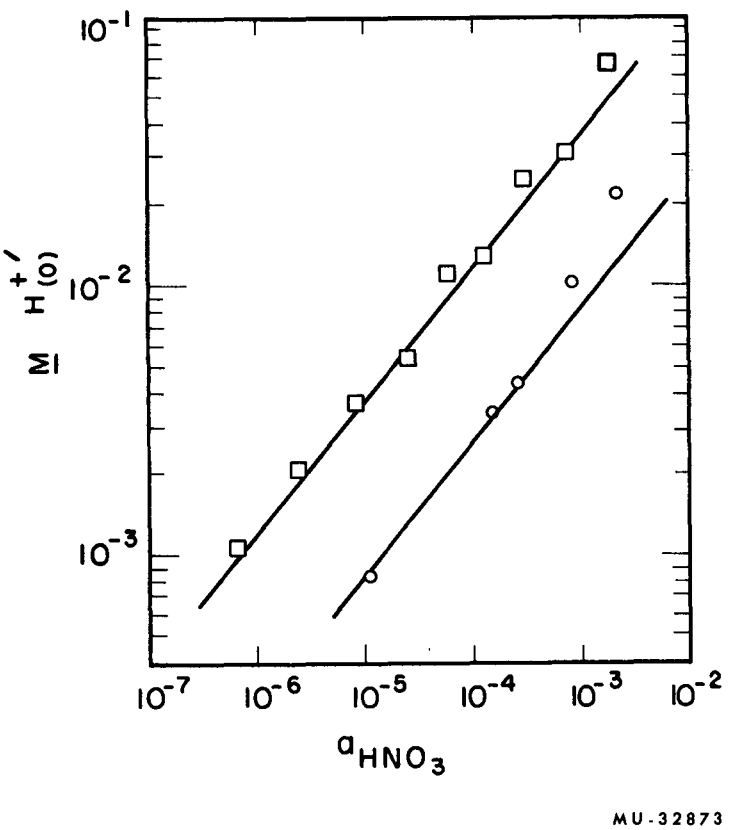


Fig. 21. Variation of organic-phase acid content (nitrobenzene diluent, corrected for solubility of HNO_3 in nitrobenzene) with aqueous HNO_3 activity for fixed TOPO concentrations: ■ 0.1 M; ▲ 0.05 M. Lines drawn with slopes 1/2.

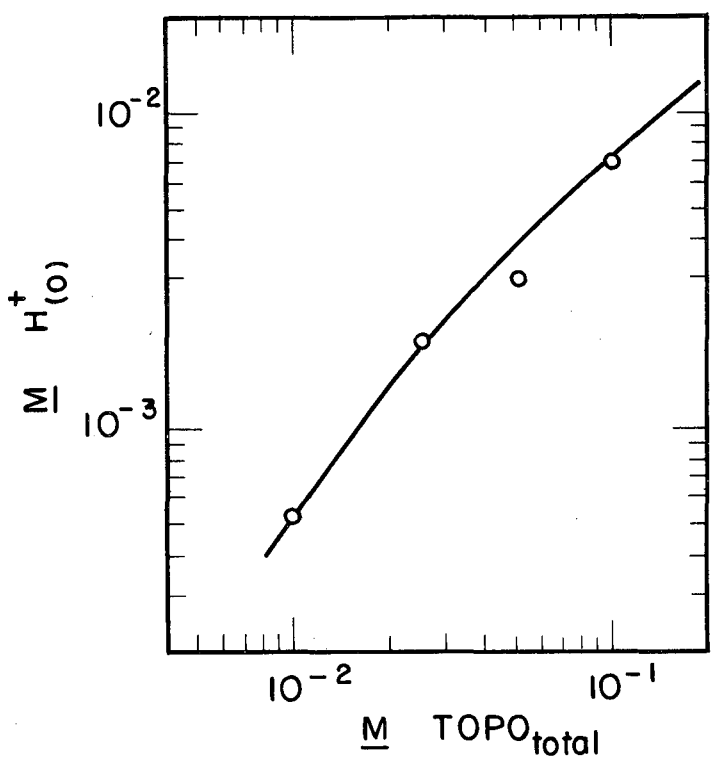


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Fig. 22. Variation of organic-phase acid content (nitrobenzene diluent) with total TOPO concentrations for aqueous HNO_3 activity of 1.0×10^{-3}.

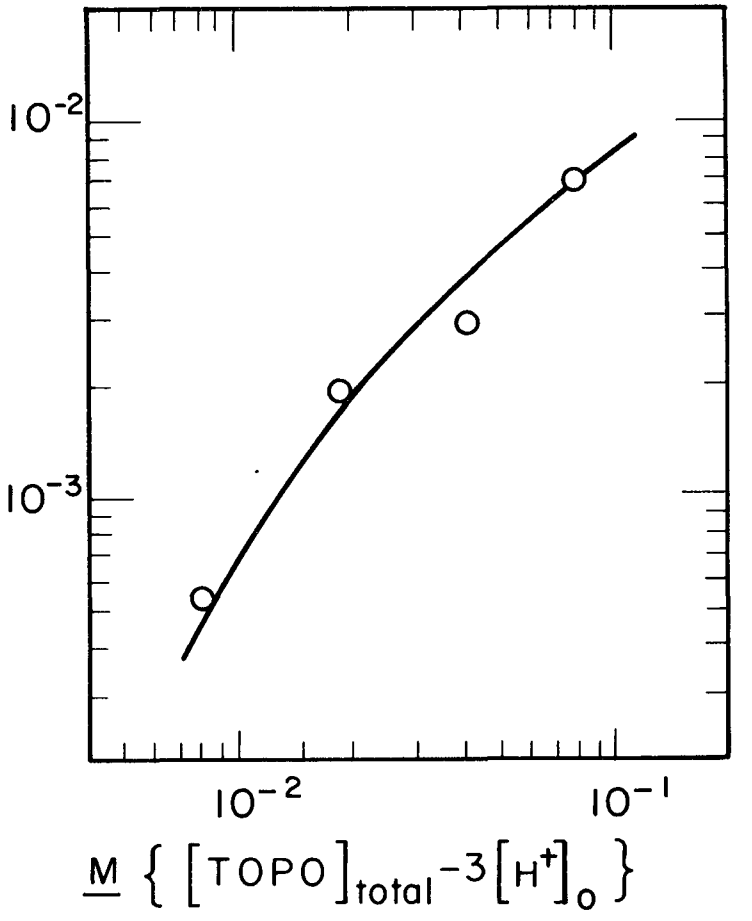

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Fig. 23A. Variation of organic-phase acid content (nitrobenzene diluent) with concentrations of TOPO not tied up with acid for aqueous HNO_3 activity of 1.0×10^{-3}.

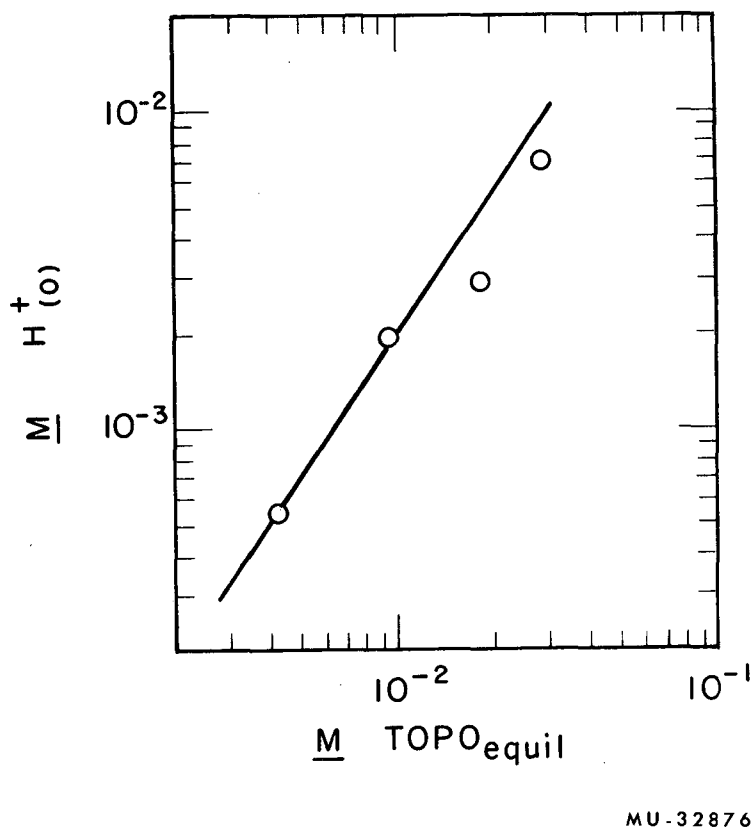

Fig. 23B. Variation of organic-phase acid content (nitrobenzene diluent) with equilibrium TOPO concentrations for aqueous HNO_3 activity of 1.0×10^{-3}. Line drawn with slope 3/2.

The extraction of HNO_3 into TOPO-nitrobenzene is entirely different from its extraction into TOPO-CCl_4. As nitrobenzene has a much higher dielectric constant than CCl_4, ionization and dissociation of the acid species is promoted; that is, the force of attraction between the proton and anion is increased by a factor of 2 over the value in water, compared to the 35-fold increase in CCl_4. Thus, HNO_3 is a strong acid like $HClO_4$ in nitrobenzene solutions, just as in dilute aqueous solutions. In CCl_4, NO_3^- wins the competition for the proton and molecular HNO_3 is extracted, whereas here the basicity of NO_3^- is reduced to the point where water wins the competition.

On the basis of the foregoing data a species can be suggested similar to that for $HClO_4$ extraction. Again, three TOPO molecules per proton in the complex implies at least a hydronium ion as the extracting acid species. The hydronium ion is probably the extracting cation, but because the amount of water extracting was not determined, there is always the possibility that the hydronium ion is further hydrated. When the stoichiometric TOPO/H^+ ratio is greater than 3, the formula may be written

$$H_3O \cdot 3TOPO \cdot yH_2O + NO_3^-,$$

where y is probably zero but is possibly as large as 3. As discussed earlier, the extraction of both HNO_3 and $HClO_4$ into TOPO-nitrobenzene is significantly greater than that into TOPO-CCl_4. For example, with 0.1 $\underline{M}$ TOPO at an aqueous activity of 1×10^{-4}, the amount of HNO_3 extracting is 1.3×10^{-4} $\underline{M}$ and the amount of $HClO_4$ is 1.0×10^{-4} $\underline{M}$. In nitrobenzene however, for 0.1 $\underline{M}$ TOPO at an aqueous acid activity of 1×10^{-6}, the $HClO_4$ extraction is 3.3×10^{-3} $\underline{M}$ and the HNO_3 is 2.3×10^{-4} $\underline{M}$. In CCl_4, the magnitudes of extraction of both $HClO_4$ and HNO_3 is comparable. This similarity is coincidental since the mechanism of extraction is different for each acid. In fact, one might expect the HNO_3 extraction to be somewhat better since no charge transfer is involved in molecular acid extraction. In nitrobenzene, both acids have the same mechanism. Because of the electrostatic free energy differences discussed in Section V. B. 4, for ions in a high-dielectric-constant media,

one would expect both acids to extract better in nitrobenzene than in CCl_4. It can be seen, however, that the extraction of $HClO_4$ into TOPO-nitrobenzene is tenfold greater than that of HNO_3. The difference in extraction can be explained in terms of the anions. The ClO_4^- ion is a large, bulky ion and when it is in aqueous solution the ion disrupts the highly oriented water structure. Water will tend to eject this anion into the organic phase in order to regain its original structure. The NO_3^- ion is a smaller ion and is better accommodated into the water structure; therefore, this anion will not be ejected as readily as will ClO_4^-.

C. TOPO-Concentrated Acid

The curves shown in Figs. 3, 5, 11, 16, and 20 for both acids in each solvent deviate from the initial slopes of 1 or 1/2 at about 0.2 M $HClO_4$ and 0.3 M HNO_3 for TOPO solutions from 0.002 to 0.1 M. The assumptions used for the interpretation of extractions into dilute solutions are probably no longer valid. Some inferences and conclusions can be drawn, however, from stoichiometric considerations.

1. TOPO-Concentrated $HClO_4$-CCl_4

In the concentrated region (0.2 to 11 M), the $\log[H^+]_{(o)}$ vs $\log[HClO_4)$ curve (Fig. 3) approaches as a limit a value of the organic-phase $[H^+]$ equal to the total TOPO concentration, although even at the highest initial $HClO_4$ concentration the stoichiometric TOPO/H^+ ratio is not quite 1. When the stoichiometric TOPO/H^+ falls below 3, a new species must be involved besides the previously described $H_3O^+ \cdot 3TOPO \cdot yH_2O \cdots ClO_4^-$. The asymptotic limit, however, suggests that at high organic-phase acid concentrations, only one TOPO molecule is associated with the proton. The water activity in concentrated $HClO_4$ has been reduced considerably and the TOPO may compete more favorably as a base for the proton. It may, in fact, become the primary solvating molecule. A complex of the form H^+ TOPO$\cdots ClO_4^-$ may be suggested. (This case is similar to that of the formation of an ammonium salt by a more basic trialkyamine.)[2,37]

However, the water content in the organic phase never goes to zero (Fig. 7), but even rises slightly from 3 to 11 M $HClO_4$; some

hydrated species may be involved to about 10% or possibly the water is just distributing due to the increased acid content in the organic phase.

2. TOPO-Concentrated HNO_3-CCl_4

Figure 11 shows that the extraction of HNO_3 increases beyond the point where the stoichiometric TOPO/H^+ ratio is equal to 1. In fact, at 14 and 16 M HNO_3 initial aqueous-acid concentration, the TOPO/H^+ ratio is less than 1/2; that is, more than one HNO_3 molecule is extracting per TOPO molecule. The concentrated acid region of the H_2O-H^+ curve also shows a change from the dilute solution trend, and the curve begins to rise; thus the new species probably involves water.

From the limited amount of data available about the concentrated acid region, an attempt was made to establish a species that involves more than one HNO_3 molecule. For example, possible species suggested are TOPO·$2HNO_3$ and TOPO·$3HNO_3$. The following equation may be written

$$\text{TOPO} \cdot HNO_3 + HNO_3 = \text{TOPO} \cdot 2HNO_3,$$

with a corresponding equilibrium constant

$$K = \frac{(\text{TOPO } 2HNO_3)}{(\text{TOPO } HNO_3)(HNO_3)} .$$

The assumption is again made that the ratio of the activity coefficients of two TOPO species is a constant, although this is not as good an assumption as in the dilute-solution cases treated earlier. This treatment may, however, indicate if a new species is being formed. A plot of log [TOPO·$2HNO_3$] vs log[TOPO·HNO_3] should yield a slope of 1. The TOPO·$2HNO_3$ concentration may be taken as the excess acid above the 1:1 point. The TOPO·HNO_3 concentration is equal to $[\text{TOPO}]_{total}$ - [TOPO·$2HNO_3$]. The results of such a plot are shown in Fig. 24. Again, it must be stated that the use of such data is limited, but the slopes of the curves are approximately 1, which lends some support to the idea of a TOPO·$2HNO_3$ complex.

Although the conclusions made from data in the concentrated acid region are limited, it appears that TOPO does extract more than one

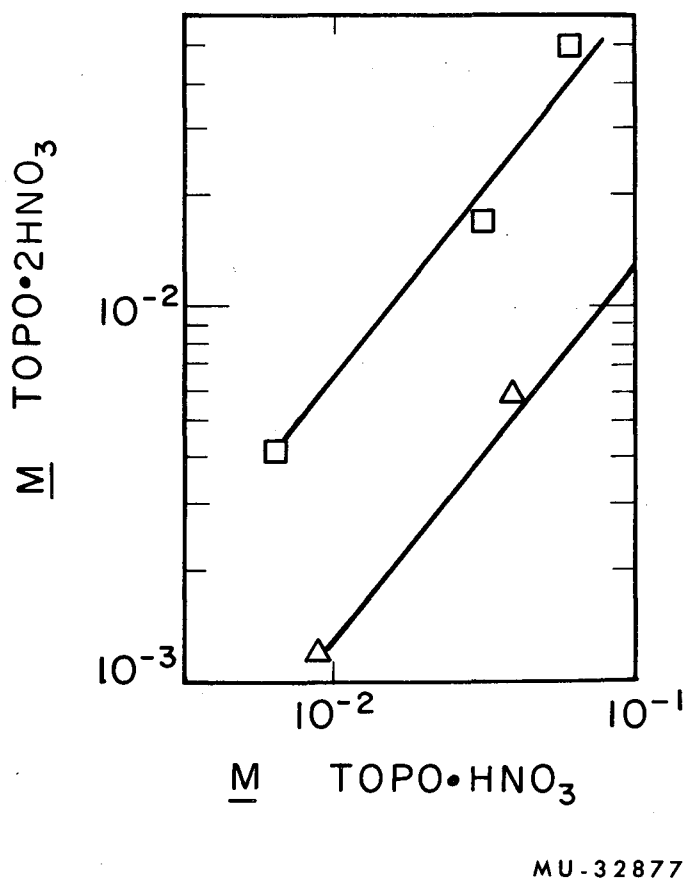

Fig. 24. Variation of concentration of TOPO · HNO_3 with TOPO · $2HNO_3$ concentration for aqueous HNO_3 concentration: ■ 8.00 M; ▲ 6.05 M. Lines drawn with slopes 1.0.

molecule of HNO_3, and that water may be tied up in the complex. Suggestions that the additional HNO_3 molecules extracted by TBP are hydrogen bonded to the ester oxygens are not correct.[5,17] There is only one basic site in TOPO, yet 0.1 M TOPO extracts even more HNO_3 above the 1:1 point than does 0.1 M TBP. TBP (0.1 M) extracts as many as 1.8 HNO_3 molecules per TBP molecule at 16 M HNO_3 while TOPO (0.1 M) extracts as many as 2.6 HNO_3 molecules per TOPO molecules. No conclusions were drawn concerning the structure of the species, but it is possible that linear chains containing TOPO and both HNO_3 and H_2O are present.

3. TOPO-Concentrated $HClO_4$-Nitrobenzene

The results for the extraction of concentrated $HCLO_4$ (> 0.3 M) by TOPO into nitrobenzene are similar to those obtained for the extraction of $HClO_4$ into TOPO-CCl_4 (Fig 16). The stoichiometric TOPO/H^+ ratio never falls below 1. One cannot conclude much about intermediate species, but in the limit a 1:1 complex is formed which probably is ionized possibly $TOPO \cdot H^+ + ClO_4^-$. Because water measurements of the organic phase were not made, the role of water in this (these) species cannot be determined.

4. TOPO-Concentrated HNO_3-Nitrobenzene

Although the extraction of HNO_3 was not determined above 6 M due to the large amount of acid extracted by nitrobenzene itself, the stoichiometric TOPO/H^+ ratio falls below 1 even at 3 M aqueous HNO_3. The ratio, in fact, decreases below 1/2 at 6 M. It is possible that species are being formed similar to those proposed for the extraction of HNO_3 by TOPO in CCl_4 but these species are probably ionized. No conclusions could be drawn, however, on the basis of these data.

VI. CONCLUSIONS

The examples for the extraction of dilute acid presented in this paper are: (a) the extraction of $HClO_4$ by TOPO into CCl_4, for which the extracting species may be written $H_3O^+ \cdot 3\ TOPO \cdots ClO_4^-$; (b) the extraction of HNO_3 and $HClO_4$ by TOPO in nitrobenzene, for which the species suggested is $H_3O^+ \cdot 3\ TOPO \cdot yH_2O + X^-$; and (c) the extraction of HNO_3 by TOPO into CCl_4, for which the proposed species is $TOPO \cdot HNO_3$.

As has been discussed the nature of the extracted species is in fact dependent upon the outcome of the competition for the proton by the extractant, water, and anion, and on the dielectric constant of the inert diluent.

When the extractant is the strongest base, anhydrous extraction occurs, and the distribution ratios are higher than when the proton is hydrated. The trialkylamines extract strong acids in this manner, e.g., trilaurylamine-$HClO_4$.[37] This may also be true for TOPO-concentrated $HClO_4$-CCl_4 as the water activity is very low and TOPO may compete more successfully for the proton.

When water best solvates the proton, extraction may proceed in one of two ways: (a) extraction of H_3O^+ or (b) extraction of higher hydrated proton complexes, in particular $H_9O_4^+$. The differentiation between these two possibilities will be dependent upon the strength and concentration of the basic organic solvent. An example is the extraction of dilute $HClO_4$ by TOPO solutions in which H_3O^+ extracts, compared to that by TBP solutions (a weaker base) into which a hydrated H_3O^+ extracts.[8]

Thirdly, the anion may form the primary solvation of the proton, and then the acid extracts as a molecule that is hydrogen bonded to the organic extractant. An example of this is the extraction of HNO_3 by TOPO[24-26] and TBP.[9-18]

Whether a particular extracting species is dissociated, ion-paired, or molecular depends markedly upon the dielectric constant of the inert solvent. In low-dielectric-constant media, the extracting

complex will exist in the form of ion pairs or neutral molecules, provided the ions are of moderate size. Examples are the extraction of HNO_3 by TBP or TOPO into CCl_4, into which molecular HNO_3 is extracted. In high-dielectric-constant media, dissociated ions are present. Examples are the extraction of HNO_3 or $HClO_4$ by TOPO into nitrobenzene. The dielectric constant of the inert diluent also affects the extent to which an acid species will extract. $HClO_4$ extracts far better into TOPO-nitrobenzene than into TOPO-CCl_4. The size of the anion of the ionized and dissociated acid also affects the degree of extraction. The larger the anion, the better the extraction. For example, $HClO_4$ extracts better than HNO_3 into TOPO in nitrobenzene.

The boundary lines between the three cases are not sharp. The mode of extraction is also dependent upon the relative activities of each component in the system. For example, as the water activity decreases with increasing $HClO_4$ concentration, the extracting species changes from a hydrated form to an anhydrous form. The extraction of $HClO_4$ by TOPO over the entire range of acid concentrations fits into two classes described above. In the extraction of dilute $HClO_4$, water wins the competition for the proton, but in concentrated $HClO_4$, TOPO wins the competition. In general, however, the knowledge of the dielectric constant of the medium and the evaluation of the relative base strengths of the extractant, water, and anion afford a method for predicting the extracting complex and mode of extraction, at least for dilute solutions of the extractant.

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REFERENCES

1. M. Davies and E. Gwynne, J. Am. Chem. Soc. 74, 2748 (1952).
2. I. Newman and P. Klotz, J. Phys. Chem. 65, 796 (1961).
3. This hydrated hydronium ion, $H_9O_4^+$, has been suggested in aqueous solutions: K. N. Bascombe and R. P. Bell, Discussions Faraday Soc. 24, 158 (1957); H. D. Beckey, Z. Naturforsch 14A, 712 (1959); M. Eigen and L. DeMaeyer, in The Structure of Electrolytic Solutions, W. J. Hamer, Ed. (John Wiley and Sons, Inc., New York, 1959). Theoretical calculations have also been made for the bonding in $H_9O_4^+$: R. Grahn, Arkiv Fysik 21, 13 (1962).
4. W. H. Baldwin, C. E. Higgins, and B. A. Soldano, J. Phys. Chem. 63, 118 (1959).
5. D. G. Tuck and R. M. Diamond, J. Phys. Chem. 65, 193 (1961).
6. S. Siekierski and R. Gwozdz, Nukleonika 5, 187 (1960).
7. K. Naito and T. Suzuki, J. Phys. Chem. 66, 983 (1962).
8. D. C. Whitney and R. M. Diamond, J. Phys. Chem. 67, 209 (1963).
9. K. Alcock, S. S. Grimley, T. V. Healy, J. Kennedy and H. A. C. McKay, Trans Faraday Soc. 52, 39 (1962).
10. T. J. Collopy and J. F. Blum, J. Phys. Chem. 64, 1324 (1960).
11. T. J. Collopy and J. H. Cavendish, J. Phys. Chem. 64, 1328 (1960).
12. V. V. Fomin and E. P. Maiorova, Russ. J. Inorg. Chem. (English Transl.) 3, No. 2, 404 (1958).
13. V. V. Fomin, R. E. Kartushova, and E. P. Maiorova, Russ. J. Inorg. Chem. (English Transl.) 5, 645 (1960).
14. D. R. Olander and M. Benedict, Nucl. Sci. Eng. 15, 354 (1963).
15. C. J. Hardy, B. F. Greenfield, and D. Scargill, J. Chem. Soc. 1961, 90.
16. A. M. Rozen and L. P. Khorkhorina, Russ. J. Inorg. Chem. (English Transl.) 2, No. 8, 389 (1957).
17. D. C. Whitney, The Effects of Ion Hydration in Solvent Extraction and Ion Exchange, University of California Radiation Laboratory Report UCRL-10505, 1962 (unpublished).
18. D. G. Tuck, Trans. Faraday Soc. 57, 1297 (1961).

19. E. Hesford, H. A. C. McKay, and D. Scargill, J. Inorg. Nucl. Chem. 4, 321 (1957).

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

21. E. Hesford, H. A. C. McKay and E. E. Jackson, J. Inorg. Nucl. Chem. 9, 229 (1959).

22. D. C. Whitney and R. M. Diamond, The Extraction of Acids by Basic Organic Solvent-II. Tributyl Phosphate-HBr, University of California Radiation Laboratory Report UCRL-10604, 1963 (unpublished).

23. M. I. Tocher, D. C. Whitney, and R. M. Diamond, The Extraction of Acids by Basic Organic Solvents - IV. Tributyl Phosphate and Trioctyl Phosphate Oxide - $HAuCl_4$ and $HAuBr_4$, University of California Radiation Laboratory Report UCRL-10912, 1963 (unpublished).

24. J. C. White and W. J. Ross, "Separations by Solvent Extraction with TOPO", National Academy of Sciences Report NAS-NS-3102, 1961.

25. R. A. Zingaro and J. C. White, J. Inorg. Nucl. Chem. 12, 315 (1960).

26. B. Martin, D. W. Ockenden, and J. K. Foreman, J. Inorg. Nucl. Chem. 21, 96 (1961).

27. W. J. Ross and J. C. White, "The Solvent Extraction of Iron with TOPO," Oak Ridge National Laboratory ORNL-2382, 1957.

28. G. E. Boyd and Q. V. Larson, J. Phys. Chem. 64, 988 (1960).

29. Half-life taken from the "General Electric Chart of the Nuclides", Fifth Ed., (Knolls Atomic Power Laboratory, April 1956).

30. J. Mitchell, Jr., and D. M. Smith, Aquametry, (Interscience Publishers, Inc., New York, 1948), p. 235.

31. G. C. Pimental and A. L. McClellon, The Hydrogen Bond (W. H. Freeman & Co., San Francisco, California, 1960), p. 80.

32. Prijana and R. M. Diamond (Lawrence Radiation Laboratory) unpublished data.

33. E. Hesford and H. A. C. McKay, J. Inorg. Nucl. Chem. 13, 156 (1960).

34. V. V. Fomin and A. F. Morgonov, Russ. J. Inorg. Chem. (English Transl.) 5, 670 (1960).

35. Handbook of Chemistry and Physics, 39th Ed. (Chemical Rubber Publishing Co., Cleveland, Ohio, 1957).

36. E. Hogfeldt and Britt Bolander, Arkiv Kemi 21, 161 (1963).

37. J. J. Bucher and R. M. Diamond, Extraction of Acid by Trilaurylamine (Lawrence Radiation Laboratory) in preparation.

APPENDIX A

List of Symbols

a	Equilibrium aqueous acid activity
$[H^+]_{aq}$	Equilibrium aqueous acid concentration
$[H^+]_{(o)}$	Organic-phase acid concentration
$[H^+]'_{(o)}$	Organic-phase acid concentration, corrected
$[H_2O]_{acid}$	Concentration of organic-phase water associated with the proton
$[H_2O]_{(o)}$	Water in the organic phase
$[H_2O]_{HNO_3}$	Concentration of organic-phase water bonded to TOPO as calculated from HNO_3 extraction data into TOPO-nitrobenzene
$[H_2O]_{IR}$	Concentration of organic-phase water bonded to TOPO as measured by infrared absorbances
$[H_2O]_{KF}$	Total concentration of organic-phase water minus the solubility of water in the pure diluent
M	Initial acid concentration in molarity
$[TOPO]_{equil}$ or $[TOPO]$	Equilibrium TOPO concentration
$[TOPO]_{total}$	Initial TOPO concentration

APPENDIX B

Table I. Extraction of water by TOPO into CCl_4.

$TOPO_{total}$	H_2O_{KF}	$H_2O_{2.75}$	$H_2O_{3.0}$	TOPO
0.0010	-	0.0003	0.0004	0.0006
0.0020	0.0007	0.0007	0.0009	0.0013
0.0035	0.0012	0.0011	0.0013	0.0023
0.0060	0.0023	0.0020	0.0025	0.0038
0.0100	0.0036	0.0035	0.0040	0.0064
0.0200	0.0070	0.0078	0.0090	0.0128
0.0350	0.0132	0.0130	0.0130	0.0220
0.0600	0.0222	0.0210	0.0200	0.0380
0.100	0.039	0.039	0.039	0.061
0.200	0.089	0.072	0.090	0.111
0.500	0.352	0.195	0.360	0.148

Table II. Extraction of water by TOPO into Nitrobenzene.

$TOPO_{total}$	H_2O_{KF}	$H_2O_{2.75}$	$H_2O_{3.0}$
0.002	-	-	-
0.005	-	-	0.0025
0.01	0.005	0.005	0.005
0.02	0.010	0.011	0.010
0.05	0.036	0.025	0.027
0.1	0.075	0.053	0.062
0.2	0.167	0.099	0.143

Table III. Extraction of $HClO_4$ by TOPO into CCl_4.

$TOPO_{total}$	M	$H^+_{(o)}$	H^+_{ag}	a	$H'^+_{(o)}$	H_2O_{KF}	H_2O_{IR}	H_2O_{calc}	H_2O_{acid}	TOPO
0.0100	0.214	0.0001	0.214	2.4×10^{-2}	0.0004	-	-	-	-	0.0062
	0.341	0.0003	0.341	6.7×10^{-2}	0.0012	-	-	-	-	0.0059
	0.640	0.0008	0.639	2.4×10^{-1}	0.0063	-	-	-	-	0.0049
	1.07	0.0019	1.07	8.5×10^{-1}	0.097	-	-	-	-	0.0027
	2.14	0.0039	2.14	7.4×10^{0}	-	-	-	-	-	-
	3.41	0.0046	3.41	6.6×10^{1}	-	-	-	-	-	-
	6.40	0.0074	6.39	2.4×10^{4}	-	-	-	-	-	-
	10.72	0.0087	10.71	3.0×10^{9}	-	-	-	-	-	-
0.0500	0.0640	0.0007	0.0633	2.7×10^{-3}	0.0028	0.0180	-	0.0173	0.0007	0.0308
	0.1072	0.0017	0.1055	6.5×10^{-3}	0.0086	0.0175	-	0.0157	0.0018	0.0292
	0.214	0.0053	0.209	2.3×10^{-2}	0.0635	0.0173	-	0.0122	0.0051	0.0219
	0.341	0.0121	0.329	6.4×10^{-2}	-	0.0150	-	0.0050	0.0100	0.0090
	0.640	0.0200	0.620	2.3×10^{-1}	-	0.0126	-	-	0.0126	-
	1.07	0.0235	1.05	8.0×10^{-1}	-	0.0101	-	-	0.0101	-
	3.41	0.0367	3.37	6.5×10^{1}	-	0.0090	-	-	0.0090	-
	6.40	0.0395	6.36	2.4×10^{4}	-	0.0086	-	-	0.0086	-
	10.72	0.0495	10.67	3.0×10^{9}	-	0.0140	-	-	0.0140	-
0.1000	0.0107	0.0001	0.0106	9.2×10^{-5}	0.00045	0.0360	0.0360	0.0359	0.0001	0.0617
	0.0214	0.0004	0.0210	3.3×10^{-4}	0.0018	-	-	-	-	0.0608
	0.0341	0.0008	0.0333	7.8×10^{-4}	0.0037	0.0360	0.0350	0.0351	0.0009	0.0606
	0.0640	0.0029	0.0611	2.5×10^{-3}	0.0165	-	-	-	-	0.0563
	0.0818	0.0045	0.0763	3.8×10^{-3}	0.028	0.0353	0.0300	0.0310	0.0043	0.0545
	0.1072	0.0071	0.1001	6.3×10^{-3}	0.056	0.0350	0.0290	0.0282	0.0067	0.0504
	0.1199	0.0075	0.1114	7.2×10^{-3}	0.062	0.0352	-	0.0276	0.0076	0.0496
	0.1500	0.0100	0.1400	1.1×10^{-2}	0.112	0.0336	-	0.0251	0.0085	0.0448
	0.214	0.0162	0.198	2.1×10^{-2}	-	0.0314	0.0185	0.0187	0.0127	0.0329
	0.341	0.0326	0.308	5.8×10^{-2}	-	0.0253	0.0087	0.0078	0.0174	0.0014
	0.400	0.0381	0.362	7.6×10^{-2}	-	0.0226	0.0065	-	0.0226	-
	0.640	0.0420	0.598	2.1×10^{-1}	-	-	-	-	0.0134	-
	1.07	0.0497	1.02	7.0×10^{-1}	-	0.0123	-	-	0.0123	-
	3.41	0.0668	3.34	6.4×10^{1}	-	-	-	-	-	-
	6.40	0.0795	6.32	2.0×10^{4}	-	0.0133	-	-	0.0133	-
	10.72	0.0951	10.62	2.9×10^{9}	-	0.0171	-	-	0.0171	-

Table IV. Extraction of $HClO_4(HReO_4)$ by TOPO into CCl_4.

$TOPO_{total}$	M	$H^+_{(o)}$	H^+_{aq}	a	$H'^+_{(o)}$	TOPO
0.0100	0.0107	9.2×10^{-7}	0.0107	1.0×10^{-4}	3.5×10^{-6}	0.0064
	0.0214	3.6×10^{-6}	0.0214	3.5×10^{-4}	1.4×10^{-6}	0.0064
	0.0341	1.0×10^{-5}	0.0341	8.0×10^{-4}	4.0×10^{-5}	0.0064
	0.0640	2.8×10^{-5}	0.0640	2.8×10^{-3}	1.10×10^{-4}	0.0064
	0.107	7.5×10^{-5}	0.107	7.0×10^{-3}	3.1×10^{-4}	0.0063
	0.214	2.98×10^{-4}	0.214	2.4×10^{-2}	1.2×10^{-3}	0.0062
	0.341	7.70×10^{-4}	0.341	6.7×10^{-2}	3.1×10^{-3}	0.0059
	0.640	2.45×10^{-3}	0.639	2.4×10^{-1}	1.9×10^{-2}	0.0049
	1.07	3.9×10^{-3}	1.07	8.5×10^{-1}	-	-
	2.14	7.29×10^{-3}	2.14	7.5×10^{0}	-	-
	6.40	1.16×10^{-2}	6.39	2.4×10^{4}	-	-
	8.58	1.02×10^{-2}	8.57	4.0×10^{6}	-	-
0.0250	.0640	2.24×10^{-4}	0.0640	2.8×10^{-3}	-	0.0159
0.0350	.0640	4.80×10^{-4}	0.0640	2.8×10^{-3}	-	0.0221
0.0500	.0640	1.26×10^{-3}	0.0640	2.8×10^{-3}	-	0.0312
0.0600	.0640	2.42×10^{-3}	0.0640	2.8×10^{-3}	-	0.0359
0.1000	0.00158	7.7×10^{-6}	0.00158	3.3×10^{-5}	2.4×10^{-6}	0.0620
	0.00222	1.6×10^{-5}	0.00222	6.6×10^{-5}	4.3×10^{-6}	0.0620
	0.00357	3.5×10^{-5}	0.00356	1.5×10^{-4}	1.0×10^{-5}	0.0619
	0.00655	1.19×10^{-4}	0.00651	5.1×10^{-4}	3.5×10^{-5}	0.0619
	0.0107	2.71×10^{-4}	0.0106	1.20×10^{-3}	9.2×10^{-5}	0.0617
	0.0214	9.84×10^{-4}	0.0210	4.5×10^{-3}	3.3×10^{-4}	0.0608
	0.0341	2.36×10^{-3}	0.0333	1.1×10^{-2}	7.8×10^{-4}	0.0606
	0.0640	7.46×10^{-3}	0.0611	4.1×10^{-2}	2.6×10^{-3}	0.0563
	0.1072	1.83×10^{-2}	0.1001	1.4×10^{-1}	6.3×10^{-3}	0.0504
	0.214	4.27×10^{-2}	0.198	-	2.1×10^{-2}	-
	0.341	5.54×10^{-2}	0.308	-	5.8×10^{-2}	-
	0.640	6.80×10^{-2}	0.598	-	2.1×10^{-1}	-
	1.07	7.64×10^{-2}	1.02	-	7.0×10^{-1}	-
	2.14	8.31×10^{-2}	2.08	-	6.6×10^{0}	-
	3.41	8.58×10^{-2}	3.34	-	6.4×10^{1}	-
	6.40	1.16×10^{-1}	6.32	-	2.0×10^{4}	-
	8.58	1.08×10^{-1}	8.49	-	3.0×10^{6}	-

Table V. Extraction of HNO_3 by TOPO into CCl_4.

$TOPO_{total}$	M	$H^+_{(o)}$	H^+_{aq}	a	$H'^+_{(o)}$	H_2O_{KF}	H_2O_{IR}	H_2O_{calc}	H_2O_{acid}	TOPO
0.0100	0.0501	0.0001	0.0500	1.6×10^{-3}	0.0002	-	-	-	-	0.0063
	0.146	0.0010	0.145	1.4×10^{-2}	0.0017	-	-	-	-	0.0057
	0.202	0.0016	0.200	2.3×10^{-2}	0.0030	-	-	-	-	0.0054
	0.395	0.0036	0.391	8.0×10^{-2}	0.0087	-	-	-	-	0.0041
	0.618	0.0063	0.612	1.9×10^{-1}	0.0256	-	-	-	-	0.0024
	4.96	0.0110	4.95	4.3×10^{1}	-	-	-	-	-	-
	6.05	0.0112	6.04	9.2×10^{1}	-	-	-	-	-	-
	12.10	0.0202	12.08	2.1×10^{3}	-	-	-	-	-	-
	14.04	0.0238	14.02	4.9×10^{3}	-	-	-	-	-	-
	15.8	0.0265	15.77	1.2×10^{4}	-	-	-	-	-	-
0.0250	0.0640	0.0006	0.0633	2.5×10^{-3}	-	-	-	-	-	0.0156
	0.146	0,0026	0.143	1.3×10^{-2}	-	-	-	-	-	0.0143
0.0500	0.0202	0.0001	0.0201	2.7×10^{-4}	0.0001	0.0180	-	0.0180	0.000	0.0319
	0.0384	0.0004	0.0380	9.0×10^{-4}	0.0006	0.0179	-	0.0179	0.000	0.0317
	0.0630	0.0009	0.0621	2.4×10^{-3}	0.0015	-	-	-	-	0.0315
	0.147	0.0036	0.143	1.3×10^{-2}	0.0061	0.0167	-	0.0166	0.0001	0.0295
	0.384	0.0161	0.368	7.2×10^{-2}	0.0369	-	-	-	-	0.0218
	0.496	0.0202	0.476	1.2×10^{-1}	0.0526	0.0108	-	0.0106	0.0002	0.0192
	0.630	0.0261	0.604	1.9×10^{-1}	0.0847	-	-	-	-	0.0154
	1.46	0.0433	1.42	1.2×10^{0}	0.504	0.0050	-	0.0048	0.0002	0.0043
	6.05	0.0567	6.00	8.9×10^{1}	-	0.0038	-	-	0.0039	-
	12.10	0.0997	12.00	2.1×10^{3}	-	0.0126	-	-	0.0126	-
	14.04	0.1100	13.93	4.8×10^{3}	-	0.0149	-	-	0.0149	-
0.1000	0.0147	0.0002	0.0144	1.5×10^{-4}	0.0003	0.0360	0.0360	0.0360	-	0.061
	0.0202	0.0004	0.0197	2.6×10^{-4}	0.0006	-	-	-	-	0.061
	0.0384	0.0009	0.0374	8.8×10^{-4}	0.0015	-	-	-	-	0.061
	0.0501	0.0014	0.0487	1.5×10^{-3}	-	0.0356	0.0350	0.0355	0.0001	0.060
	0.0630	0.0020	0.0609	2.3×10^{-3}	0.0032	-	-	-	-	0.060
	0.0807	0.0031	0.0775	4.6×10^{-3}	0.0052	0.0355	0.0340	0.0349	0.0006	0.0590
	0.147	0.0085	0.139	1.3×10^{-2}	0.0150	0.0344	0.0330	0.0331	0.0013	0.0565
	0.202	0.0130	0.189	2.1×10^{-2}	0.0240	0.0332	0.0310	0.0313	0.0019	0.0540
	0.294	0.0244	0.269	4.0×10^{-2}	0.052	-	-	-	-	0.0470
	0.384	0.0364	0.348	6.6×10^{-2}	0.0898	0.0276	0.0220	0.0227	0.0049	0.0408
	0.395	0.0370	0.358	6.9×10^{-2}	0.0997	0.0270	-	0.0224	0.0046	0.0405
	0.496	0.0482	0.448	1.1×10^{-1}	0.146	0.0236	0.0180	0.0185	0.0051	0.0331
	0.618	0.0580	0.560	1.6×10^{-1}	0.215	0.0199	-	0.0135	0.0064	0.0269
	0.630	0.0646	0.565	1.7×10^{-1}	0.285	0.0176	0.0120	0.0125	0.0051	0.0227
	1.46	0.0837	1.38	1.1×10^{0}	0.805	0.0108	-	0.0056	0.0052	0.0104
	2.93	0.0958	2.83	8.6×10^{0}	-	0.0059	-	0.0014	0.0045	0.0027
	6.05	0.110	5.94	8.6×10^{1}	-	-	-	-	-	-
	6.13	0.120	6.01	8.9×10^{1}	-	0.0071	-	-	0.0071	-
	12.10	0.191	11.89	2.1×10^{3}	-	0.0153	-	-	0.0153	-
	14.04	0.234	13.79	4.8×10^{3}	-	0.0206	-	-	0.0206	-
	15.80	0.261	15.54	1.1×10^{4}	-	-	-	-	-	-

Table VI. Extraction of $HClO_4$ by TOPO into Nitrobenzene.

$TOPO_{total}$	M	$H^+_{(o)}$	H^+_{aq}	a
0.1000	0.00158	0.0012	0.00035	1.2×10^{-7}
	0.00222	0.0017	0.00047	2.1×10^{-7}
	0.00357	0.0028	0.00074	5.2×10^{-7}
	0.00655	0.00500	0.00151	2.3×10^{-6}
	0.01072	0.0082	0.00248	5.4×10^{-6}
	0.0214	0.0154	0.00520	2.3×10^{-5}
	0.0341	0.0237	0.0103	9.0×10^{-5}
	0.0640	0.0367	0.0273	5.5×10^{-4}
	0.1072	0.0412	0.0658	2.6×10^{-3}
	0.214	0.0557	0.158	1.4×10^{-2}
	0.640	0.0648	0.575	2.0×10^{-1}
	0.858	0.0955	8.48	3.0×10^{6}

Table VII. Extraction of $HClO_4(HReO_4)$ by TOPO into Nitrobenzene.

$TOPO_{total}$	M	$H^+_{(o)}$	H^+_{aq}	a	$H'^+_{(o)}$	TOPO
0.0020	0.000655	0.000019	0.000637	3.8×10^{-7}	0.000056	0.0010
	0.00158	0.000056	0.00152	2.3×10^{-6}	0.000179	0.0009
0.0100	0.000158	0.000028	0.00012	1.5×10^{-8}	0.00008	0.0050
	0.000222	0.000040	0.00017	2.9×10^{-8}	0.00012	0.0050
	0.000357	0.000079	0.00026	6.4×10^{-8}	0.00023	0.0049
	0.000655	0.00015	0.00048	2.2×10^{-7}	0.00048	0.0048
	0.00158	0.00036	0.00120	1.5×10^{-6}	0.00119	0.0045
	0.00222	0.00054	0.00170	2.6×10^{-6}	0.00198	0.0042
	0.00357	0.00082	0.00270	6.2×10^{-6}	0.00354	0.0038
	0.00655	0.00147	0.00503	2.1×10^{-5}	0.00992	0.0028
	0.01072	0.00207	0.00858	6.0×10^{-5}	-	-
	0.0214	0.00306	0.0182	2.6×10^{-4}	-	-
	0.0341	0.00378	0.0302	6.4×10^{-4}	-	-
	0.0640	0.00466	0.0592	2.4×10^{-3}	-	-
	0.1072	0.00526	0.102	6.3×10^{-3}	-	-
	0.341	0.00590	0.335	6.5×10^{-2}	-	-
	0.640	0.00645	0.633	2.4×10^{-1}	-	-
	1.072	0.00712	1.06	9.0×10^{-1}	-	-
	3.41	0.0080	3.40	6.6×10^{1}	-	-
	6.40	0.0098	6.38	2.4×10^{4}	-	-
	8.58	0.0105	8.55	5.08×10^{6}	-	-
0.0500	0.00222	0.00145	0.00077	5.6×10^{-7}	0.00571	0.0201
	0.00357	0.00240	0.00117	1.5×10^{-6}	0.01042	0.0188
0.1000	0.000158	0.00012	0.000038	1.4×10^{-9}	0.00060	0.034
	0.000222	0.00017	0.000052	2.7×10^{-9}	0.00086	0.034
	0.000357	0.00027	0.000089	7.9×10^{-9}	0.00136	0.034
	0.000655	0.00051	0.00014	1.9×10^{-8}	0.00257	0.034
	0.00158	0.00125	0.00035	1.2×10^{-7}	0.00595	0.034
	0.00222	0.00177	0.00047	2.1×10^{-7}	0.00871	0.033
	0.00357	0.00285	0.00074	5.2×10^{-7}	0.0154	0.033
	0.00655	0.00535	0.00151	2.3×10^{-6}	0.0311	0.032
	0.01072	0.00875	0.00248	5.4×10^{-6}	0.0599	0.028
	0.0214	0.0165	0.0052	2.3×10^{-5}	-	-
	0.0640	0.0377	0.0273	5.5×10^{-4}	-	-
	0.1072	0.0475	0.0658	2.6×10^{-3}	-	-
	0.214	0.0558	0.158	1.4×10^{-2}	-	-
	0.640	0.0619	0.575	2.0×10^{-1}	-	-
	1.07	0.0651	1.01	6.8×10^{-1}	-	-
	3.41	0.0750	3.34	6.4×10^{1}	-	-
	6.40	0.115	6.37	1.8×10^{4}	-	-
	8.58	0.107	8.48	3.0×10^{6}	-	-

Table VIII. Extraction of HNO_3 by TOPO in Nitrobenzene.

$TOPO_{total}$	M	$H^+_{(o)}$	H^+_{aq}	a	$H'^+_{(o)}$	TOPO
0.0100	0.0202	0.0003	0.0199	2.6×10^{-4}	0.0009	0.0046
	0.0501	0.0007	0.0493	1.5×10^{-3}	0.0028	0.0040
	0.0807	0.0012	0.0795	4.0×10^{-3}	0.0066	0.0032
	0.146	0.0026	0.143	1.25×10^{-2}	-	-
	0.293	0.0056	0.286	4.5×10^{-2}	-	-
	0.630	0.0064	0.623	2.0×10^{-1}	-	-
	1.46	0.0115	1.31	9.6×10^{-1}	-	-
	2.02	0.0121	1.80	2.3×10^{0}	-	-
	6.05	0.0260	5.90	8.4×10^{1}	-	-
0.0250	0.0384	0.0015	0.0369	8.8×10^{-4}	0.0057	0.0103
	0.0630	0.0027	0.0603	2.2×10^{-3}	0.0136	0.0085
0.0500	0.00384	0.00023	0.0036	1.1×10^{-5}	0.0008	0.021
	0.0147	0.0009	0.0138	1.5×10^{-4}	0.0033	0.021
	0.0202	0.0011	0.0190	2.5×10^{-4}	0.0043	0.020
	0.0384	0.0024	0.0358	8.4×10^{-4}	0.0102	0.019
	0.0630	0.0044	0.0586	2.1×10^{-3}	0.0222	0.017
	0.147	0.0124	0.134	1.1×10^{-2}	-	-
	0.395	0.0309	0.364	1.0×10^{-2}	-	-
	0.618	0.0418	0.576	1.7×10^{-1}	-	-
	0.807	0.0483	0.758	2.9×10^{-1}	-	-
	1.04	0.0535	0.983	4.0×10^{-1}	-	-
	2.02	0.0633	1.95	2.5×10^{0}	-	-
	6.05	0.126	5.80	8.2×10^{-1}	-	-
0.1000	0.00104	0.0002	0.00085	6.8×10^{-7}	0.0011	0.0344
	0.00202	0.0004	0.00164	2.4×10^{-6}	0.0021	0.0388
	0.00384	0.0007	0.00312	8.3×10^{-6}	0.0035	0.0339
	0.00630	0.0010	0.00520	2.5×10^{-5}	0.0051	0.0340
	0.0104	0.0020	0.00840	5.8×10^{-5}	0.0111	0.032
	0.0147	0.0023	0.0124	1.2×10^{-4}	0.0116	0.0341
	0.0202	0.0043	0.0159	2.9×10^{-4}	0.0249	0.031
	0.0384	0.0053	0.0330	7.0×10^{-4}	0.0307	0.031
	0.0630	0.0093	0.0537	1.8×10^{-3}	0.0661	0.027
	0.0807	0.0125	0.0681	2.8×10^{-3}	-	-
	0.104	0.0164	0.0875	4.8×10^{-3}	-	-
	0.147	0.0243	0.123	9.6×10^{-3}	-	-
	0.294	0.0449	0.249	3.4×10^{-2}	-	-
	0.384	0.0599	0.324	5.4×10^{-2}	-	-
	0.630	0.0774	0.552	2.2×10^{-1}	-	-
	1.46	0.0935	1.36	1.05×10^{0}	-	-
	2.02	0.100	1.91	2.5×10^{0}	-	-
	6.05	0.282	5.65	7.1×10^{1}	-	-

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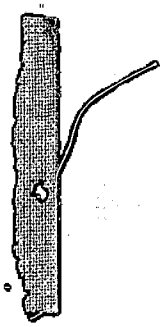
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