

University of California  
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Radiation Laboratory

THE EXTRACTION OF ACIDS  
BY BASIC ORGANIC SOLVENTS

IV. TRIBUTYL PHOSPHATE AND TRIOCTYL  
PHOSPHINE OXIDE— $\text{HAuCl}_4$  AND  $\text{HAuBr}_4$

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Berkeley, California

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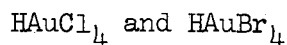
$\text{HAuCl}_4$  and  $\text{HAuBr}_4$

M. I. Tocher, D. C. Whitney, and R. M. Diamond

August 1963

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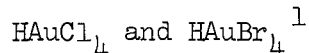
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ABSTRACT

A study has been made of the extraction of tracer amounts of  $\text{HAuCl}_4$  and  $\text{HAuBr}_4$  from aqueous solutions of the corresponding hydrohalic acids into dilute solutions of tributyl phosphate (TBP) in xylene,  $\text{CCl}_4$ , and iso-octane, and of trioctyl phosphine oxide (TOPO) in  $\text{CCl}_4$ . It was found that the extracting species has the formula  $\text{H}^+ \cdot 3\text{R}_3\text{PO} \cdot x\text{H}_2\text{O} \dots \text{AuX}_4^-$ , where R is the butoxy or octyl group and X is Br or Cl. Such a tri-solvated species is almost certainly analogous to the tri-solvated hydronium species previously found for  $\text{HClO}_4$ ,  $\text{HReO}_4$ , and  $\text{HBr}$  extracted into dilute TBP solutions and for  $\text{HClO}_4$  and  $\text{HReO}_4$  into dilute TOPO solutions, so that its formula can be written  $\text{H}_3\text{O}^+ \cdot 3\text{R}_3\text{PO} \cdot y\text{H}_2\text{O} \dots \text{AuX}_4^-$ , and it conforms to the model for strong acid extraction proposed in previous papers in this series.

## THE EXTRACTION OF ACIDS BY BASIC ORGANIC SOLVENTS

## IV. Tributyl Phosphate and Trioctyl Phosphine Oxide -



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## INTRODUCTION

A class of compound which shows high extraction into basic oxygenated organic solvents (ethers, ketones, organophosphorous esters, etc.) is the monobasic halometallic acids,  $\text{HMx}_4$ , where M is a transition metal and X is a halogen; examples are  $\text{HFeCl}_4$ ,  $\text{HAuBr}_4$ ,  $\text{HSbCl}_6$ , etc. A considerable amount of data has been published on their extraction. However, a great deal of this data was obtained by elemental analysis of the extracting species in the pure organic solvent, which in general precludes the possibility of determining the role of the solvent in the metal complex. In addition, the problem of being certain that the analysis corresponds to only a single species may make the interpretation of such data a difficult task.

Of the work which draws its conclusions mainly from organic phase stoichiometry, probably the most extensive is that of Clark, et al.,<sup>4</sup> on the Fe(III) complexes in ethers. These workers have identified  $\text{HFeCl}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{HFeBr}_4 \cdot 4\text{H}_2\text{O}$  as the extracting species into ethyl and iso-propyl ethers. Fomin and Morgunov,<sup>5</sup> on the other hand, found that  $\text{HFeCl}_4 \cdot 3-4\text{H}_2\text{O}$  was the principal species extracting into ethyl, butyl, and iso-amyl ethers and have questioned some of Clark's results. Another type of work, but of significance to these studies, is the report by McCusker, et al.,<sup>6</sup> on the crystallization

of a species from dioxane solutions which they characterize as  $[\text{FeCl}_2(\text{dioxane})_2(\text{H}_2\text{O})(\text{HCl})]^+[\text{Cl}]^- \cdot \text{dioxane}$ ; further comment on this structure is reserved for the conclusions.

Hesford and McKay<sup>7</sup> have described a method involving the extraction of tracer amounts of the acid into organic solvents diluted with inert liquids which allows treatment of the organic phase as a quasi-ideal system. That is, simple equilibrium expressions may be used to describe the extraction, and in these, the activities of the organic phase solutes may be replaced by concentrations. In several reported examples of halometallic acid extraction, this method of concentration variation has been used, but the metal ion concentrations were so high as to cast some doubt on the validity of the assumption that the organic phases were quasi-ideal. Also, in several cases there is no indication that corrections were made for the co-extraction of the hydrohalic acid or for loading of the extractant. As pointed out by Hesford et al.,<sup>8</sup> results under these conditions may give an inaccurate picture of the nature of the extracting species, and caution may have to be used in interpreting such data. Reports of this type include the identification of  $\text{HFeCl}_4 \cdot 3\text{TBP}$  at low (2-4 M) HCl concentrations but  $\text{HFeCl}_4 \cdot 2\text{TBP}$  at high (6-9 M) HCl concentrations,<sup>9</sup> and  $\text{HFeCl}_4 \cdot 2\text{TOPO}$  at very high Fe concentrations.<sup>10</sup>

The final set of reported results includes those which more or less fulfill the requirements outlined by Hesford. These actually cover the widest range of examples; the reported species are  $\text{HTlCl}_4 \cdot 3\text{TBP}$ ,<sup>11</sup>  $\text{HFeCl}_4 \cdot 3[\text{butyl ether}]$ ,<sup>12</sup>  $\text{HMcCl}_4 \cdot 3[\text{di-iso-propyl carbinol}]$  (M = Pa, Fe, Au),<sup>13</sup>  $\text{HAuCl}_4 \cdot 3\text{TBP}$ ,<sup>14</sup>  $\text{HMF}_6 \cdot 3\text{TBP}$  and  $\text{HMOF}_4 \cdot 3\text{TBP}$  (M = Nb, Ta),<sup>15</sup> and  $\text{HCrO}_3\text{X} \cdot 3\text{TBP}$  (X = Br or Cl) at low HX concentrations (1-3 M).<sup>16</sup> It may be noted that in every case the acid shows a solvation (as opposed to hydration) number of 3; in none of these examples was the hydration of the acid determined.

Other papers in this present series on strong acids have dealt with the extraction of simple mineral acids into dilute ( $\leq 0.3$  M) tributyl phosphate (TBP) and trioctyl phosphine oxide (TOPO) solutions. In these studies, it was shown that very strong acids such as  $\text{HClO}_4$ ,<sup>17,18</sup>  $\text{HReO}_4$ ,<sup>17,18</sup> and  $\text{HBr}$ <sup>19</sup> extract with the trisolvated, and in the case of TBP, partially hydrated, hydronium ion as the cation. Acids not quite as strong, such as  $\text{HNO}_3$ ,<sup>20,21</sup> however, extract primarily as the anhydrous, monosolvated molecular acid. An interpretation was present in terms of a competition for solvating the proton among the water molecules, the basic organic extractant, and the anions.

In this paper the study is extended to the mixed acid systems  $\text{HAuCl}_4$ -HCl and  $\text{HAuBr}_4$ -HBr, where the metal acid is in tracer concentration and is the species being investigated. The results reported herein, plus those reported by the other authors cited, can be formulated in terms of the previously proposed model, and this is done in the conclusion section.

## EXPERIMENTAL

Reagents. All acids and salts used were reagent grade. Of the diluents, the xylene was a reagent-grade mixture of the three isomers (see the Results Section for comments on the purity), while the iso-octane and  $\text{CCl}_4$  were of spectroscopic quality. The TBP (Fisher Scientific Co.) was purified as described previously,<sup>17</sup> while the TOPO (Eastman White Label) was used as purchased. The  $\text{Au}^{198}$  tracer was prepared by neutron irradiation of 99.9% Au foil in the Livermore Pool-Type Reactor or the General Electric Test Reactor, Vallecitos, and was certified radiochemically pure by half-life and gamma-ray spectrum measurements. The  $\text{HAuCl}_4\text{-HCl}$  solutions were prepared by dissolving the gold foil in aqua regia, taking to dryness three times with 6 M  $\text{MCl}$ , and finally dissolving the resulting  $\text{HAuCl}_4$  in  $\text{HCl}$  of the desired concentration. These solutions were stored in the dark to prevent any possible decomposition.

Procedure. Between 5 and 10  $\mu\text{l}$  of tracer solution was injected with a micro-pipet into a two-phase mixture consisting of equal volumes of acid solution and extractant solution (generally 5.00 ml of each phase) in a 60-ml glass-stoppered bottle. The samples were shaken on a mechanical wrist-type shaker for 15-30 min., transferred to 12-ml centrifuge cones, and centrifuged for 2 minutes. Duplicate 2.00-ml aliquots were taken from the upper phase, and one 2.00-ml aliquot was taken from the lower phase, the aliquots being placed in 1-dram screw cap vials. The vials were gamma-counted using a well-type  $\text{Na(Tl)I}$  scintillation counter and a single channel pulse-height analyzer; the ratio of the counts/min in each phase (after correction for background) is the distribution ratio,  $D$ , for the tracer acid.

Since in some cases a variation in the value of  $D$  was observed with a change in the tracer gold concentration over the range  $10^{-7}$  to  $10^{-2}$  M, most of the work reported in this paper was done at a fixed gold concentration, namely,  $10^{-5}$  M.



The time required for the samples to come to equilibrium is presumably of the order of a few minutes or less, since variation of the shaking time over the range of 5-120 minutes did not produce significant differences in distribution ratios. The normal range of 15-30 minutes used in these experiments was a convenient period. The centrifugation time was also arbitrarily chosen, since longer times showed no changes in the distribution ratios except for a tendency to promote evaporation of the organic phase.

Analysis of the  $\text{HAuCl}_4$  complex was done by shaking a  $6 \text{ M LiCl}$ - $0.4 \text{ M HCl}$ - $0.01 \text{ M HAuCl}_4$  solution with 10% TBP in iso-octane, back-extracting the complex completely into  $\text{H}_2\text{O}$ , and determining the H: Au: Cl ratios by standard analytical methods—namely,  $\text{Au}^{+3}$  by peroxide precipitation and weighing of the metal,  $\text{Cl}^-$  by the Volhard method, and  $\text{H}^+$  by titration using a pH meter. The results gave a ratio of 1.00:1.00:4.01. (LiCl solutions were used in order to lower the amount of HCl extracting into the TBP solution in competition with the  $\text{HAuCl}_4$ .) Analyses were not done on  $\text{HAuBr}_4$ , but it can be assumed to be analogous to  $\text{HAuCl}_4$ .

All experimental work was done at room temperature,  $23 \pm 2^\circ\text{C}$ , with no apparent changes in extraction occurring over this small temperature range.

## RESULTS

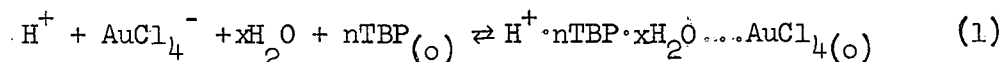
The distribution ratios,  $D$ , of the gold tracer as a function of the TBP or TOPO concentration in various organic solvents for various aqueous hydrohalic acid concentrations are shown as log-log plots in Figs. 1-6.

In some cases (notably some xylene solutions) the inert diluent was found to yield an appreciable distribution ratio, even with no extractant present. This same problem was noted by Tuck<sup>14</sup> in  $\text{HAuCl}_4$ -TBP extractions using xylene diluent, and is possibly due to basic impurities in the solvent; no such behavior was found when spectroscopic grade m-xylene was used in place of reagent-grade mixed xylenes. Whatever the cause, the distribution ratios obtained for the pure solvents were subtracted from those with extractant present to yield the corrected distribution ratios which are plotted in the figures.

## DISCUSSION

In the following derivation of the equations describing the extraction system, only those for TBP and  $\text{HAuCl}_4$  will be shown explicitly. Completely analogous equations would apply if TBP is replaced by TOPO or  $\text{HAuCl}_4$  is replaced by  $\text{HAuBr}_4$ , since the types of equations are general. Due to the low dielectric constants ( $\epsilon \sim 2$ ) of the solvents, the extracting species in these systems will probably be in the form of an ion pair, as has been earlier established for the extracting species of  $\text{HClO}_4$ ,  $\text{HReO}_4$ , and  $\text{HBr}$  under these conditions.<sup>17-19</sup>

The equation for the extraction can be written then as



where (o) denotes the organic phase, and aqueous ion hydration has been omitted. The corresponding equilibrium constant is

$$K_{\text{HAuCl}_4} = \frac{(\text{H}^+ \cdot n\text{TBP} \cdot x\text{H}_2\text{O} \dots \text{AuCl}_4^-)_{(o)}}{(\text{H}^+) (\text{AuCl}_4^-) (\text{H}_2\text{O})^x (\text{TBP})^n_{(o)}} \quad (2)$$

$$= \frac{[\text{H}^+ \cdot n\text{TBP} \cdot x\text{H}_2\text{O} \dots \text{AuCl}_4^-]_{(o)} \gamma_{(o)}}{[\text{TBP}]_{(o)}^n \gamma_{\text{TBP}}^n (\text{H}_2\text{O})^x [\text{H}^+] [\text{AuCl}_4^-] \gamma_{\text{H}^+} \gamma_{\text{AuCl}_4^-}}$$

where parentheses represent activities, and brackets stand for concentrations. By the proper choice of conditions, it is possible to considerably simplify Eq. (2). Since HCl extracts relatively poorly,  $(\text{H}_2\text{O})^x [\text{H}^+] \gamma_{\text{H}^+}$  is constant for a given HCl concentration. Also, since  $\text{HAuCl}_4$  is in dilute (tracer) concentration,  $\gamma_{\text{AuCl}_4^-}$  is very close to being constant for a given  $[\text{H}^+]$ . As long as the concentration of all acid in the organic phase is kept small compared to the TBP concentration, the equilibrium TBP concentration,  $[\text{TBP}]$ , will be proportional to the total TBP concentration, differing only by the amount of  $\text{TBP} \cdot \text{H}_2\text{O}$  formed (the proportion of the latter depends upon  $a_{\text{H}_2\text{O}}$  and the equilibrium constant for the extraction of water by TBP; see ref.17). Little is known concerning the activity coefficients of inorganic species in organic solvents, so it has been assumed that for the dilute organic phases used in this study, the ratio of activity coefficients of the two species present, i.e.,  $\gamma_{(o)} / \gamma_{\text{TBP}}^n$ , is a constant. When these various considerations are applied to Eq. (2), and it is noted that  $[\text{H}^+ \cdot n\text{TBP} \cdot x\text{H}_2\text{O} \dots \text{AuCl}_4^-]_{(o)} / [\text{AuCl}_4^-]$  is the distribution ratio for gold,  $D$ , the resulting expression is

$$K'_{\text{HAuCl}_4} = \frac{D}{[\text{TBP}]^n} \quad (3)$$

Taking logarithms,

$$\log D = n \log [\text{TBP}] + \log K'_{\text{HAuCl}_4} \quad (4)$$

Thus, a plot of  $\log D$  vs  $[\text{TBP}]$  should yield a straight line of slope  $n$ , giving the dependence of the extracting species (if it is an ion pair) on TBP. Such plots are shown for  $\text{HAuCl}_4$  extracting from 2, 6, and 10 M HCl into TBP in iso-octane (Fig. 1), xylene, (Fig. 2), and  $\text{CCl}_4$  (Fig. 3) and for  $\text{HAuBr}_4$  extracting from 1, 2, 4, and 6 M HBr into TBP in xylene (Fig. 4); the slopes are seen to range in value from 2.8 to 3.2.

The tendency for the curves from 10 M HCl solutions to bend over to a slope below 3.0 has its explanation in the assumption that the extraction of HCl is negligibly small. Although this is certainly true in 2 M HCl (where  $[\text{H}^+]_{(o)} \approx 10^{-4}$  M for 0.15 M TBP in iso-octane,  $[\text{H}^+]_{(o)}$  denoting organic phase HCl concentration), the extraction has started to become appreciable ( $[\text{H}^+]_{(o)} \approx 0.003$  M) at 6 M and is actually quite large ( $[\text{H}^+]_{(o)} \approx 0.04$  M) at 10 M; Since the effect of decreasing  $[\text{TBP}]$  is a greater lowering of  $D$ , the  $D$ 's in 10 M HCl fall below their expected values by a factor of 5 or more for the most concentrated TBP solutions; the same effects, although somewhat due to the lower extractions of HCl, are also noticeable for xylene and  $\text{CCl}_4$  solutions. The rapid reduction of HCl extraction with decrease in TBP concentration ( $\propto [\text{TBP}]^3$ ) causes this effect to diminish, and the  $D$ 's to become closer to the expected values, as the TBP concentration is reduced. The effect is even more apparent in the 6.3 M HBr system (Fig. 4), since HBr extracts better than HCl.

This problem could be avoided in some cases by doing the extraction from a 6.0 M LiCl-0.1 M HCl aqueous phase. The results of such an experiment

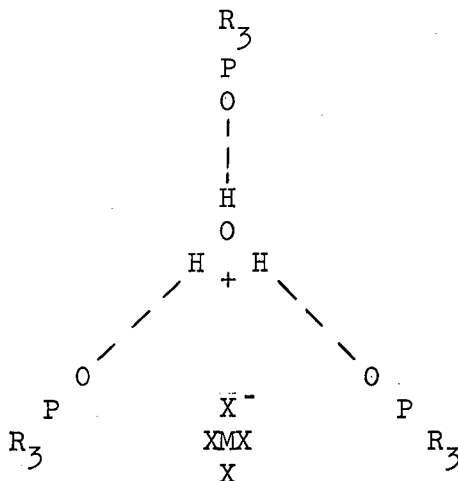
are shown in Fig. 5, and it is seen that good results are achieved in iso-octane solutions of TBP (slope  $\sim 3.2$ ).

Extraction of  $\text{HAuCl}_4$  from aqueous HCl solutions were also made into trioctyl phosphine oxide (TOPO) dissolved in  $\text{CCl}_4$ . Equation (3) may be used to represent the extraction, provided [TOPO] is substituted for [TBP]. The results of plotting  $\log D$  vs  $\log [\text{TOPO}]$  for these systems are shown in Fig. 6 and again slopes near, but usually below, 3 were found. The lowered values of the slopes can again be ascribed to the extraction of HCl, which, because of the greater basicity of TOPO, extract from a 0.2 M solution to give a value of  $[\text{H}^+]_{(o)} \approx 0.005 \text{ M}$  for 0.1 M TOPO, corresponding to a complexing of 15% of the total TOPO. Actually, because of TOPO's greater extraction of water ( $[\text{TOPO} \cdot \text{H}_2\text{O}] \approx 0.35 [\text{TOPO}]$ ),<sup>18</sup> this amount to a 25% reduction of the actual equilibrium TOPO concentration.

Thus, it is seen that in each case involving a complex haloauric acid and either TBP or TOPO, there are 3 extractant molecules per gold atom. Since the formula for the extracting chloro-acid was shown to be  $\text{HAuCl}_4$  (and most surely the bromo-complex is  $\text{HAuBr}_4$ ), this leaves only the number of water molecules unaccounted for. Unfortunately, it is very difficult to determine water in sub-milligram quantities in the presence of an easily reducible metal ion, and such measurements were not attempted. However, it is possible to make a reasonable inference as to the minimum amount of water present in the complex.

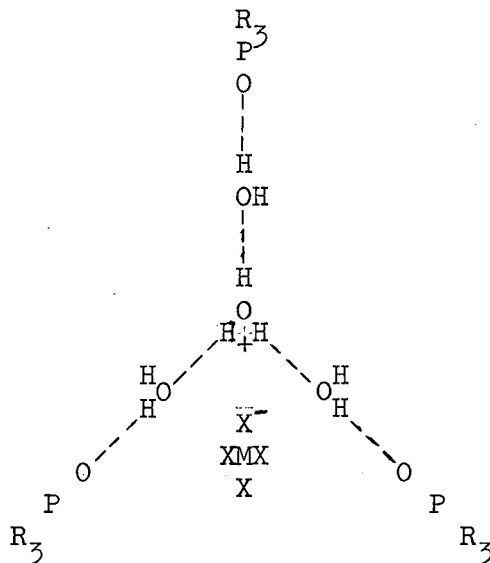
From the fact that there are 3 TBP or TOPO molecules per  $\text{HAuCl}_4$ , it may be assumed that there are 3 acidic bonding sites in the extracting acid. Since  $\text{AuCl}_4^-$  would not be expected to be an electron acceptor, the basic extractant molecules must be bonding to the proton. Since tri-coordinate protons are highly unlikely species, especially in view of the steric

hindrance among the TBP (TOPO) molecules, it seems reasonable to assign to the proton an additional water molecule, making the cationic species  $H_3O^+$ . Each TBP(TOPO) molecule is thus coordinated to one of the protons of the hydronium ion to make a total of 3 TBP (TOPO) per  $H_3O^+$ . Indeed, in the previous studies of  $HClO_4$ -TBP,<sup>17</sup>  $HBr$ -TBP,<sup>19</sup> and  $HClO_4$ -TOPO,<sup>18</sup> it was shown that the proton is extracted as the hydronium ion, with a TBP or TOPO molecule hydrogen-bonded to each of the three hydrogen atoms. It seems that this model should also apply to  $HAuCl_4$ , since the only difference in this case is that the metal complex acid, owing to the greater size of the anion, probably is a slightly stronger acid and will extract better. By this reasoning, it is apparent that the minimum value of  $x$  in the haloauric systems may be set at 1, leading to the structure shown below.



This species should occur when the extractant is basic enough to compete with the water molecules for coordination to the hydrogen atoms of the hydronium ion. These conditions are met by the use of dilute TOPO solutions in  $CCl_4$ , octane, etc., and so this is the species found for  $HClO_4$  extracted by such systems,<sup>18</sup> and is the species assumed for the similar

extraction of the haloauric acids. But with solutions of a more weakly basic extractant, additional molecules of water may appear in the complex. For example, the less basic nature of TBP enables water to compete more successfully with TBP for coordination to the  $H_3O^+$  ion. As a result, in the studies of the  $HClO_4$ -TBP and  $HBr$ -TBP systems,<sup>17,19</sup> it was found that the number of water molecules per proton extracted increased from 1 at an infinitely dilute TBP solution to about 2.5 at 10% by volume TBP in  $CCl_4$ . The limiting case in pure TBP might well correspond to the fully tri-hydrated hydronium ion shown below which has the three TBP molecules hydrogen-bonded to the first shell of water molecules. Several accounts of the existence and unusual stability of the ion  $H_3O(H_2O)_3^+$  in aqueous solution have been published,<sup>22-26</sup> and



several authors have reported a ratio of  $4H_2O/H^+$  for extraction into pure TBP.<sup>27-29</sup> Again it might be expected that the haloauric acids would behave similarly to  $HClO_4$ , and that the number of water molecules bound in the extracting complex would vary from 1 to 4 as the experimental conditions were varied.

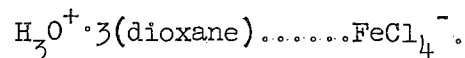
## CONCLUSION

It thus appears that the formula for the extracting species can best be written as,



and that a similar formula can be written for almost all of the other halometallic acids mentioned in the introduction. That is, the general case will involve the extraction and trisolvation of a hydronium ion; the extent of hydration of the hydronium ion in the organic phase depends upon the base strength of the extractant and upon its concentration in the organic phase. It is worth noting at this point that the ratio  $3\text{TBP}/\text{H}^+$  is not confined to acids of the general formula  $\text{HMX}_4$ , but should be found for any strong acid. Preliminary studies on the extraction of  $\text{Ag}^+$  from  $\text{HBr}$  solutions as, presumably,  $\text{HAgBr}_2$  have also shown slope 3 in log-log plots of  $D$  vs  $\text{TBP}$ .<sup>30</sup> It appears that  $\text{HSbCl}_6$  may also behave similarly,<sup>30</sup> although the experimental difficulties in the latter case are much greater.

Special mention should be made of the crystalline compound obtained by McCusker, et al.,<sup>6</sup> since it is one of the few reported cases of the isolation from solution of a hydrated halometallic acid. The structure indicated in the introduction seems a rather unlikely one for this type of compound, and, on the basis of the ideas presented in this paper, it might perhaps be more reasonable to formulate it as





Lastly, a comment should be made on the role of the anion in such strong acid extraction systems. If the anion is large, and very weakly basic, it passes into and remains in the organic phase as an ion. It does not coordinate with the basic extractant, but is essentially ejected from the aqueous into the organic phase because of its disturbance of the hydrogen-bonded water structure, much as is a molecule of  $\text{CCl}_4$ . (The halometallic anions are similar to a molecule of  $\text{CCl}_4$  carrying a single negative charge.) The degree of extraction is greater the larger, more weakly basic, and more hydrophobic is the anion. In low dielectric constant solvents, such as the  $\text{CCl}_4$ , iso-octane, and xylene of the present work, the anion ion-pairs with the hydronium complex; in higher dielectric constant media, the ions are dissociated.<sup>21</sup> If the anion is moderately basic, it will enter into the competition with water and extractant for solvating the proton. If it wins, forming the molecular acid, the extracting species into dilute extractant solutions will be mono-solvated (e.g.,  $\text{TBP}\cdot\text{HONO}_2$ ,  $\text{TBP}\cdot\text{HO}_2\text{CCCl}_3$ ,  $\text{TOPO}\cdot\text{HONO}_2$ ), as there is then only one acidic site with which the extractant can bond.

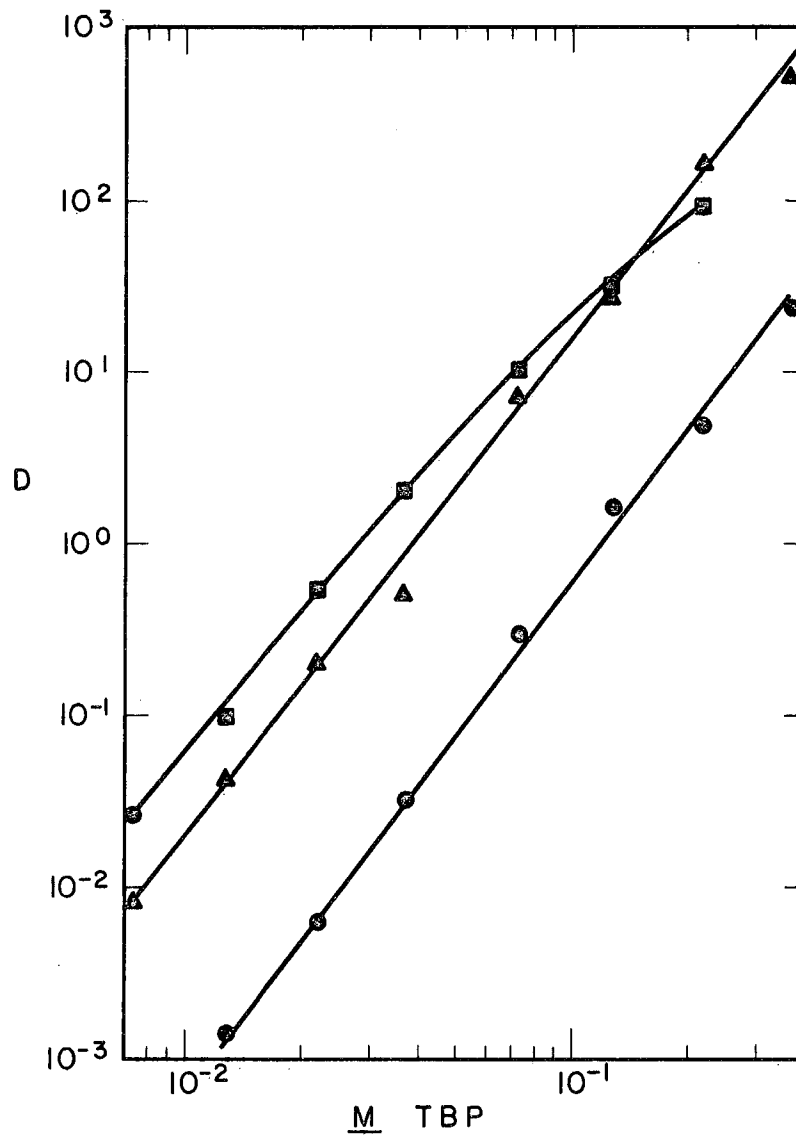
#### ACKNOWLEDGMENT

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FOOTNOTES AND REFERENCES

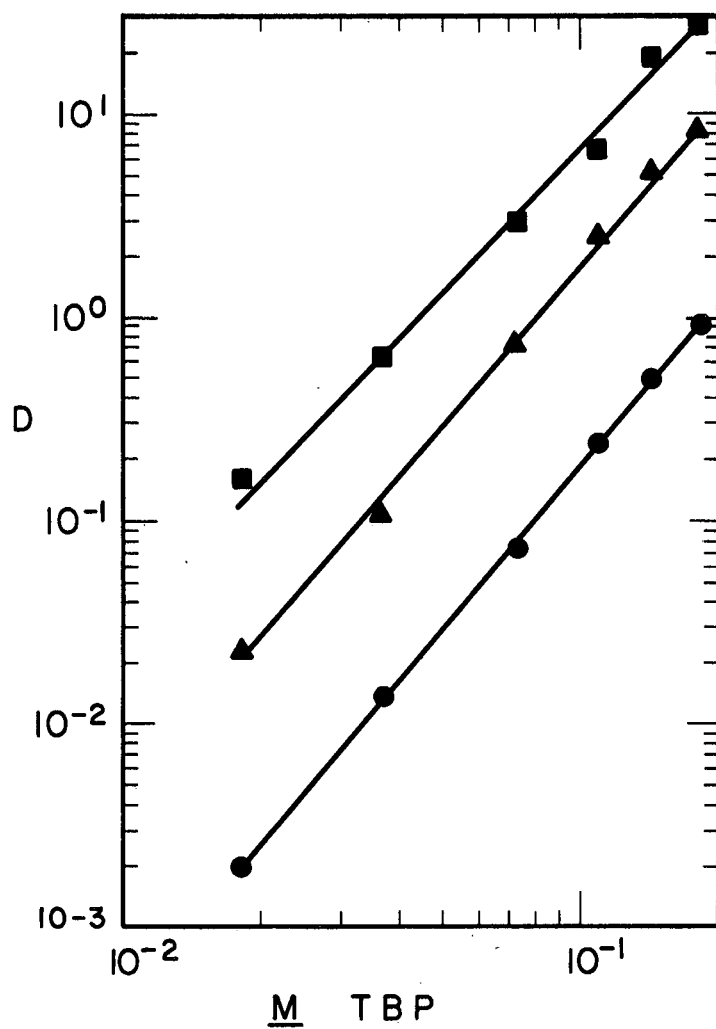
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3. Author to whom requests for reprints should be addressed.
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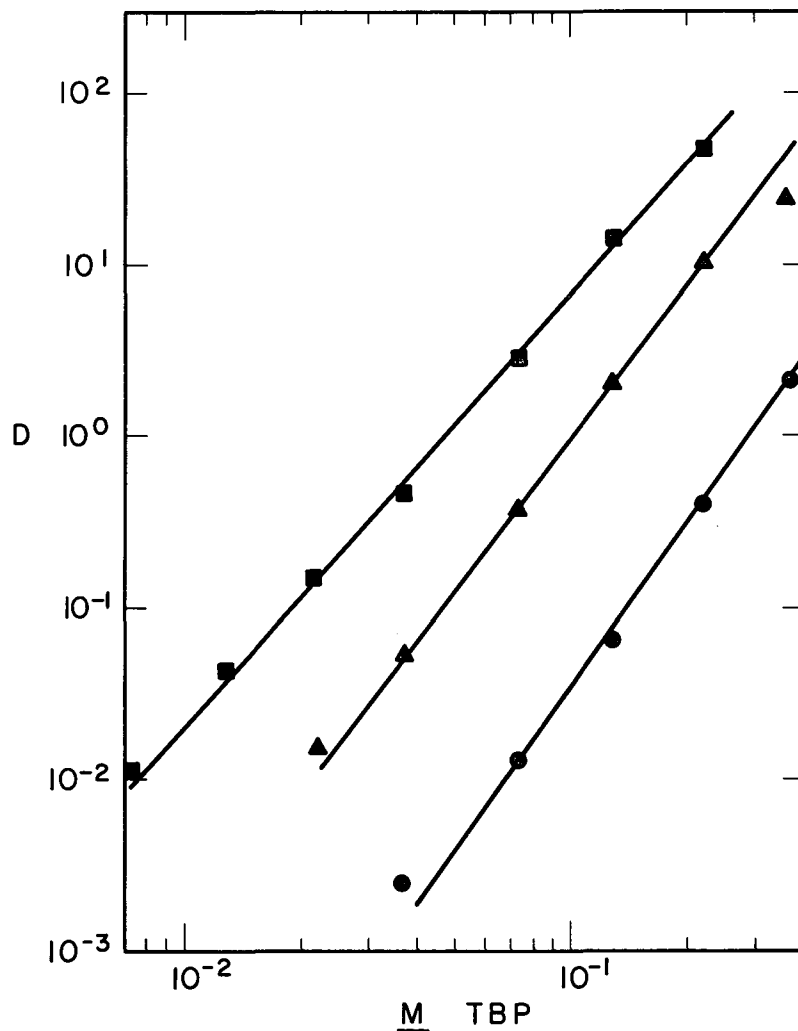
MU-31337

Fig. 1. Variation of distribution ratio of  $\text{HAuCl}_4$  with total TBP concentration (in iso-octane) for initial aqueous Au concentration of  $1 \times 10^{-5}$  M and acid concentrations of : ●, 2.0 M HCl; ▲, 6.0 M HCl; ■, 10.0 M HCl.



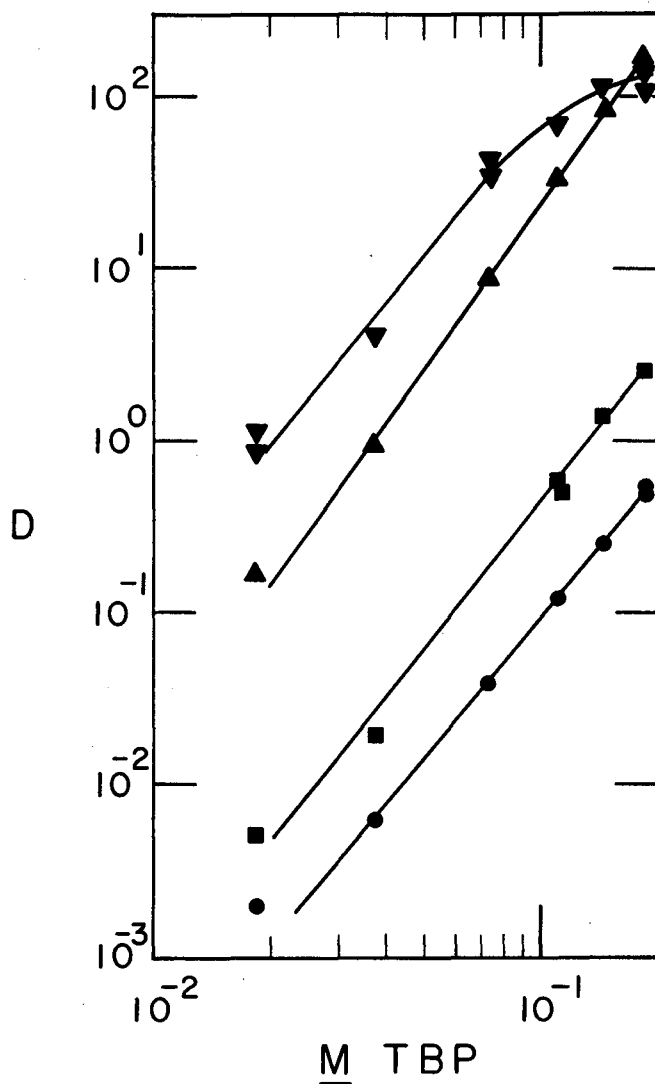
MU-31335

Fig. 2. Variation of distribution ratio of  $\text{HAuCl}_4$  with total TBP concentration (in xylene) for initial aqueous Au concentration of  $1 \times 10^{-5}$  M and acid concentrations of:  $\bullet$ , 2.0 M HCl;  $\blacktriangle$ , 6.0 M HCl;  $\blacksquare$ , 10.0 M HCl.



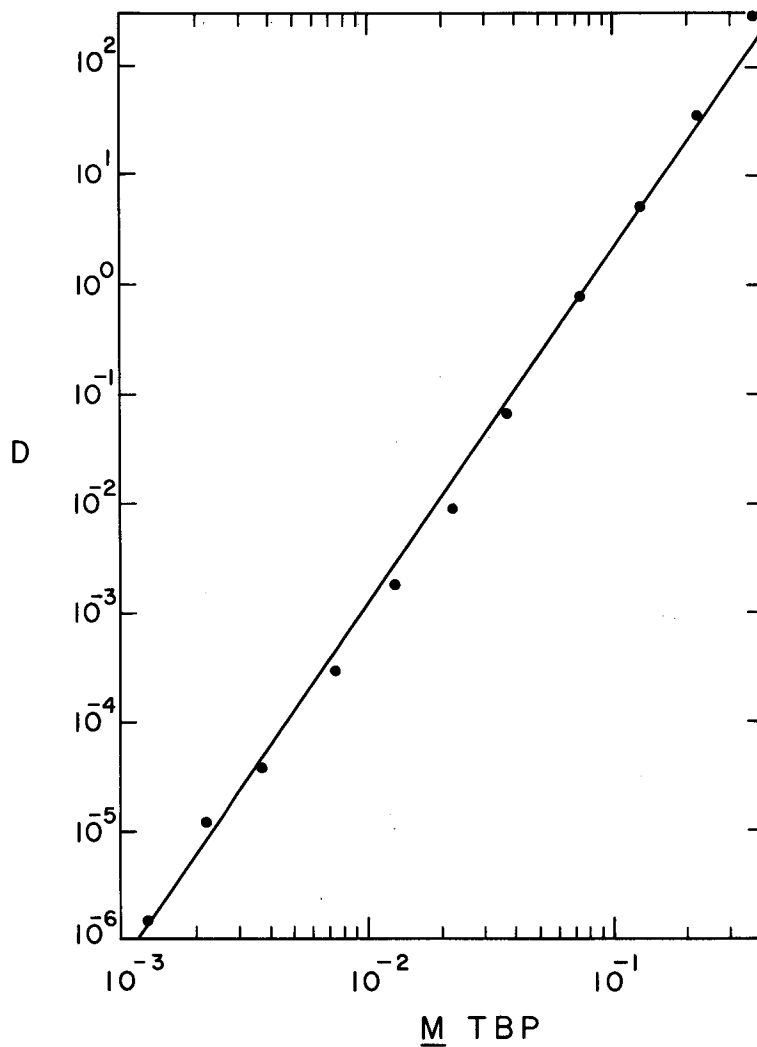
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Fig. 3. Variation of distribution ratio of  $\text{HAuCl}_4$  with total TBP concentration (in  $\text{CCl}_4$ ) for initial aqueous Au concentration of  $1 \times 10^{-2}$  M and acid concentrations of :  $\circ$ , 2.0 M HCl;  $\blacktriangle$ , 6.0 M HCl;  $\blacksquare$ , 10.0 M HCl.



MU-28745-A

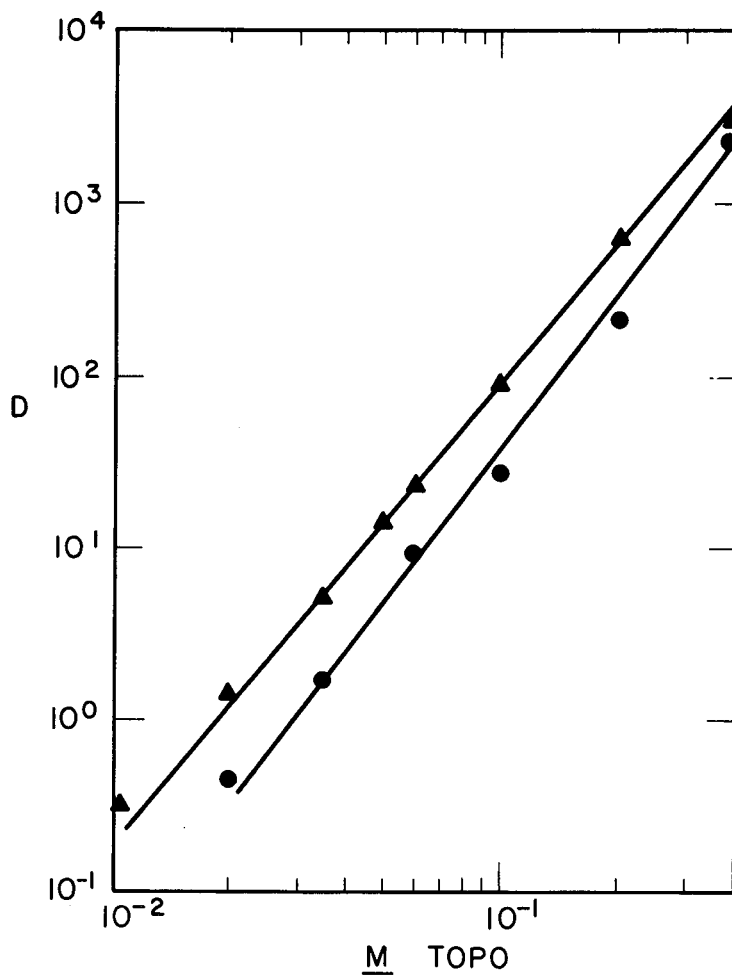
Fig. 4. Variation of distribution ratio of  $\text{HAuBr}_4$  with total TBP concentration (in xylene) for initial aqueous concentrations of:  
 ●, 1.1 M HBr,  $1 \times 10^{-5}$  M  $\text{HAuBr}_4$ ; ■, 2.0 M HBr,  $1 \times 10^{-6}$  M  $\text{HAuBr}_4$ ;  
 ▲, 4.1 M HBr,  $1 \times 10^{-5}$  M  $\text{HAuBr}_4$ ; ▼, 6.3 M HBr,  $1 \times 10^{-6}$  M  $\text{HAuBr}_4$ .



MU-28719-K

Fig. 5. Variation of distribution ratio of  $\text{HAuCl}_4$  with total TBP concentration (in iso-octane) from 6.0 M LiCl-0.1 M HCl solutions,  $1 \times 10^{-5}$  M  $\text{HAuCl}_4$  initial aqueous concentration.





MU-31338

Fig. 6. Variation of distribution ratio of  $\text{HAuCl}_4$  with total TOPO concentration (in  $\text{CCl}_4$ ) for initial aqueous Au concentration of  $1 \times 10^{-5} \text{ M}$  and acid concentrations of:  $\bullet$ ,  $0.05 \text{ M HCl}$ ;  $\blacktriangle$ ,  $0.20 \text{ M HCl}$ .

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