

AN ABSTRACT OF THE THESIS OF

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Title: THE STUDY OF FLUO-TANTALUM SPECIES BY SOLVENT  
EXTRACTION

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Abstract approved: \_\_\_\_\_

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The extraction of tantalum fluoride complexes by large cationic extractants (tetraphenylarsonium ion, TPA, and crystal violet) and by methyl isobutyl ketone (MIBK) has been investigated as a function of fluoride concentration using  $^{182}\text{Ta}$  as tracer. Extractions by the cationic extractants into chloroform were carried out in the absence of a constant ionic medium because of the high extractability of perchlorate; aqueous phases contained only HF. Dependence of the distribution ratio  $\phi$  of Ta upon extractant concentration is approximately linear; at HF concentrations above  $10^{-3}$  M the distribution is independent of metal concentration ( $10^{-7}$  to  $10^{-6}$  M) indicating absence of polynuclear Ta species in this range. Both TPA and crystal violet exhibit a distribution maximum at 0.4 M HF (approximately  $1 \times 10^{-2}$  M  $[\text{F}^-]$ ) which is probably due to the extraction of  $\text{TaF}_6^-$  through ion pair formation; the extraction drops sharply at higher fluoride

concentrations. At HF concentrations below  $10^{-3}$  M evidence was found for hydrolytic polymerization with one of the products extracting at about  $10^{-4}$  M HF.

Distribution of  $^{182}\text{Ta}$  between pre-equilibrated MIBK and MIBK-saturated aqueous 1.0 M perchlorate (constant  $[\text{H}^+] = 0.40, 0.70$  and 1.0 M) and 2.0 M perchlorate (constant  $[\text{H}^+] = 2.0$  M) media maintained by  $\text{HClO}_4$  and  $\text{NaClO}_4$  was studied as a function of free fluoride concentration calculated from known HF and  $\text{HClO}_4$  concentrations. Increasing distribution ratios with increasing  $(\text{H}^+)$  within the 1.0 M perchlorate system, as well as comparison of the function  $\phi [(\text{F}^-)]$  with that expected from published tantalum fluoride formation constants, indicate the primary extracting species to be  $\text{TaF}_6^-$  paired with the hydrated and solvated hydronium ion. A shift in the distribution maximum to lower fluoride concentrations with increasing  $(\text{H}^+)$  is probably due to changes in activity coefficients. This shift continues, accompanied by a change in slope of the distribution curve and a decrease in the maximum extraction, as the background electrolyte concentration is increased from 1.0 M to 2.0 M  $\text{HClO}_4$ ; the reasons for this behavior are not clear but may involve changes in hydration and solvation numbers of the extracting species as well as activity effects.

Mutual solubilities of MIBK and the various aqueous media have been investigated. MIBK solubility in perchlorate solutions increases

with  $\text{HClO}_4$  concentration. Extraction of  $\text{NaClO}_4$  into MIBK is practically negligible but the distribution ratio of  $\text{HClO}_4$  is significant, increases with acid concentration and is accompanied by the extraction of water. Evidence was found for the dissociation of  $\text{HClO}_4$  in MIBK. Hydrofluoric acid extracts as molecular HF and appears to be monomeric at concentrations up to about 1 M in the MIBK phase. Significant and changing aqueous phase MIBK solubilities and MIBK phase  $\text{HClO}_4$  and HF concentrations make it questionable whether reliable tantalum fluoride formation constants can be obtained from distribution data in this system.

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by

Marjory Carol Coker

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For Howard

Jon, Mary Kay and Steven

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# THE STUDY OF FLUO-TANTALUM SPECIES BY SOLVENT EXTRACTION

## INTRODUCTION

Tantalum and its sister element niobium are bright metals of high melting point, tensile strength, thermal conductivity and corrosion resistance. These properties have earned them a market in modern industry. A small amount of niobium alloyed with stainless steel considerably enhances the corrosion resistance of the steel at high temperatures; tantalum, the more resistant and higher melting of the two, is used to construct heat exchangers, valves and surgical instruments.

Tantalum and niobium are members of group VB of the periodic chart. They possess nearly the same ionic radius and exhibit much the same chemical behavior. Occurring together in nature, they were thought for many years to be one and the same element. The separation of the two metals has thus presented a challenge to the analytical chemist.

Since the oxides of niobium and tantalum are most readily dissolved either by bisulfate or alkali fusion or through the action of concentrated HF, and since the best solvent for the metals themselves is a mixture of  $\text{HNO}_3$  and HF, it is not surprising that many of the methods developed for separation and determination of tantalum

and niobium have involved fluoride solutions. One of the oldest and most popular separation methods, developed by Marignac (60), makes use of the fact that  $K_2TaF_7$  is much less soluble than  $K_2NbOF_5$  and thus may be separated from it by fractional crystallization.

Other analytical and industrial methods for separating the metals have been described by Moshier (65, p. 27-113) and Kallmann (51, p. 269-277) and include fractional precipitation by such reagents as tannin, fractional distillation of the chlorides and oxychlorides, column and cellulose chromatography, and ion exchange. However, the procedure most widely used in industry today is that of solvent extraction of the fluorides. The appeal of this method lies in its ability to produce, through continuous processes, niobium and tantalum of high purity while at the same time separating them from a number of other metals.

Extraction systems in commercial use involve the preferential distribution of tantalum into methyl isobutyl ketone, MIBK (sometimes called hexone) from aqueous HCl-HF or  $H_2SO_4$ -HF media. The separation of niobium and tantalum using the HCl-HF-MIBK system was suggested by Werning and co-workers (97) on the basis of studies involving the extracting properties of several ketones. At lower acid concentrations a high percentage of tantalum was extracted accompanied by a very low percentage of niobium; at higher acid concentrations the separation was poor due to a decrease in the

tantalum extraction and a large increase in the extraction of niobium.

During the development of solvent extraction methods for industrial separation of the metals in the 1950's, a number of investigations were carried out to determine optimum conditions. The study of Werning and co-workers (97) had been preceded by that of Stevenson and Hicks (82), whose investigation of various mineral acid media for the extraction of tantalum fluorides by diisopropyl ketone (DIPK) suggested that the  $\text{H}_2\text{SO}_4$ -HF medium provided best specificity. Wilhelm and Kerrigan (99), however, preferred the HCl-HF medium for DIPK extraction, while the method of Faye and Inman (34) involved extraction of tantalum from 7 M HF-5 M  $\text{HNO}_3$  solution by MIBK. Chernikhov and co-workers (17) favored the use of cyclohexanone over DIPK as extractant; optimum conditions for extraction of tantalum in the cyclohexanone- $\text{H}_2\text{SO}_4$ - $\text{NH}_4\text{F}$  system were studied by Goroschenko and colleagues (44). Other proposed separation procedures involved extraction of the chloride complexes of tantalum and niobium (57, 96, 14).

A host of additional extraction systems of analytical interest involving fluoride complexes of tantalum and niobium have been described in the literature; a number of these are reviewed in a later section.

While industrial necessity encouraged the proliferation of methods of separation for the two elements, knowledge of the actual

chemistry involved lagged far behind. Little was known of the state of tantalum and niobium in aqueous solution, much less of their chemical form in non-aqueous solvents. Improvements in methods for separation and analysis were made largely on the basis of trial and error.

It was this situation which prompted L. P. Varga to undertake a study of aqueous tantalum fluoride complexes and their stabilities; tantalum was chosen for the initial investigations because its tendency toward hydrolysis in fluoride solutions is less pronounced than that of niobium. Using an acid 1 M perchlorate medium to repress hydrolysis and to control ionic activity coefficients, Varga and Freund (92, 93) were able to obtain formation constants of a series of tantalum fluoride complexes from computer analysis of data involving anion and cation exchange, potentiometric  $H^+$  ion and tantalum electrode potential studies. Over the range of fluoride concentration investigated, evidence was found for existence of tantalum fluoride complexes of fluoride number four through nine.

One of the most interesting features of Varga's results was, of course, the indication of a tantalum coordination number of nine. It was thought that the method of solvent extraction which was becoming popular for the study of complex formation could be applied to higher fluoride concentrations than the other methods used and thus provide confirmation of the nine-coordinated fluorotantalum complex.

This, then, was the original purpose of the present work.

After some preliminary experiments were carried out, however, there was a few years' delay before experimental work was resumed. During this period the understanding of solvent extraction chemistry grew considerably and bits and pieces were added to the picture of tantalum fluoride complexation and extraction by several workers; little mention, however, was made of complexes other than  $\text{TaF}_6^-$  and  $\text{TaF}_7^{2-}$  which were thought to be the predominant species in aqueous solution. An important contribution was made by Varga and co-workers (94) who utilized the extractants N-benzoylphenylhydroxylamine (BPHA), tri-n-octylphosphine oxide (TOPO) and MIBK to study tantalum fluoride complexation in 3 M perchloric acid. In the lower range of fluoride concentrations studied, the species indicated were  $\text{TaF}_3^{2+}$ ,  $\text{TaF}_4^+$ ,  $\text{TaF}_5$ ,  $\text{TaF}_6^-$  and  $\text{TaF}_7^{2-}$ . Formation constants obtained through computer least-squares curve fitting showed the complexes to be considerably more stable in 3 M than in 1 M perchlorate. The use of the higher acid medium, thought advisable to insure repression of hydrolysis, prevented extension of fluoride concentrations to the higher values necessary for formation of such species as  $\text{TaF}_8^{3-}$  and  $\text{TaF}_9^{4-}$ .

In the light of the additional work which had been done and of the question of possible hydrolysis of tantalum occurring in the 1 M perchlorate medium, the scope of the present work was modified.

It was felt worthwhile to further investigate the MIBK extraction system because of its industrial importance and because of concern about the dependence of this extraction upon the aqueous phase acid concentration.

Extractions of tantalum fluoride into MIBK, traced by  $^{182}\text{Ta}$  were carried out from series of aqueous 1.0 M perchlorate phases at three different constant ( $\text{H}^+$ ) and varying ( $\text{F}^-$ ), and also from 2.0 M perchloric acid medium to provide a basis for comparison with the results of Varga. Special attention was paid to the solubility of MIBK in the various aqueous media and to the extraction of varying concentrations of  $\text{HClO}_4$  and HF into MIBK.

The extraction of tantalum fluoride from aqueous HF solution into chloroform by large cationic extractants was also studied; however, these investigations were necessarily carried out in the absence of a constant perchlorate medium and thus could not be directly correlated with the MIBK studies.

## USE OF SOLVENT EXTRACTION TO STUDY COMPLEX FORMATION

### General

As it became generally accepted that formation of metal-ligand complexes in aqueous solution occurs in stepwise fashion, methods were developed for the determination of the identity and stability of the complexes involved. In a simple system containing the species metal  $M^{n+}$ , ligand  $A^-$ , and a series of complexes  $MA^{(n-1)+}$ ,  $MA_2^{(n-2)+}$  ..., a certain amount of information is necessary to define the equilibrium. That minimum amount of information varies with the experimental method and type of mathematical treatment chosen, but often consists of the total metal concentration, total ligand concentration and the concentration of at least one of the individual species.

Experimental procedures for the study of complex formation include potentiometry, spectrophotometry, polarography, amperometry, solubility, reaction kinetics, cryoscopy, ion exchange and solvent extraction. Some or all of these methods have been described by Rossotti and Rossotti (72), Fronaeus (39), Tobias (85) and Yatsimirskii and Vasilév (101, p. 13-58). While potentiometric and optical methods enjoy perhaps the greatest accuracy, solvent extraction has gained in popularity because it usually offers a wider

range of possible ligand concentration than other methods and because it involves radioactive tracer concentrations of metal, thus giving it special appeal for the study of complexes of those metals which tend to hydrolyze and polymerize.

The method of solvent extraction, sometimes called the liquid-liquid partition or distribution method, has been reviewed by Rydberg (75, 76), Irving, Rossotti and Williams (50), Yatsimirskii and Vasil'ev (101, p. 27-30), Zozulya and Peshkova (104), Rossotti and Rossotti (72, p. 203-239), Starý (81) and Dyrssen (28). The theoretical basis for the method was laid down by Nernst (67) late in the nineteenth century. In 1902 it was applied to the study of mercury (II) chloride complexes by Morse (64) who noted that  $\text{HgCl}_2$  molecules, but not  $\text{HgCl}^+$  ions, were soluble in toluene. However, the quantitative relationships between distribution data and complex formation were not clearly defined until late in the 1940's, and it has been in the last two decades that the distribution method has come into its own as a means of investigating complex equilibria.

### Solvent Extraction Theory

There are two approaches to the distribution of a solute between two immiscible phases: the Gibbs phase rule, and the distribution law derived by Nernst.

## Gibbs Phase Rule

The phase rule may be stated  $F = C - P + 2$ , where  $F$  is the number of degrees of freedom,  $C$  the number of components, and  $P$  the number of phases. For distribution of a solute between two phases  $C = 3$  and  $P = 2$ , therefore  $F = 3$ . At constant temperature and pressure, one degree of freedom remains. Thus if the concentration of solute in one phase is fixed, the concentration of solute in the other phase follows.

## Distribution Law

The distribution or partition law, demonstrated empirically by Berthelot and Jungfleisch (10) in the nineteenth century, was derived thermodynamically by Nernst (67) from the assumption of equal chemical potentials in the two phases. For distribution of a solute  $A$  between immiscible aqueous and organic phases at constant temperature and pressure, the ratio of solute concentrations in the phases is (approximately) a constant:

$$\phi = \frac{(A)_{\text{org}}}{(A)_{\text{aq}}}$$

where  $\phi$  is the distribution ratio (sometimes called  $D$ ).

The distribution law necessitates the following assumptions:

(1) that the mutual solubilities of the phases do not vary with solute concentration, (2) that the activity coefficients of the solute do not vary with solute concentration and (3) that the solute does not associate or dissociate in either phase. Obviously, many systems, indeed all those which involve complex formation in the aqueous phase, do not obey the third requirement. In such systems the distribution ratio varies with concentration and may be expressed

$$\phi = \frac{\text{concentration of extractable complex(es)}_{\text{org}}}{\text{total concentration of all forms solute}_{\text{aq}}} \quad (1)$$

Even though complex formation occurs, however, the distribution of the extractable form of the solute conforms to the distribution law and is described by the distribution coefficient (sometimes designated P).

$$\lambda = \frac{\text{concentration of extractable complex}_{\text{org}}}{\text{concentration of extractable complex}_{\text{aq}}} \quad (2)$$

In the case where no association or dissociation occurs in either phase, the expression (1) for  $\phi$  reduces to the constant  $\lambda$ .

For a rigorous mathematical treatment of nonideal extraction systems, the reader is referred to the article by Rozen (73). This author points out that many workers in the complex formation field have regarded nonideality as due almost exclusively to complex

formation, while ignoring the effects of miscibility and activity coefficients; such a primitive approach may lead to the "discovery" of nonexistent complexes. Thus it must be kept in mind that extraction systems which do not obey the third assumption of the distribution law mentioned above may not comply with the first or second assumption either.

Such considerations aside for the time being, it can be seen from the expression for the distribution ratio, equation (1), that measurement of the quantity  $\phi$  as a function of solute concentration should lead to a knowledge of stabilities of aqueous phase complexes. However, this cannot be done unless the composition of the extracted complex or complexes is known. It was once assumed that only inert, neutral compounds would extract into organic solvents of low dipole moment and thus of a series of complexes  $MA^{(n-1)+}, \dots, MA_n, \dots, MA_N^{(N-n)-}$ , only the uncharged species  $MA_n$  would extract. With the introduction of new and different types of extractants and the development of solvent extraction chemistry, it is now known that species existing in the aqueous phase as charged complexes may be extracted through formation of ion pairs (sometimes preceded by chelation or solvation of ionic species), and that the composition of extracted species may change with conditions. Thus the determination of extracted species composition is a problem in its own right, but it is one which is being elucidated by research on extraction

mechanisms.

## Solvent Extraction Mechanisms

### General

For inorganic compounds to be extracted into organic solvents from aqueous solution, the basic requirement is some means of compensating for the loss in hydration energy. Any system of classifying types of extraction systems is arbitrary, for there are gradual transitions from one type to another. The same solvent may participate in different extraction mechanisms under different conditions; some extractions involve a combination of mechanisms. The means by which inorganic species are extracted into organic solvents have been the subject of reviews by Martin and Holt (62), Diamond and Tuck (23), Marcus (59), Morrison and Freiser (63), Freiser (36, 37) and Katzin (52). The classification scheme of Diamond and Tuck best represents the kinds of extraction studied in this work and thus is presented here. The headings refer to the type of compound or ion association complex extracted.

### A. Simple Molecules

This class represents the simplest of all extraction systems, in which the solute exists in both phases as the same covalent

molecule. The Nernst distribution law holds well in the case of immiscible phases, and the distribution coefficient  $\lambda$  is approximately equal to the ratio of solubility of the solute in the organic phase to that in the aqueous phase. An example of this extraction class is the distribution of molecular iodine between water and carbon tetrachloride.

Covalent molecules are readily extracted into organic solvents because they prefer the disordered solvent into which they can fit with little or no energy barrier over the highly ordered aqueous phase. The structure of water must be disrupted in order to insert the covalent molecule; the degree of disruption is related to the molecule size, thus larger molecules generally show a greater extractability. The chemical nature of the solvent is not so important unless it contains functional groups capable of bonding with the solute.

### B. Pseudomolecular Species

This class of compounds exists as a molecular species in the organic phase but is partially ionized in the aqueous phase. The weak acids and bases are of this type but the most important compounds are the metal chelates. Diamond and Tuck have also placed the monoalkyl and dialkyl phosphoric acid, phosphonic and phosphinic acid extractants, as well as the carboxylic acids, under this heading.

In chelate formation there is a considerable loss in solvation energy since the primary hydration shell of the metal ion is completely destroyed by union with the appropriate number of bidentate, uninegative ligands. This loss, however, is compensated for by the energy gained in formation of the chelate. The larger, bulkier and more hydrophobic the resulting molecule, the better it will be extracted; as with simple molecules, the extractability is not significantly dependent upon the nature of the solvent.

### C. Coordinately Unsolvated Salts

In extraction classes A and B the loss in hydration energy is compensated for by energy gained in bond formation. However, if the species extracted are to be ionic, there is no energy gain due to bond formation and the loss in hydration energy must be compensated for by some other means. In the case of coordinately unsolvated salts, the ionic species involved are so large that they do not have any primary hydration as such, and therefore possess little hydration energy to be lost. Such salts exist in the organic phase as ionized, though not completely dissociated "ion pairs."

Examples of this class are the extraction of  $\text{ClO}_4^-$  by the tetraphenylarsonium cation, and of  $\text{Cs}^+$  by the tetraphenylborate ion. Other extractants are the large cationic dyes and high molecular weight secondary and tertiary alkylammonium salts. Chloroform

is a popular solvent for these extractions. The extent of distribution is greatest when the ions to be extracted by large ionic reagents are large, low in charge and hydration (polyvalent ions, which have considerable primary hydration, are poorly extracted), and are hydrophobic in structure. Extractability should be increased through the use of solvents of higher dielectric constant which enhance the electrostatic solvation energy in the organic phase.

A feature of all ion association extractions (classes C through F) is the dissociation of ion pairs in solvents of high dielectric constant and association to higher aggregates in low dielectric constant solvents. These phenomena may lead to depression or enhancement of the distribution ratio through "common ion" effects or formation of mixed aggregates.

#### D. Mineral Acids

This is the simplest of the remaining systems which involve extraction of ionic compounds through formation of some type of solvent-solute complex, which may involve either hydrogen bonding or actual coordinate bonding of the solvent to the metal. These extractions are strongly dependent upon the nature of the solvent, especially upon its basic strength and steric availability of the donor atom, and also upon the nature of the aqueous phase.

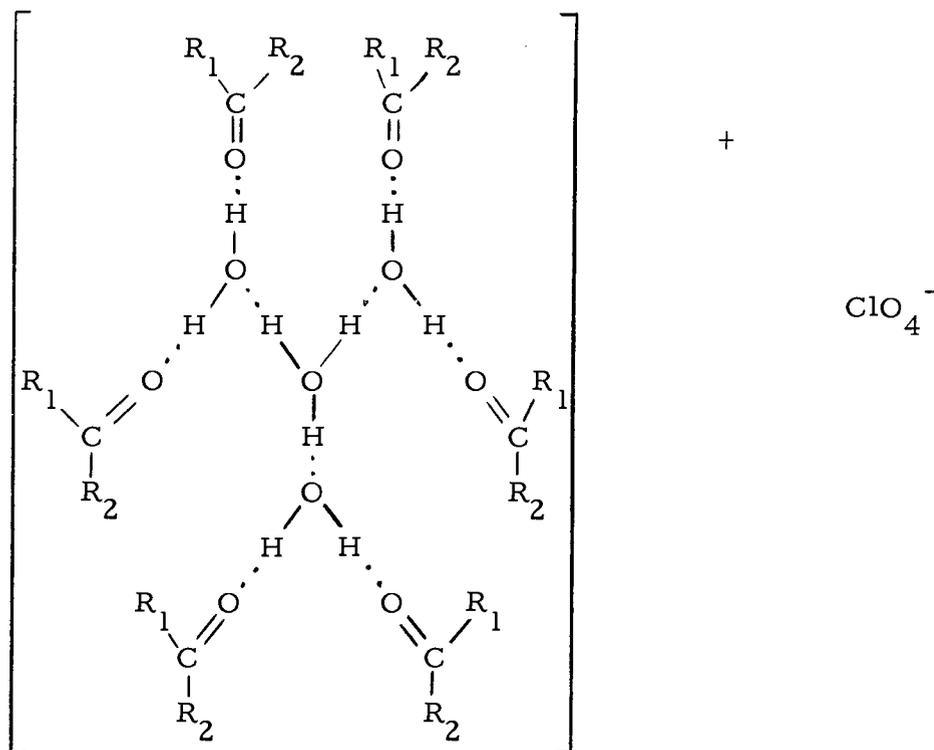
Oxygenated solvents such as ethers and ketones have some

basicity owing to the availability of a pair of electrons of the oxygen atom for donor-acceptor bonding, and thus are able to compete with water for coordination with some ions. The hydrogen ion possesses properties which make it especially suitable for solvation by oxygenated solvents.

Evidence points to the likelihood that the aqueous hydronium ion  $\text{H}_3\text{O}^+$ , is hydrogen bonded to three other water molecules to form the symmetrical species  $\text{H}_9\text{O}_4^+$ . The positive charge of the hydronium ion is apparently situated at the three hydrogen ions through a unique proton jump mechanism; therefore the additional water molecules are rather strongly bound. The hydrated structure may be further solvated either by more water molecules or by the basic organic solvent. This secondary solvation is more favorable for the hydrated hydronium ion than for any other small cation because of the proton jump mechanism; thus mineral acids are much better extracted than their alkali metal salts.

#### Solvation of the Proton

Tuck and Diamond (88) found that the  $\text{H}_9\text{O}_4^+$  configuration is maintained in the extraction of perchloric acid by diisopropyl ketone and dibutyl cellosolve; four moles of water are extracted for each mole of  $\text{HClO}_4$ . For such a case the extraction of perchloric acid by ketones may be represented:



Alcohols have some hydrogen bonding ability, and Turner and Diamond (89) found 1-decanol to participate in the primary hydration sphere of the hydronium ion. The extraction of perchloric acid into the diluents isooctane or 1,2-dichloroethane was accompanied by approximately one mole of water and three moles of 1-decanol.

The same configuration appears to occur in the extraction of  $\text{HClO}_4$  by the basic extractants tributyl phosphate and tri-*n*-octylphosphine oxide. The investigations of Whitney and Diamond (98) and of Conocchioli, Tocher and Diamond (21) indicate that the cationic species in these extractions is a hydronium ion around which three molecules of extractant are coordinated at the three sites of positive

charge; lower coordination numbers with respect to TBP and TOPO are also possible.

Numerical values of the hydration and solvation numbers in particular systems are not always easy to obtain, and Zolotov (103) has pointed out that they are to some extent devoid of meaning since they are apt to vary with conditions and thus apply only under certain circumstances. Zolotov (103) and Diamond and Tuck (23, p. 151) have agreed, however, that the organic solvent adds on to the water hydrating the hydrogen ion and only rarely directly solvates the proton.

The extraction of acids through primary or secondary solvation of the hydronium ion has been termed the "hydroxonium" or "hydrate-solvate" mechanism.

#### Factors Influencing Extractability

Factors affecting the extraction of mineral acids by organic solvents have been reviewed by Tuck (87). For the solvent, important considerations are solvent basicity and steric availability of the donor atom. For a given solvent the relative extractability of acids is influenced by three factors: acid strength, anion hydration and anion size. Weak acids should be better extracted for two reasons; the  $H^+A^-$  affinity is greater and the neutral molecule has greater tendency to be rejected by the aqueous phase. If the anion is strongly hydrated, it will prefer the aqueous phase (this is the reason for poor

extraction of polyvalent anions). As pointed out before, the disruption of the water structure is dependent upon the size of the particle to be inserted; thus larger anions are better extracted. Of the acids considered, the extractability of perchloric acid was exceeded only by that of nitric acid.

#### E. Complex Metal Acids

Anions formed by some of the transition metals with halide ions or pseudohalide ions may be extracted from acid solutions by the same hydrate-solvate mechanism described for extraction of mineral acids. Conditions of extractability are essentially identical, with the added complication that the metal halide anion must be formed by reaction of the metal ion with the appropriate number of halide ions. The extraction of these species is enhanced by the fact that they generally have no primary hydration shell; the metal is buried in the halogens which react only weakly with the surrounding water.

The system of this type which has been most thoroughly studied is the extraction of  $\text{HFeCl}_4$  by ethers and esters.

An excess of hydrohalic acid is necessarily present in such extraction systems and some of it also extracts into the organic phase, causing irregularities in the distribution behavior of the metal; this effect is even more pronounced when a third acid is

added to the system, such as the extractable  $\text{HClO}_4$ .

Effects of association or dissociation of the extracted species in the organic phase have been discussed by Diamond and Tuck (23, p. 163-168) and Zolotov (102).

#### Association of Complex Acids in the Organic Phase

In solvents of low dielectric constant such as ethers, where there is a tendency for ion pairs to associate into dimers and higher aggregates, the distribution of the complex metal acid may be enhanced by the formation of mixed aggregates. Impurity metals may also be coextracted by this means.

#### Dissociation of Complex Acids in the Organic Phase

In solvents of higher dielectric constant, such as ketones, complex metal acids upon dilution dissociate into separate ions: the hydrated, solvated hydronium ion and the metal complex anion. If the hydrogen ion is furnished primarily by dissociation of the complex metal acid  $\text{HMX}_{(n+1)}$  in the organic phase and by dissociation of another species such as the hydrohalic acid  $\text{HX}$  in the aqueous phase, the result will be a lowering of the distribution of  $\text{HMX}_{(N+1)}$  as the aqueous phase metal concentration increases. This "common ion" effect also occurs when a readily extractable acid such as  $\text{HClO}_4$  is added to the system. The perchloric acid extracts and dissociates

in the organic phase furnishing an excess of hydrogen ion, which forces the association of some of the  $H^+$  and  $MX_{(n+1)}^-$  ions and thus reduces the distribution of the metal.

#### F. Coordinately Solvated Salts

These are formed through coordination of the solvent molecules directly to the cation. More basic solvents are required to solvate cations other than the hydronium ion; a class of extractants which shows remarkable solvating properties for inorganic compounds consists of the esters of orthophosphoric acid and related compounds whose essential functional group is the phosphoryl bond. This group has a basic oxygen atom with good steric availability. The most popular extractant of this type is tributyl phosphate, TBP, which has been extensively used for the extraction of such compounds as uranyl nitrate. Another extractant with even stronger solvating properties is tri-n-octyl phosphine oxide, TOPO.

Both cationic and anionic species may be solvated by the higher aliphatic alcohols. For example, 2-octanol will extract  $ZnCl_2$  and  $CoCl_2$ . Under certain circumstances the ketones, ethers and esters usually extracting via the hydrate-solvate mechanism (classes D and E) may also become involved in coordinate solvation of cations. Specker (80) found that MIBK extracts some salts from neutral solution; complexes identified included  $HgBr_2 \cdot 2MIBK$ ,  $Hg(SCN)_2 \cdot$

4 MIBK and  $\text{CdI}_2 \cdot 2\text{MIBK}$ .

The solvation numbers of extracted complexes may be determined from the dependence of the distribution ratio on extractant concentration in an inert diluent. Again, however, solvation numbers may vary according to the conditions.

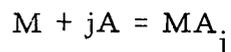
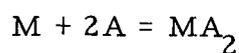
### Quantitative Relationships between Complex Formation and Distribution Data

#### Complex Formation System

The distribution method is adaptable to the study of hydrolytic, weak acid and even polynuclear metal complexes. However, the treatment of these systems becomes quite complicated, especially when more than one type of complex formation is involved. For purposes of illustration the simplest possible kind of aqueous system involving mononuclear complexes is presented here.

Notations include  $M$ , the central metal ion;  $A$  the ligand,  $j$  the ligand number of any of a series of complexes  $\text{MA}_j$ , and  $N$  the maximum ligand number. Charges of ions are not indicated.  $C_m$  is the total metal concentration,  $(M)$  the free (unbound) metal concentration,  $C_A$  the total ligand concentration and  $(A)$  the free ligand concentration.

Complex formation is represented by the following overall equations:



The overall formation constant,  $\beta_j$ , of the complex  $MA_j$  is given by

$$\beta_j = \frac{(MA_j)}{(M)(A)^j} \quad (3)$$

and is equal to the product of the stepwise formation constants or  $k_i$ 's of the individual complexes up to and including  $MA_j$ :

$$\beta_j = \prod_{i=1}^j k_i \quad (4)$$

#### Distribution of Complexes

For the usual case in which the distribution of the central atom M is followed by means of a radioactive tracer technique, the distribution ratio  $\phi$ , equation (1), is simply the ratio of the activity of a given volume of organic phase to the activity of an equal volume of aqueous phase, and equation (1) becomes, more specifically,

$$\phi = \frac{\text{concentration of extractable complex(es) of } M_{\text{org}}}{C_{M_{\text{aq}}}}$$

Through the introduction of the appropriate terms, the following relationships are adaptable to the extraction of complex metal acids or other types of species (classes B, C, E and F). Again, however,

for purposes of illustration the simplest possible case is chosen in which only the uncharged complex, designated  $MA_n$ , is extracted, and in which free metal ion and all simple complexes of M up to and including  $MA_N$  are present in the aqueous phase. Then

$$\phi = \frac{(MA_n)_{org}}{(M) + (MA) + \dots (MA_j) + \dots (MA_N)_{aq}} \quad (5)$$

The distribution coefficient  $\lambda$ , equation (2), determines the distribution of the species  $MA_n$  between aqueous and organic phases:

$$\lambda = \frac{(MA_n)_{org}}{(MA_n)_{aq}} \quad (6)$$

$$\text{therefore } \phi = \frac{\lambda (MA_n)}{(M) + (MA) + \dots (MA_j) + \dots (MA_N)} \quad (7)$$

in which all concentrations refer to the aqueous phase.

Introducing formation constants and ligand concentrations from equation (3) into equation (7), we obtain

$$\phi = \frac{\lambda \beta_n (M)(A)^n}{(M) + \beta_1 (M)(A) + \dots \beta_j (M)(A)^j + \dots \beta_N (M)(A)^N} \quad (8)$$

(M) cancels out of the equation which may then be expressed

$$\phi = \frac{\lambda \beta_n (A)^n}{1 + \sum_{j=1}^N \beta_j (A)^j} \quad (9)$$

Distribution data are customarily presented as a plot of  $\log \phi$  vs  $\log (A)$  over a wide range of free ligand concentration; this plot is called the distribution curve. The curve will rise to a maximum at the free ligand concentration corresponding to the greatest concentration of extractable complex, and will then fall off again if higher complexes are formed.

### Mathematical Treatment of $\phi, (A)$ Data

#### General

Solution of the function  $\phi [(A)]$ , equation (9) or modifications thereof, to obtain the formation constants (and the distribution coefficient  $\lambda$  if it cannot be conveniently determined independently) may be accomplished through the use of simultaneous equations, graphical methods, least-squares curve fitting, or combinations of these methods. The procedures available have been described and compared by Sullivan and Hindman (84), Rossotti and Rossotti (72, p. 213-221 and 83-117), and Fronaeus (39, p. 3-10). Konečný (55) has reviewed numerical-graphical methods for treatment of distribution data giving special attention to systems containing more than one extractable species.

The widespread availability of high-speed computers has greatly simplified the task of solving simultaneous equations in systems

containing more than 2 or 3 complexes, and has also given impetus to the solution of expressions for  $\phi$  such as that given in equation (9) (rearranged to polynomial form) through computer least-squares curve fitting. Such an approach was used by Varga and co-workers (94). Another article describing the application of least-squares computer calculations to extraction data is that of Rydberg and Sullivan (77).

One of the numerical-graphical methods recommended by Sullivan and Hindman (84) which is applicable to  $\phi, (A)$  data is the average ligand number method of Bjerrum. This procedure, which involves graphical differentiation of the distribution curve and (usually) solution of simultaneous equations, is described here because it further clarifies the relationship between complex formation and distribution data.

### Bjerrum's Average Ligand Number Method

#### General

The average ligand number,  $\bar{n}$ , is the average number of ligand ions bound to the central ion M in the aqueous phase; it will vary with ligand concentration. Use of the quantity  $\bar{n}$  is limited to systems which do not contain polynuclear or mixed complexes (including mixed hydroxy or weak acid species).

$$\bar{n} = \frac{\text{total concentration of bound ligand}}{C_M}$$

$$\bar{n} = \frac{(MA) + \dots j (MA_j) + \dots N(MA_N)}{(M) + (MA) + \dots (MA_j) + \dots (MA_N)} \quad (10)$$

Introducing the formation constants,

$$\bar{n} = \frac{\beta_1(M)(A) + \dots j\beta_j(M)(A)^j + \dots N\beta_N(M)(A)^N}{(M) + \beta_1(M)(A) + \dots \beta_j(M)(A)^j + \dots \beta_N(M)(A)^N} \quad (11)$$

(M) cancels out and the expression reduces to

$$\bar{n} = \frac{\sum_{j=1}^N j \beta_j(A)^j}{1 + \sum_{j=1}^N \beta_j(A)^j} \quad (12)$$

Relationship between  $\bar{n}$  and  $\phi$

The mathematical relationship between the average ligand number and the distribution ratio is derived by first taking the derivative of  $\phi$  with respect to (A), equation (9). Through manipulation and introduction of

$$\frac{d \log \phi}{d \log (A)} = \frac{(A) d \phi}{\phi d (A)}$$

the equation eventually reduces to this expression:

$$\bar{n} = n - \frac{d \log \phi}{d \log (A)} \quad (13)$$

where  $n$  is the ligand number of the extractable complex, which must be properly identified. Thus the average ligand number is simply the difference between  $n$  and the slope of the distribution curve at a particular value of  $(A)$ . The value of a positive slope may be considered to be the average number of ligands being added to complexes already existing at that value of  $(A)$  to form the extractable complex; correspondingly, a negative slope indicates the number of ligands being added to the extractable complex.

#### Computation of Formation Constants

Graphical differentiation of the smoothed distribution curve,  $\log \phi$  vs  $\log (A)$ , and knowledge of the ligand number of the extractable complex yields  $\bar{n}$  as a function of  $(A)$  by equation (13). Rearrangement of equation (12) leads to simultaneous equations of the type

$$\bar{n} + (\bar{n}-1)\beta_1(A) + \dots + (\bar{n}-j)\beta_j(A)^j + \dots + (\bar{n}-N)\beta_N(A)^N = 0 \quad (14)$$

which may then be solved for the formation constants. It is customary to take the  $(A)$  values at half-integral values of  $\bar{n}$ , e. g.  $n = 1.5$ ,  $2.5$  and so on; this spaces the values for a good representation of the formation function and simplifies the coefficients when the

simultaneous equations are solved by determinants.

A computer curve-fitting approach to the calculation of stability constants from the formation function has been described by Varga (91) as an improvement over the simple approach described above.

### Experimental Considerations of the Distribution Method

#### Control of Activity Coefficients

##### General

The goal of obtaining thermodynamic formation constants for stepwise complexes at infinite dilution, besides being difficult if not impossible to obtain for complicated systems, becomes rather meaningless when it is realized that many complexes do not exist in dilute solution. It has been recognized that variation of the ligand concentration over a wide range necessitates some means of minimizing changes in activity coefficients of the ligand and metal complexes. Thus most workers have settled for determination of concentration formation constants for a given medium containing an excess of non-complexing electrolyte, whose presence reduces the changes occurring in activity coefficients of lesser constituents.

While some investigators have kept the total ionic strength constant by adjusting the concentration of bulk electrolyte as the ligand concentration increases, in many experiments the simpler

method has been chosen of maintaining a constant concentration of the bulk electrolyte. Such an aqueous solution is referred to as a constant ionic medium or swamping medium, and is effective in limiting variations in activity coefficients. Brönsted (13) found that small changes in the concentration of solute had a negligible effect upon its activity coefficient, provided that its concentration was never comparable to that of the background salt. Tobias (85) claimed that the use of a constant ionic medium is more effective than maintaining a constant ionic strength; this contention has been also supported by Fomin (35).

Prue and Read (70), however, have pointed to the lack of experimental work on variations of activity coefficients under swamping conditions. They found that in at least one mixture of electrolytes, HCl and  $\text{NaClO}_4$ , the activity coefficient of HCl was better controlled under conditions of constant ionic strength. When the concentration of HCl was varied from 0-0.2 m in two different mixtures, one in which  $m_{\text{HCl}} + m_{\text{NaClO}_4} = 2.85$  and the other having a constant ionic medium  $m_{\text{NaClO}_4} = 2.85$ , the respective changes in the activity coefficient of HCl were 1.8% and 6%. Neither figure can be considered negligible.

Sodium perchlorate is probably the most popular ionic medium which has been used. Perchlorate ion has less tendency to participate in metal complex formation than do most other anions; however,

it cannot be used with metal ions which are powerful reducing agents. Perchloric acid or mixtures of  $\text{HClO}_4$  and  $\text{NaClO}_4$  may be used for systems requiring an acid medium. A number of studies have been carried out in 1.0 M perchlorate medium, although molarities of two, three, four or even higher have been employed for the study of weak complexes requiring a high ligand concentration. The 3.0 M perchlorate medium was recommended as a standard by Tobias (85).

Investigation by Choppin and co-workers (18) of the stability constant of  $\text{Eu}(\text{NO}_3)_2^{2+}$  in solutions of various nitrates and perchlorates at ionic strengths of 0.5 and 1.0 supports the contention that stability constants measured in one ionic medium should not be compared with those measured in another medium.

Other general considerations in the control of activity coefficients and the types of formation constants which may be obtained from complex systems have been discussed by Rossotti and Rossotti (72, p. 17-35) and Fomin (35).

#### Activity Coefficient Control in Extraction Systems

The control of activity coefficients in two-phase systems unfortunately has added complications. Since few solvent-aqueous solution pairs are completely immiscible, it becomes necessary to qualify formation constants to an even greater extent by stating that they have been determined for a given ionic medium which is saturated

with the specific solvent used. The requirement of a specific constant temperature becomes even more important. It must also be demonstrated that the mutual solubilities of the phases do not vary with ligand concentration or else changes in activity coefficients are to be expected.

While information on the significance and magnitude of activity coefficients in non-aqueous solvents is scarce, it is safe to assume that they also change with solute concentration. Control of organic activity coefficients presents a difficult problem, especially for systems in which the acid HA (used to provide the ligand A) is extractable. The composition of the organic phase then changes with variation of (HA). The perchlorate ion used to provide a constant ionic medium in the aqueous phase is extracted by a number of cationic extractants. Although sodium perchlorate is poorly extracted by oxygenated solvents, perchloric acid is easily extracted and may cause irregularities in distribution behavior of complex metal acids, as has already been mentioned.

In conclusion, the study of complex formation by the distribution method presents special problems in the control of activity coefficients, particularly in systems involving significant mutual solubilities of the phases and their constituents. The use of a constant ionic medium may not be sufficient to effectively control activity coefficients in such systems.

## Experiment Design

### Range of Free Ligand Concentration

One of the main considerations in the planning of complex formation studies is the desirability of varying the free ligand concentration over as wide a range as possible. This range is enhanced by the use of radioactive tracer metal, for the ligand concentration may be increased to higher levels without exceeding the solubility product of the uncharged complex; it may also be decreased to lower levels without a significant amount of ligand being involved in complexing with the metal (this simplifies the calculations if the free ligand concentration is determined indirectly and eliminates the need for accurate knowledge of the metal concentration). However, the ligand range may be limited by the useful range of the method used to determine the free ligand concentration.

If no second-order electrode is available for the specific anion, and if the ligand is the anion of a weak acid, its concentration may be indirectly determined by measurement of the hydrogen ion concentration when the acid dissociation constant for the appropriate medium and temperature is known.

### Range of Metal Concentration

The concentration of metal used is generally kept to a minimum consistent with the specific activity of the available radiotracer metal and the efficiency of the counting equipment; this is especially advisable in the study of metals which tend toward hydrolytic polymerization. Since a total of  $10^4$  counts is required for a standard deviation of 1% in the count rate of each portion of aqueous or organic phase, the metal concentration should be such as to provide for the attainment of this total count rate in a reasonable length of time for less active samples, while not exceeding the limit of resolution of the counter for the most active samples. Although Friedlander and Kennedy (38, p. 122) refer to "tracer concentrations" as reaching as low as  $10^{12}$  to  $10^{-15}$  M, it is sometimes necessary to increase the concentration to as high as  $10^{-5}$  M for metals of low specific activity; this in turn limits the lower end of the free ligand scale.

The use of low level tracer metal is often assumed to preclude formation of polynuclear species; however, this assumption should be checked by measuring  $\phi$  as a function of (A) at various  $C_M$ . If all distribution curves coincide this is generally interpreted to mean that polynuclear species are absent over that  $C_M$  range. If the curves do not coincide polynuclear complex formation is likely, although in special cases the behavior may be attributable to common ion

effects in high  $\epsilon$  solvents or formation of mixed ion aggregates in low  $\epsilon$  solvents.

### Acidity

The study of easily hydrolyzable metals requires an acid medium such as perchloric acid in order to repress hydrolysis. Again, it is advisable to test for the presence of hydrolytic species. If the extraction mechanism does not depend upon the presence of hydrogen ion, the function  $\phi[(A)]$  should not depend upon the hydrogen ion concentration in the absence of hydrolytic or weak acid species. However, it is not generally convenient to vary  $(H^+)$  greatly in systems in which the ligand is added to the solution through the weak acid HA. Rydberg (75) has suggested plotting  $\log \phi$  as a function of  $\log \left[ \frac{(HA)}{(H)} \right]$  at different (HA). If all the curves coincide, only simple complexes  $MA_j$  are formed. If the curves coincide at high values of  $\log \left[ \frac{(HA)}{(H)} \right]$  but not at low values, complexes of the type  $MA_j(OH)_p$  are formed. If the curves never coincide, complexes of the type  $MA_j(OH)_p(HA)_r$  are likely.

### Choice of Solvent

A solvent or extractant-diluent combination should be selected which gives measurable distribution ratios (generally in the range  $\phi = 10^{-3}$  to  $10^3$ ) over the range of free ligand concentration, and

which possesses other desirable characteristics, including a low miscibility with the aqueous phase and a density sufficiently different from water so that separation is easily accomplished. Another consideration is the dielectric constant; associations of ion pairs occur in solvents of low dielectric constant and the ion pairs themselves dissociate at least partially in solvents of dielectric constant above about ten, according to Dulova, Lichkova and Ivleva (27).

#### Determination of Extracted Complex Composition

The identity of the extracting metal complex is sometimes determined by analysis of the organic phase after equilibration to obtain the ligand:metal mole ratio. This ratio must be corrected for any excess ligand which extracts. Spectra of the organic phase are helpful in demonstrating the type of bonds involved in the complex.

A method which appears to be a favorite of Russian workers is the isomolar series method. This procedure apparently involves preparation of a series of aqueous phases of different ligand:metal mole ratios, such as 4:1, 5:1 and 6:1, which are then equilibrated with the organic solvent, and the optical density of the organic phase is measured to find which ratio results in the greatest extraction.

Information on the number of chelating or solvating molecules involved in the extracted complex may be obtained through measurement of the distribution ratio as a function of extractant concentration

in an inert diluent.

### Equilibration Procedure

#### Preparation of Samples

So that changes in composition and volume of the aqueous phase do not occur in the final equilibration, each phase is presaturated with the other. For the aqueous phase this involves addition of the appropriate amount of solvent as the phases are made up. The organic solvent is pre-equilibrated with fresh portions of the aqueous phase with which it is to be equilibrated; a knowledge of the extent of extraction of HA and of the supporting electrolyte is desirable in order to determine the number of pre-equilibrations necessary. Addition of radioactive tracer metal in the form of a small aliquot is generally delayed until equal volumes of aqueous phase and pre-equilibrated solvent are brought together in the equilibration sample.

#### Containers

Containers for the equilibration warrant some consideration. Glass offers the advantage that the interface is easily detectable, but some metals tend to hydrolyze out on glass surfaces; the use of glass is also precluded for fluoride systems. Polyethylene bottles are often used but are permeable to such solvents as benzene and

chloroform unless the equilibration time is very short. Teflon offers the greatest chemical resistance but its opacity renders separation of phases more difficult.

### Equilibration

Equilibrations are carried out in a bath or room of constant temperature, usually 25°C. Shaking insures more rapid, complete extraction. While many extractions are complete within a few minutes, that of chelates may require a longer period. After the equilibration period the samples are sometimes centrifuged to hasten a clean separation of the phases. Aliquots of both phases are then removed for counting, and the free ligand concentration of the aqueous phase is measured.

### Measurement of the Distribution Ratio

For radionuclides which are mixed beta-gamma emitters, scintillation counting of the gamma radiation offers definite advantages. Aliquots of the liquids may be counted without corrections for self-absorption and scattering; use of a well counter increases the liquid volume which may be counted and also the counting efficiency.

Pure beta emitters are usually counted as thin solid samples obtained through evaporation of the liquids, using a thin-window counter. Reproducibility may be a problem due to self-absorption

and scattering effects, for which corrections must be applied.

Due to the low resolving time of modern counters, counting rates of at least  $10^5$  cpm may often be handled without coincidence loss. At the other extreme, the minimum count rate distinguishable above background is about 10 cpm; however, the time required to accumulate enough total counts to obtain any measure of precision is prohibitive. Therefore a more realistic lower limit is approximately  $10^2$  cpm. The distribution ratio, then, may range from values of about  $10^{-3}$  to  $10^3$ .

## THE LITERATURE OF TANTALUM (V) FLUORIDES

General

Although tantalum itself is decidedly metallic, its V oxidation state chemistry, like that of niobium, resembles that of nonmetals. Tantalum forms few cationic complexes; most of its chemistry is anionic in nature. Oxides, oxyhalides and halides constitute the most important simple compounds, and these have been studied much more extensively in the solid state than in solution.

The most commonly known fluorides and oxyfluorides are  $\text{TaF}_5$ ,  $\text{TaOF}_3$ , and salts of  $\text{TaOF}_5^{2-}$ ,  $\text{TaOF}_6^{3-}$ ,  $\text{TaF}_6^-$ ,  $\text{TaF}_7^{2-}$  and  $\text{TaF}_8^{3-}$ . In addition, Buslaev and Kokunov (15) have prepared the compound  $\text{CsTaOF}_4$ , and  $\text{Na}_2\text{TaF}_7 \cdot \text{H}_2\text{O}$  has been described by Balke (8) and Eberts and Pink (29). Solid phases in the  $\text{TaF}_5$  ( $\text{Ta}_2\text{O}_5$ )- $\text{H}_2\text{O}$  system observed by Buslaev and Nikolaev (16) included  $\text{HTa}_2\text{F}_{11} \cdot 4.5 \text{H}_2\text{O}$  and  $\text{HTaF}_6 \cdot 1.5 \text{H}_2\text{O}$ . Repeated evaporations of  $\text{K}_2\text{TaF}_7$  with water result in the formation of insoluble  $\text{K}_4\text{Ta}_4\text{O}_5\text{F}_{14}$  (Marignac's salt), according to Ruff and Schiller (74).

Electrical conductivity studies of molten  $\text{TaF}_5$  carried out by Fairbrother, Frith and Woolf (31) indicated partial ionization of  $\text{TaF}_5$  to  $\text{TaF}_6^-$  and  $\text{TaF}_4^+$ . Fairbrother, Grundy and Thompson (32) found that  $\text{TaF}_5$  forms colored adducts, such as  $\text{TaF}_5 \cdot \text{Et}_2\text{O}$ ,  $\text{TaF}_5 \cdot 2\text{Me}_2\text{O}$  and  $\text{TaF}_5 \cdot \text{Me}_2\text{O}$ , with various donor ligands.

## Tantalum Coordination in the Solid State

It is evident from the above observations that tantalum exhibits various coordination numbers with respect to fluoride in the solid state. The structure of some compounds has been investigated by techniques of x-ray diffraction and infrared and Raman spectroscopy, establishing the existence of coordination numbers six through eight.

### Six-Coordination

Keller and Chetham-Strode (54) found the Raman spectrum of solid  $\text{CsTaF}_6$  to be consistent with the octahedral structure for  $\text{TaF}_6^-$  suggested by Hoard and Vincent (48); thus the salt contains  $\text{TaF}_6^-$  ions showing a tantalum coordination number of six.

### Seven-Coordination

Two seven-coordinated species of tantalum have been investigated. Surprisingly, they possess different structures. Hoard's X-ray studies of the  $\text{TaF}_7^{2-}$  ion in  $\text{K}_2\text{TaF}_7$  (47) showed it to have approximately  $C_{2v}$  symmetry, while Keller and Chetham-Strode (54) found the Raman spectrum of  $\text{TaOF}_6^{3-}$  ion to be very similar to that of  $\text{NbOF}_6^{3-}$  whose cubic holohedral ( $C_{3v}$ ) symmetry had been established by Williams and Hoard (100) using X-ray methods.

### Eight-Coordination

The  $\text{TaF}_8^{3-}$  ion in  $\text{Na}_3\text{TaF}_8$  has the structure of a square Archimedian antiprism, according to the X-ray data of Hoard and co-workers (49). This assignment has been confirmed by infrared and Raman studies of crystalline  $\text{Na}_3\text{TaF}_8$  conducted by Hartman and Miller (46).

### Tantalum Coordination in Aqueous Solution

The question of possible coordination states of tantalum in aqueous solution is basic to an understanding of the aqueous complex chemistry of tantalum. On the basis of limited information available up to the present time, it appears likely that in fluoride solutions tantalum may have coordination numbers of six, seven, eight and possibly even nine.

Studies of tantalum fluoride complexation in aqueous solution by Varga and co-workers (92, 93, 94) have indicated the existence of mononuclear complexes of fluoride number three through nine. However, their data do not preclude the likelihood of some of the lower species being present as hydrates.

Lassner and Püschel (56) have presented a detailed case for a single tantalum coordination number of eight in aqueous solution, but their presentation neglected the important work of Keller and Chetham-Strode (54). The latter authors found the Raman spectra of aqueous

Ta-HF-NH<sub>4</sub>F solutions to be closely comparable to those of solid CsTaF<sub>6</sub> and K<sub>2</sub>TaF<sub>7</sub>. This correspondence strongly indicates that the structures, and therefore coordination states, of aqueous TaF<sub>6</sub><sup>-</sup> and TaF<sub>7</sub><sup>2-</sup> are unchanged from the solid state.

### Hydrolysis of Tantalum in Fluoride Solutions

Most of the work that has been done on hydrolysis of tantalum has involved a comparison with the behavior of niobium. The evidence is convincing that the tendency of tantalum toward hydrolysis in fluoride solutions is much less pronounced than that of niobium. The oxyfluorides of tantalum seem to be less stable than the fluorides, while the reverse is true for niobium.

While NbF<sub>5</sub> reacts with water upon contact, forming NbOF<sub>3</sub> or H<sub>2</sub>NbOF<sub>5</sub>, TaF<sub>5</sub> is soluble in water without immediate hydrolysis (51, p. 210).

According to Schäfer (78) the compositions of solid phases in equilibrium with HF solutions differ for niobium and tantalum. As the HF concentration increases the solid phase in equilibrium with solutions of tantalum soon changes from K<sub>4</sub>Ta<sub>4</sub>O<sub>5</sub>F<sub>14</sub> to K<sub>2</sub>TaF<sub>7</sub>, while the solid phase in equilibrium with niobium solutions has the composition K<sub>2</sub>NbOF<sub>5</sub> · H<sub>2</sub>O throughout much of the HF range, finally changing to K<sub>2</sub>NbF<sub>7</sub> at a considerably higher HF concentration than was required to form K<sub>2</sub>TaF<sub>7</sub>.

Allan and Gahler (5), in a study of the near-infrared absorption of HF in solutions containing  $\text{TaF}_5$  and  $\text{NbF}_5$ , found that in HF solutions of below about 5 N the HF concentration increased when  $\text{NbF}_5$  was dissolved in the solutions. This phenomenon was attributed to formation of one or more soluble niobium oxyfluoride complexes with consequent release of fluoride ion, resulting in additional HF. Increase of HF concentration upon addition of  $\text{TaF}_5$  occurred over a much narrower range of initial HF concentration; in most of the solutions the effect was to decrease the HF concentration indicating formation of anionic fluorotantalum species.

The potentiometric  $\text{H}^+$  ion data of Varga and Freund (92) indicated that no appreciable hydrolysis of tantalum occurred when the ratio of total acid molarity (stoichiometric sum of hydrofluoric and perchloric acids present) to tantalum molarity exceeded about 150.

In Raman studies of  $\text{HF-NH}_4\text{F}$  solutions approximately 1 M in tantalum, Keller and Chetham-Strode (54) found no evidence for oxyfluorotantalum species except in solutions containing a low HF concentration (near 0 M) along with a high  $\text{NH}_4\text{F}$  concentration (5-9 M). They concluded that the oxyfluorotantalate disappears at about 0.1 M HF, leaving simple fluoro complexes of tantalum. By contrast, Keller (53) had found evidence for  $\text{NbOF}_5^{2-}$  ion in solutions of up to 19 M HF.

### Polymerization of Tantalum in Fluoride Solutions

Available data suggest that mononuclear complexes of tantalum predominate in solutions containing an appreciable excess of fluoride concentration over tantalum, although the total acidity is probably also a factor. This is not surprising in view of the foregoing discussion on hydrolysis, for while hydrolysis may occur without polymerization, the reverse does not appear to be true. Hydrolytic species are considered to be a prerequisite to the formation of Ta-O-Ta bonds present in polynuclear complexes.

Babko and Gridchina (7) used the method of dialysis to study polymerization in alkaline and HCl solutions of tantalum. Large poly-ions occurred in these solutions even at 11 N HCl. However, the dialysis coefficient increased upon addition of HF and reached a maximum at an HF:Ta molar ratio of 20 (at a metal concentration of  $2.5 \times 10^{-3}$  M) indicating complete depolymerization.

A similar electro dialysis study conducted by Nabivanets (66) indicated that partial decomposition of polynuclear species begins when the ratio of fluoride to tantalum reaches 2:1 in solutions of 0.5 N HCl and  $2.5 \times 10^{-3}$  M Ta. Monomeric, anionic tantalum fluoride complexes were formed upon further addition of HF.

No evidence was found by Djordjević (24) for polynuclear tantalum species in solutions containing  $10^{-6}$  to  $10^{-4}$  M tantalum,

0.2 M oxalate and HF concentrations of 0.04 and 0.4 M. The distribution ratio of tantalum with three different long-chain amine extractants was not a function of metal concentration; infrared spectra of the organic phases did not contain lines due to a Ta-O-Ta bridging vibrational absorption.

### Formation of Tantalum Fluoride Complexes

The identity of fluoride complexes of tantalum in aqueous solution has been the subject of few rigorous investigations.

#### Raman Spectroscopy Method

The Raman studies of Keller and Chetham-Strode (54) established that within the range of concentrations investigated the predominant tantalum species in Ta-HF-NH<sub>4</sub>F solutions were TaF<sub>6</sub><sup>-</sup> and TaF<sub>7</sub><sup>2-</sup>. TaF<sub>7</sub><sup>2-</sup> is the more stable complex as it was found to be present in all the solutions examined; TaF<sub>6</sub><sup>-</sup> was replaced by TaF<sub>7</sub><sup>2-</sup> as NH<sub>4</sub>F was added.

### Discussion

Unfortunately the probable range of free fluoride concentrations in these solutions cannot be readily estimated from the relatively high concentrations of HF (~0-24 M) and of NH<sub>4</sub>F (0-11 M). The use of such large concentrations of fluoride was occasioned by

the necessity of using up to 1 M tantalum to make Raman lines detectable. Because the activity of water and the ionic activity coefficients of tantalum species are bound to be significantly affected at the higher fluoride concentrations, and because of the uncertainty in the lower limit of fluoride concentration (0-0.5 M HF), there is some question whether the range of concentrations included conditions favorable to the formation of species either higher or lower than  $\text{TaF}_6^-$  and  $\text{TaF}_7^{2-}$ . At the same time, however, an unidentified line (thought to originate from a simple fluoro complex) appearing in the spectra of the least concentrated fluoride solutions may reasonably have been due to hydrated  $\text{TaF}_5$ , if not to a mixed hydroxy-fluoro species.

#### Formation Constants of Tantalum Fluoride Complexes

The only quantitative studies of stabilities of tantalum fluoride complexes have been made by Varga and co-workers.

##### 1.0 M Perchlorate Medium

Studies in an acid 1 M perchlorate medium containing from  $10^{-5}$  to  $5 \times 10^{-3}$  M free fluoride were carried out by Varga and Freund (92). The presence of  $\text{TaF}_4^+$ ,  $\text{TaF}_5$  and  $\text{TaF}_6^-$  was inferred from cation and anion exchange data using tracer concentrations of tantalum. Potentiometric  $\text{H}^+$  ion studies at about millimolar tantalum concentrations suggested the existence of the species  $\text{TaF}_6^-$ ,

$\text{TaF}_7^{2-}$ ,  $\text{TaF}_8^{3-}$  and  $\text{TaF}_9^{4-}$  and indicated that hydrolytic and polynuclear species of tantalum were absent when the ratio of total acid concentration to metal concentration exceeded about 150. Tantalum electrode potential data (93) supported the formation of tantalum fluoride complexes up to and including  $\text{TaF}_9^{4-}$ .

The average ligand number method of Bjerrum was chosen for mathematical treatment of the data. The average ligand number,  $\bar{n}$ , was determined as a function of  $(\text{F}^-)$  for the anion exchange and potentiometric  $\text{H}^+$  ion data. With the assistance of a high-speed computer, simultaneous equations of the type (14) described in the previous section were solved by determinants, and through a process of trial and error the set of positive formation constants was found which best fit the experimental data.

The stepwise formation constants given for the 1 M perchlorate medium at 25°C were as follows:

$$k_5 = \frac{(\text{TaF}_5)}{(\text{TaF}_4^+) (\text{F}^-)} = 6.47 \times 10^4$$

$$k_6 = \frac{(\text{TaF}_6^-)}{(\text{TaF}_5) (\text{F}^-)} = 4.13 \times 10^3$$

$$k_7 = \frac{(\text{TaF}_7^{2-})}{(\text{TaF}_6^-) (\text{F}^-)} = 2.20 \times 10^3$$

$$k_8 = \frac{(\text{TaF}_8^{3-})}{(\text{TaF}_7^{2-})(\text{F}^-)} = 9.39 \times 10^2$$

$$k_9 = \frac{(\text{TaF}_9^{4-})}{(\text{TaF}_8^{3-})(\text{F}^-)} = 3.73 \times 10^3$$

### 3 M Perchlorate Medium

A second study of tantalum fluoride complexation was conducted by Varga and co-workers (94), this time in 3 M  $\text{HClO}_4$  to further reduce the possibility of hydrolytic polymerization. The method of solvent extraction was used incorporating data from three different types of extractant; radioactive tracer concentrations of tantalum were employed. Free fluoride ion concentrations varied from  $2 \times 10^{-7}$  to  $2.5 \times 10^{-4}$  M; the range was considerably lower than that covered in the 1 M perchlorate studies because of the higher acidity.

The distribution curve of tantalum fluoride with N-benzoylphenylhydroxylamine (BPHA) in chloroform was interpreted as indicating the presence of  $\text{TaF}_4^+$ ,  $\text{TaF}_5$ ,  $\text{TaF}_6^-$  and  $\text{TaF}_7^{2-}$ . Extractions with tri-n-octylphosphine oxide (TOPO) in  $\text{CHCl}_3$  gave evidence for the species  $\text{TaF}_3^{2+}$ ,  $\text{TaF}_4^+$  and  $\text{TaF}_5$ . The extractant methyl isobutyl ketone (MIBK) gave results consistent with the existence of  $\text{TaF}_5$ ,  $\text{TaF}_6^-$  and  $\text{TaF}_7^{2-}$ .

Least-squares curve fitting with the aid of a computer was

utilized for calculation of the formation constants. Mathematical models similar to equation (9) of the previous section were set up for each of the extraction systems and the computer used to search for the formula of the extractable complex and for the formation constants which best fit the  $\phi$ , ( $F^-$ ) data and were consistent with results obtained from the other extraction systems.

Overall formation constants obtained for the 3 M  $HClO_4$  medium at 25°C were:

$$\beta_4 = \frac{(TaF_4^+)}{(TaF_3^{2+})(F^-)} = (7.3 \pm 2.1) \times 10^5$$

$$\beta_5 = \frac{(TaF_5)}{(TaF_3^{2+})(F^-)^2} = (5.9 \pm 2.0) \times 10^{10}$$

$$\beta_6 = \frac{(TaF_6^-)}{(TaF_3^{2+})(F^-)^3} = (4.7 \pm 1.4) \times 10^{15}$$

$$\beta_7 = \frac{(TaF_7^{2-})}{(TaF_3^{2+})(F^-)^4} = (1.4 \pm 0.6) \times 10^{20}$$

These formation constants revealed considerably greater stabilities than those observed for the tantalum fluoride complexes in 1 M perchlorate; no explanation was offered.

Formation constants combining the results from 1 M and 3 M perchlorate media have also been published by Varga (91).

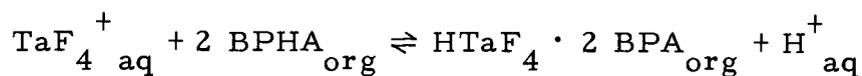
## Solvent Extraction of Tantalum Fluoride Complexes

Solvent extraction methods for the analytical and commercial separation and determination of tantalum and niobium have been reviewed by Moshier (65, p. 67-92) and Kallmann (51, p. 192, 263-269). Mention here is limited to those systems for which the extraction mechanism or composition of the extractable complex has been investigated. Extraction systems are classified according to the scheme of Diamond and Tuck (23).

### Pseudomolecular Compounds

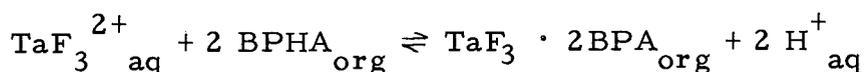
#### N-Benzoylphenylhydroxylamine

The extraction of tantalum fluorides from 3 M HClO<sub>4</sub> into CHCl<sub>3</sub> through the chelating action of BPHA was studied by Varga and co-workers (94). The F:Ta mole ratio in the organic phase after equilibration was determined to be 3.8 ± 0.1. This ratio was consistent with computer analysis of the distribution data indicating HTaF<sub>4</sub> · 2BPA to be the most probable formula of the extracting species. The reaction for the extraction equilibrium was postulated as follows:



with  $K_{\text{BPHA}} = (1.25 \pm 0.27) \times 10^8$ .<sup>1</sup>

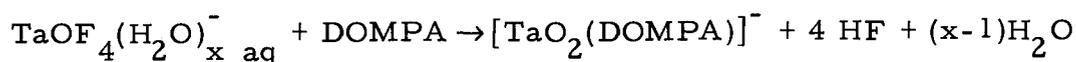
In 4 to 5 M  $\text{HClO}_4$ , however, Erskine, Sink and Varga (30) found the best extraction model to be  $\text{TaF}_3 \cdot 2\text{BPA}$ :



with  $K = 2.0 \times 10^{10}$ .

### Diocetyl Methylene bis (Phosphonic acid)

Experiments with a chelate phosphoryl agent, DOMPA, by Djordjević and Gorican (25) led them to propose, from the dependence of distribution upon the reagent and fluoride concentration, the following mechanism for the extraction:



The maximum extraction was observed at low HF concentration, 0.02-0.05 N. The extracting species isolated from the organic phase was found to be polymeric.

### Coordinately Unsolvated Salts

#### Tetraphenylarsonium Ion

Alimarin and Makorova (4) reported that tantalum fluoride

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<sup>1</sup>K is the notation used by Varga for the extraction equilibrium constant. In the present work this type of constant is considered to be a modification of the distribution coefficient and thus has the designation  $\lambda$ .

could be extracted from sodium fluoride solutions by tetraphenylarsonium chloride, probably in the form of  $C_6H_5As(TaF_6)$  ion pairs. The complex was extractable into dichloroethane and chloroform, but not into benzene and carbon tetrachloride.

### Large Cationic Dyes

An investigation of crystal violet fluorotantalate extraction by the same authors (3) showed fluorotantalum species, under conditions of  $(Ta) = 0.7 \times 10^{-5}$  M and a pH of 2 (acidity supplied by sulfuric acid) to be best extracted at a crystal violet concentration of  $3 \times 10^{-4}$  M and 0.05 M sodium fluoride. In contrast to the view expressed by Diamond and Tuck (23, p. 140), that ion pairs of this type should be better extracted by solvents of higher dielectric constant, Alimarin and Makorova found no relation between the dielectric constant of a solvent and its ability to extract the crystal violet-fluorotantalum complex. The best solvents were chloro-substituted hydrocarbons: chloroform, dichloroethane and chlorobenzene.

In a later study on the mechanism of extraction of fluorotantalate by crystal violet and other basic dyes (butylrhodamine, Rhodamine 3B and Rhodamine 6G), Makorova and Alimarin (58) established that the spectra of these dyes extracted as fluorotantalates are identical to the spectra of solution of dyes present as singly charged cations. Thus it was concluded that a 1:1 complex is formed between

the large dye cation and the fluorotantalum species; the identity of the latter was assumed to be  $\text{TaF}_6^-$ .

### Amine Extractants

Some long chain amine type extractants for tantalum and niobium were investigated by Djordjević (24) and Djordjević and Sevdic (26). Included were trioctylamine, dioctylaminobutanone, and di-n-octylaminopropanol; however, the extraction studied most thoroughly was that involving di-n-octylaminoethanol (DOAE) in chloroform.

Extractions were carried out from aqueous solutions containing approximately  $10^{-5}$  M metal and three different concentrations of hydrofluoric acid: 0.04, 0.4 and 1 M. Distribution ratios were highest from the 0.04 M HF solution; infrared spectra of the organic phase showed the presence of a Ta=O bond and an analysis of the organic phase residue corresponded to a formula of  $(\text{DOAEH})(\text{TaOF}_4)$ . At 0.4 M HF, however, an analysis of the species extracted agreed well with an equimolar mixture of  $(\text{DOAEH})(\text{TaOF}_4)$  and  $(\text{DOAEH})_2(\text{TaF}_7)$ . From organic phases in equilibrium with 1 M HF, substances corresponding to the formula  $(\text{DOAEH})_2(\text{TaF}_7)$  were isolated. It was pointed out that the analytical data from 0.4 M and 1 M HF systems could also be due to mixtures of two or more extracting species containing an excess of free extractant; the picture is also complicated by the extraction of HF, probably as  $(\text{DOAEH})(\text{HF}_2)$ .

## Complex Metal Acids

### Cyclohexanone Extraction

The extraction of tantalum from HF and  $H_2SO_4$ -HF solutions into cyclohexanone was investigated by Goroschenko, Andreava and Babkin (44). On the basis of studies of the F:Ta ratio during re-extractions of tantalum from the organic phase by water, it was concluded that tantalum is extracted from HF by cyclohexanone in the form of  $H_2TaF_7$  and from aqueous  $H_2SO_4$ -HF media as a mixed sulfato-fluoro complex,  $H_2TaF_x[(SO_4)_{\frac{1}{2}}]_{(7-x)}$ . However, a more recent study of the cyclohexanone extraction by Babkin and Goroschenko (6) established that complexes extracted from solutions of the composition 2.5 M  $H_2SO_4$ , 1 M  $(NH_4)_2SO_4$ , 2.3 M Nb, 0.5 M Ta and varying amounts of HF contained six fluoride ions, no sulfate ions and one to four molecules of cyclohexanone per metal atom (Ta or Nb). The F:Ta mole ratio of six was deduced from analysis of the organic phase, with correction of fluoride content for the amount of HF extracted in a blank experiment, and agreed with results obtained from the isomolar series method.

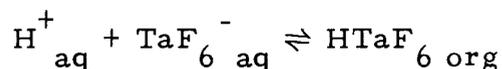
### Furfural Extraction

Chufarova and Petunina (19) studied the extraction of tantalum

and niobium fluorides by furfural, a heterocyclic aldehyde. The dependence of the extraction upon furfural concentration in an inert diluent showed four molecules of furfural to be involved in the extracting species. The F:Ta ratio during re-extraction of organic phases by water indicated that the extracting fluorotantalum complexes were  $\text{HTaF}_6$  and  $\text{H}_2\text{TaF}_7$ .

#### Methyl Isobutyl Ketone Extraction

The extraction of fluorotantalum species from 3 M  $\text{HClO}_4$  by methyl isobutyl ketone, MIBK, proceeds according to the following equilibrium according to Varga and co-workers (94):



with  $K_{\text{MIBK}} = 5.00 \pm 0.21$  for the extraction.

The F:Ta mole ratio in the organic phase after equilibration was determined by analysis to be  $6.1 \pm 0.2$ , and the extraction of  $\text{TaF}_6^-$  was in agreement with the distribution data as subjected to computer analysis and correlated with results using other extractants.

#### Discussion

The general consensus of the above results is that  $\text{TaF}_6^-$  is probably extracted by oxygenated solvents of this classification from

moderately high acid media (3-5 N) and is paired in the organic phase with the hydrated and solvated hydrogen ion, thus the reference to extraction of  $\text{HTaF}_6$ .

The report of Chufarova and Petunina (19) that  $\text{H}_2\text{TaF}_7$  is also extracted by furfural is not considered conclusive in view of the fact that the re-extraction data of Goroschenko, Andreava and Babkin (44) proved to be misleading. While it is possible that  $\text{H}_2\text{TaF}_7$  is extracted from systems containing very high acid concentrations, this has yet to be established.

In a recent article describing the industrial extraction and recovery of tantalum, Alexander (2) assumed  $\text{H}_2\text{TaF}_7$  to be the species extracted by MIBK but gave no supporting references. Such assumptions appear to be based upon evidence that  $\text{TaF}_7^{2-}$  is the predominant fluorotantalum complex in aqueous solution. Schäfer (78), for example, deduced (from the composition of solid phases in equilibrium with HF solutions of tantalum and niobium) that  $\text{TaF}_7^{2-}$  and  $\text{NbOF}_5^{2-}$  were virtually the only species present over a wide range of fluoride concentration; thus the fact that niobium was poorly extracted by ketones in this range was apparently due to the oxygen content of  $\text{NbOF}_5^{2-}$ . If, however,  $\text{TaF}_6^-$  and  $\text{NbF}_6^-$  are the primary extracting species as suggested by the most reliable results to date, then the nonextraction of  $\text{NbOF}_5^{2-}$  may be at least as much a consequence of its double charge as of its oxyfluoro character.

## Coordinately Solvated Salts

Tributyl Phosphate

Several studies have been made on the extraction of tantalum fluorides by tributyl phosphate (TBP), and it is in this system that the greatest variety of formulae for extracting species have been postulated. Giganov, Ponomarev and Khan (41) first determined the extracting species to be  $H_2TaF_7 \cdot 2TBP$ , but later also reported  $HTaF_6 \cdot 3TBP$  (42); Giganov and Ponomarev (40) found evidence for  $HTaF_6 \cdot 3TBP$  and  $H_2TaF_7 \cdot 3TBP$ . Nishimura, Moriyama and Kushima (68) reported the same formulae as the latter authors with some additional speculations; it was their opinion that weak acid species are present in the aqueous phase and that  $H_3TaF_8$  exists in solutions of high HF concentration (above 9 N).

Baram, Kaplan and Laskorin (9), in a more recent attempt to clarify the TBP extraction picture, found that at high concentrations of tantalum the number of TBP molecules in the extracted species is two, whereas at low and trace tantalum concentrations the number rises to three or four. The composition of the extracted fluorotantalum complex may also vary according to the conditions.

Diluents for TBP in the above studies included kerosene and benzene.

Tri-n-Octylphosphine Oxide

The results of Varga and co-workers (94) indicated that perchlorate ion participates in the extraction of fluorotantalum complexes by chloroform solutions of TOPO, which has stronger basic properties than does tributyl phosphate. Independent experiments on the variation of distribution with TOPO concentration in cyclohexane suggested that one to two molecules of TOPO are involved in the extraction. For extraction from aqueous 3 M  $\text{HClO}_4$  the following equilibrium was considered probable:



with  $K_{\text{TOPO}} = (1.00 \pm 0.26) \times 10^4$  for  $m=2$ .

## PRELIMINARY AND LARGE CATION EXTRACTIONS

Miscellaneous Extraction Attempts

## Non-Polar Solvents

At the onset of this work the expectation was that a suitable solvent could be found to extract the neutral complex  $\text{TaF}_5$  from aqueous solution. Aqueous phases containing  $\text{HClO}_4$  and HF in such concentration as would be expected, according to the work of Varga and Freund (92), to result in the formation of  $\text{TaF}_5$  were prepared. Portions were spiked with  $^{182}\text{Ta}$  tracer solution and equilibrated with equal volumes of three "inert" solvents: chloroform, cyclohexane and benzene.

When the radioactivity of aliquots of both phases was assayed, no significant amount of tantalum was found to be present in any of the organic phases. It is not clear whether the failure of these solvents to extract  $\text{TaF}_5$  is an indication that this species does not exist in aqueous solution, for other factors may inhibit its extraction. For example, tantalum may have a minimum coordination number of six in aqueous solution, so that  $\text{TaF}_5$  would be present as the hydrate and thus extract poorly.

### Preliminary Extractions with Methyl Isobutyl Ketone

Although methyl isobutyl ketone (MIBK) was known to be a successful extractant for tantalum fluoride, the mechanism for the extraction had not been elucidated. Preliminary extraction runs at total acid concentrations of 1.0 and 0.5 M and varying tantalum concentrations revealed the distribution to be markedly dependent on acidity. Since it could not be ascertained whether this dependence was due to the extraction mechanism or to the presence of hydrolytic or weak acid species of tantalum, other extractants known to be independent of acidity were sought in order to clarify the situation. Later, of course, it was established that the extraction mechanism in systems of this type involves a hydrated and solvated proton as the cationic portion of the extracted complex; thus the distribution is dependent upon the hydrogen ion concentration regardless of the existence of hydrolytic or weak acid metal species.

### Sodium Tetrphenylborate

It was thought that the large anion tetrphenylborate could be used to extract the complex  $\text{TaF}_4^+$  whose existence had been indicated by the cation exchange work of Varga and Freund (92). Attempts to extract tantalum into chloroform from aqueous HF solution in the presence of 1.0 M  $\text{HClO}_4$  and a small amount of sodium

tetraphenylborate failed. It was learned that the acid medium necessary to control hydrolysis of tantalum causes decomposition of tetraphenylborate (22).

#### Extraction by Tetraphenylarsonium Ion and Crystal Violet

Attempts to extract tantalum fluoride with large cationic extractants met with somewhat greater success. The extraction of tantalum from fluoride solutions, probably as  $\text{TaF}_6^-$ , by tetraphenylarsonium chloride and the cationic dye crystal violet had been reported by Alimarin and Makarova (3, 4) and appeared to have possibilities for the study of complex formation.

The distribution of tetraphenylarsonium ion (TPA) was found to be independent of pH by Bock and Beilstein (11) who studied the extraction of a number of anions into chloroform by the large cation. Perchlorate ion, with a distribution ratio of over 200, was one of those best extracted. This fact made it impossible to control activity coefficients through the use of a 1.0 M perchlorate medium during TPA distribution studies. Trial extractions from such a medium with  $(\text{Ta}) \leq 5 \times 10^{-7}$  M and  $(\text{TPA}) = 10^{-4}$  to  $10^{-5}$  M in chloroform showed that the extraction of tantalum fluoride was completely repressed by the large excess of perchlorate. The other large cation, crystal violet, was expected to behave in the same manner with regard to perchlorate ion.

Some effort was made to find a suitable ionic medium other than perchlorate to control activity coefficients in the aqueous phase during investigations with these extractants. Of the more than 25 anions whose extraction behavior with TPA had been studied by Bock and Beilstein, however, each had one or more drawbacks precluding its use as a swamping medium. Those anions which did not extract well into chloroform either formed water-insoluble precipitates with TPA or were expected to participate in the formation of complexes with tantalum.

A rigorous study of tantalum fluoride complexation using large cationic extractants was therefore abandoned; however, several runs of a less quantitative nature were carried out. Aqueous phases for each run consisted of a series of HF solutions of increasing concentration, to which small aliquots of radioactive  $^{182}\text{Ta}$  tracer and of TPA or crystal violet stock solutions were added. Equilibration with equal volumes of chloroform (usually pre-equilibrated) was followed by radioactive counting of aliquots of both phases to determine the distribution ratio. Determination of the change in distribution upon increasing the tantalum or extractant concentration was facilitated by using the same equilibration samples two or three times; they were spiked with additional reagent following removal of aliquots for counting and were again equilibrated.

## Experimental

### Reagents

#### Hydrofluoric Acid Solutions

Stock hydrofluoric acid solutions approximately 0.01, 0.1, 1 and 5 N in HF were diluted from reagent grade 48% HF (Baker and Adamson) and stored in new polyethylene bottles. The HF concentrations of these solutions were determined by titration with 0.01, 0.1 or 1 N carbonate-free sodium hydroxide (standardized against potassium biphthalate) using phenolphthalein as indicator.

In addition, three less concentrated HF solutions were prepared by successive tenfold dilutions of the approximately 0.01 N solution.

#### $^{182}\text{Ta}$ Stock Solutions

Processed  $^{182}\text{Ta}$  tracer from Oak Ridge National Laboratory was received in the form of tantalate in 0.92 N KOH solution. The tantalum content of the solution was 1.3 mg/ml and the specific activity was 4538 mc/g tantalum at the time of shipping. The solution, received in a polyethylene bottle to avoid adsorption on glass, was found to contain a tantalate precipitate. Most of the tantalum had hydrolyzed out of solution as the supernatant liquid was low in radioactivity.

A known amount of hydrofluoric acid was added to the tantalate solution, dissolving most of the precipitate; a portion of the resulting solution was diluted with water to give a stock  $^{182}\text{Ta}$  solution approximately  $3 \times 10^{-4}$  M (or less) in Ta and  $2.4 \times 10^{-2}$  M in total fluoride. Small aliquots (generally 0.025 ml) of this solution, designated  $\text{Ta}_B$ , were added to aqueous phases via glass micropipet.

In the meantime, further precipitation occurred in the original tantalum solution requiring addition of more HF. The stock solution  $\text{Ta}_C$  resulting from this addition consisted of  $3 \times 10^{-4}$  M Ta (or less) and  $3.9 \times 10^{-2}$  M fluoride; it was used to spike aqueous phases when the supply of solution  $\text{Ta}_B$  was exhausted.

The fluoride concentration added to 15.0 ml of aqueous phases by 0.025-ml aliquots of solutions  $\text{Ta}_B$  and  $\text{Ta}_C$  was from 4.0 to  $6.5 \times 10^{-5}$  M, and was included in the total HF concentration.

#### Extractant Stock Solutions

Considering the approximate character of these studies and the tedious procedure required to convert tetraphenylarsonium chloride and crystal violet (hexamethyl rosaniline chloride) into the corresponding fluorides, it was decided to leave the extractants in the chloride form throughout most of the runs. However, the range of aqueous phase extractant concentration ( $10^{-5}$  to  $2 \times 10^{-4}$  M) overlapped with the range of free fluoride ion concentrations

(approximately  $6 \times 10^{-5}$  to  $2 \times 10^{-2}$  M). Thus at the low end of the fluoride scale the formation of mixed chloro and fluoro tantalum species appeared possible. Because of this factor it was thought advisable to carry out an additional run in the absence of chloride, using tetraphenylarsonium perchlorate as the extractant.

Tetraphenylarsonium chloride stock solutions. Tetraphenylarsonium chloride dihydrate (reagent grade, 99% purity) was obtained from K & K Laboratories. For convenience in varying the aqueous phase TPA concentration, three stock solutions of TPA chloride were prepared:

0.0138 g  $(C_6H_5)_4AsCl \cdot 2H_2O$ /10.0 ml  $H_2O$ , or  $3 \times 10^{-3}$  M

0.1364 g/10.0 ml or  $3 \times 10^{-2}$  M

0.6825 g/10.0 ml or 0.15 M

Aliquots (0.025-0.050 ml) of these stock solutions were added to 15.0 ml of aqueous phases to obtain the desired concentration of TPA.

Crystal violet stock solution. A 0.3% solution of Fisher Certified crystal violet, corresponding to a molarity of approximately  $7.4 \times 10^{-3}$ , was made by dissolving 0.0302 g of the dye in 10.0 ml water. An attempt to prepare a 3% solution failed as the material did not completely dissolve. Hence it was necessary to add larger aliquots (0.3 ml) of 0.3% stock to equilibration samples to substantially increase the crystal violet concentration after the first series.

The values of aqueous phase HF concentrations were adjusted accordingly.

Tetraphenylarsonium perchlorate. Tetraphenylarsonium perchlorate was prepared according to the method of Bock and Beilstein (11) for gravimetric determination of TPA, based on the scant water solubility of TPA perchlorate. Approximately 5 g of tetraphenylarsonium chloride was dissolved in 10 ml water; to this solution was added 5.5 ml of 10%  $\text{HClO}_4$ . A suspension of a fine white precipitate resulted; this was chilled before suction filtration. The precipitate was twice washed thoroughly by suspending in distilled water, chilling and filtering again. The final product was dried at 105-110°C and powdered. Owing to its insolubility in water, the compound was dissolved in chloroform; two solutions were prepared of  $10^{-4}$  and  $10^{-5}$  molarity for equilibration with aqueous HF phases. Contrary to Bock and Beilstein's observation of a marked solubility of TPA perchlorate in chloroform, the compound was difficult to dissolve even at these low concentrations. The  $10^{-4}$  solution required two days for complete solution.

Chloroform. Chloroform used in these studies was Baker and Adamson reagent grade. That used in the TPA chloride and crystal violet runs was twice pre-equilibrated with fresh portions of the appropriate HF solution, using 20 ml of each phase at a time. This precaution was probably unnecessary since later experiments

showed the extraction of HF into  $\text{CHCl}_3$  to be negligible. Pre-equilibrations were neglected for TPA perchlorate runs to avoid possible loss of TPA from the chloroform in which it had been dissolved.

#### Preparation of Samples for Equilibration

Graduated cylinders of polypropylene and glass were used to measure 15.0 -ml portions of HF solution and pre-equilibrated  $\text{CHCl}_3$  (or  $\text{CHCl}_3$  containing TPA perchlorate) into one-ounce polyethylene bottles. Aliquots of extractant stock solution (where appropriate) and  $^{182}\text{Ta}$  tracer solution were added via micropipet to the sample bottles which were then tightly capped and shaken well. Equilibration times varied from a few hours to a total of four days including additional series; the samples were not always kept at constant temperature during the entire period but were brought to  $25 \pm 0.5^\circ\text{C}$  in a water bath for a few hours before taking aliquots for counting.

Four runs were carried out: TPA chloride run I (three series at varying TPA chloride concentrations), TPA chloride run II (three series at different Ta concentrations), crystal violet (three series including two different crystal violet and two different Ta concentrations) and TPA perchlorate (two series involving two different  $\text{TPaClO}_4$  concentrations and two Ta concentrations).

### Chloroform Permeability of Polyethylene

Loss of chloroform from the polyethylene bottles proved to be a problem, especially over equilibration times of more than one day. Independent experiments showed that an estimated 0.9 ml of  $\text{CHCl}_3$  escapes from bottles of this size standing in air for a period of 24 hours; however, if the bottles are stored in water, the loss is reduced to about 0.6 ml per day. Since the solubility of HF in chloroform is very slight, loss of  $\text{CHCl}_3$  volume should not affect the fluoride concentration of the aqueous phase and the distribution ratio of tantalum should not be greatly affected by a change in the volume ratio.

### Removal of Aliquots for Counting

After equilibration of the samples, aliquots for counting were removed using 1.50-ml pipets which had been drawn from polypropylene tubing. The pipet used for the aqueous phase had been calibrated with water, which scarcely wets the plastic; the pipet used for the organic phase had been calibrated with carbon tetrachloride since polypropylene is wet by solvents.

Aliquots of the lower, chloroform phase were taken by carefully lowering the pipet through the aqueous phase, meanwhile gently forcing air through the pipet so that none of the upper phase could enter.

A few chloroform phases sampled by this method in preliminary runs showed zero counts above background, all of the activity remaining in the aqueous phase. Therefore this procedure is successful in minimizing contamination of the lower phase by the upper.

Each aliquot for counting was transferred to a planchet cup of Teflon or stainless steel and covered with a square of Parafilm secured by a wire ring.

### Radioactive Counting

Gamma radiation from the  $^{182}\text{Ta}$  radioisotope was counted by a Tracerlab P-20 scintillation detector with a thallium-doped sodium iodide crystal, in conjunction with a Tracerlab Superscaler. The P-20 probe was operated at maximum amplifier gain and at 1200 volts operating potential, determined to be the optimum by running a response vs voltage curve. Under these conditions the background count rate was approximately 130 cpm.

In order to limit standard deviation of counting rates to 1%, the total count for each aliquot was kept above  $10^4$  for all but the least active aliquots. In these cases and for most of the background counts, the total count was  $3 \times 10^3$  giving a standard deviation of approximately 1.8% for the total count. All counting rates were corrected for background; coincidence corrections were unnecessary due to the low resolving time of the equipment.

### Calculation of Free ( $F^-$ ) in HF Solutions

For the purpose of plotting distribution curves from the data, it was necessary to know the approximate free fluoride concentration in each of the various aqueous phases. The ( $F^-$ ) values for several solutions of known total hydrofluoric acid concentration  $C_{HF}$  were calculated on the basis of available acid dissociation constants for HF and a curve,  $\log (F^-)$  vs  $\log C_{HF}$ , was prepared from which were taken the free fluoride concentrations in the aqueous phases.

The following dissociation constants had been reported (79) for zero ionic strength:

$$K_{a_1} = \frac{(H^+)(F^-)}{HF} = 6.7 \times 10^{-4}$$

$$K_{a_2} = \frac{(HF)(F^-)}{(HF_2^-)} = 0.26$$

These values were used for solutions of total HF concentration up to 0.6 M; above that strength the value of  $K_{a_1} = 1.23 \times 10^{-3}$  reported for solutions of 0.5 ionic strength was utilized. The same value of  $K_{a_2}$  was used throughout as none was reported for the higher ionic strength.

The ( $F^-$ ) and (HF) values for each  $C_{HF}$  were determined through successive approximation using the relationships for  $K_{a_1}$  and  $K_{a_2}$ . Calculations involving the higher  $C_{HF}$  values where the concentration

of  $\text{HF}_2^-$  was significant were aided by the following relationships derived from conservation of mass and of charge:

$$\frac{C_{\text{HF}}}{C_{\text{HF}} - (\text{F}^-)} = \frac{K_{a_1} K_{a_2} + (\text{F}^-)^2 + K_{a_2} (\text{F}^-)}{K_{a_2} (\text{F}^-) + 2(\text{F}^-)^2} \quad (15)$$

$$(\text{HF}) = \frac{C_{\text{HF}} - (\text{F}^-)}{1 + \frac{2(\text{F}^-)}{K_{a_2}}} \quad (16)$$

Since the value of (HF) for each solution was a usual byproduct in the process of obtaining ( $\text{F}^-$ ), it was a simple matter to calculate ( $\text{H}^+$ ) as well. Hydrolysis in the tantalum fluoride system depends upon the hydrogen ion concentration as well as the fluoride concentration, so it was thought worthwhile to include  $\log (\text{H}^+)$  in the plot of  $\log (\text{F}^-)$  vs  $\log C_{\text{HF}}$  (Figure 1). At  $C_{\text{HF}}$  below  $10^{-2}$  M, equal amounts of ( $\text{H}^+$ ) and ( $\text{F}^-$ ) result from the ionization of HF. At higher  $C_{\text{HF}}$  the formation of  $\text{F}^-$  levels off while  $\text{HF}_2^-$  and correspondingly  $\text{H}^+$  are formed in increasing amounts, considerably enhancing the acidity of the solution.

## Results

Data and results for the four runs are summarized in Tables 1 through 11 and include aqueous phase compositions and approximate

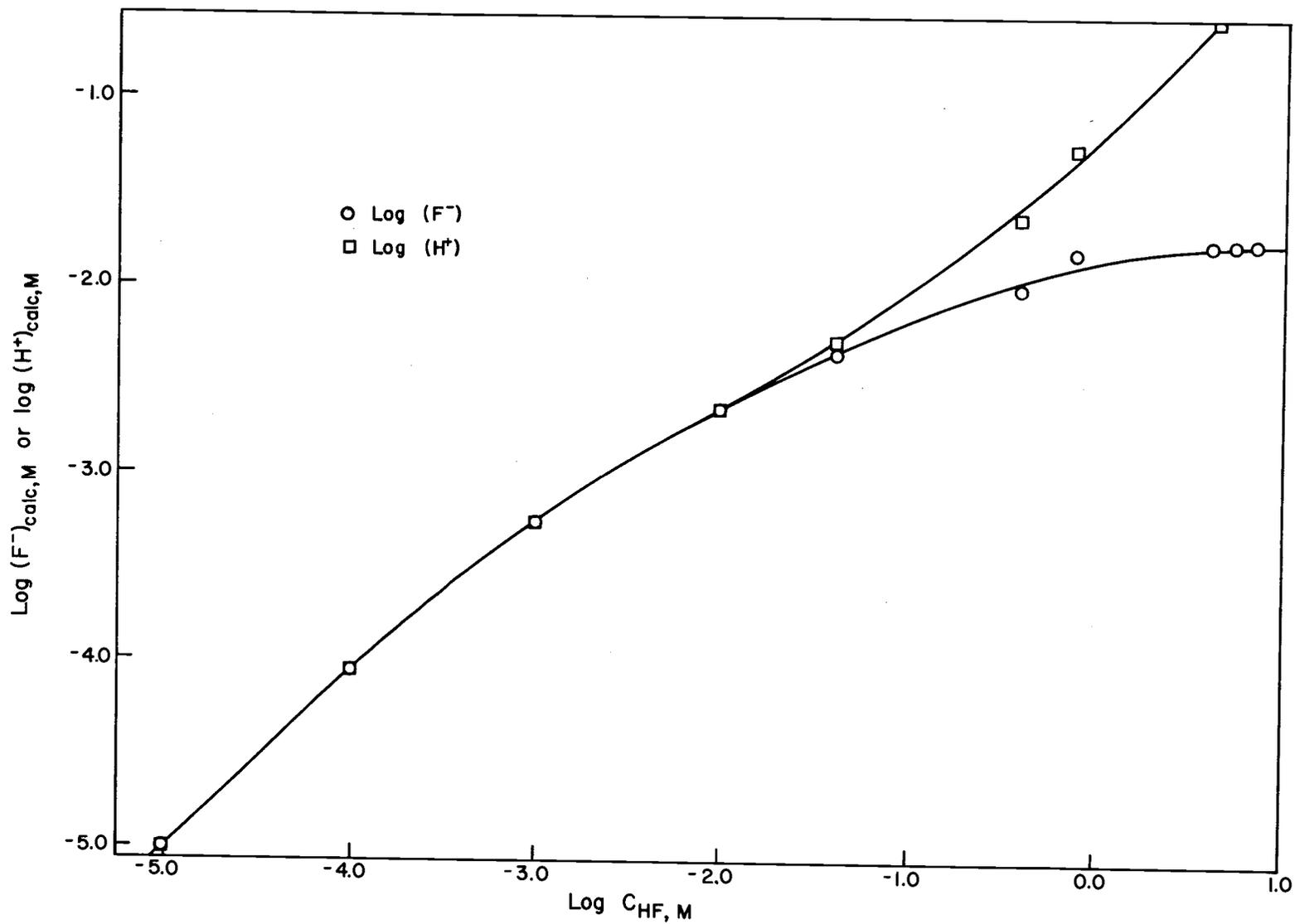


Figure 1.— Calculated free (F<sup>-</sup>) and (H<sup>+</sup>) in aqueous HF solutions.

Table 1. Tetraphenylarsonium chloride extraction data.

Sample #	$C_{HF}, M$	Run I, series 1 ( $Ta \cong 5 \times 10^{-7} M$ (TPA Cl) = $1 \times 10^{-5} M$ )		$\log (F^-)_{calc}$	$\phi$	$\log \phi$	Total count rate, cpm
		$(H^+)_{calc}, M$	$(F^-)_{calc}, M$				
IB <sub>1</sub>	$6.5 \times 10^{-5}$	$6.0 \times 10^{-5}$	$6.0 \times 10^{-5}$	-4.22	$1.09 \times 10^{-1}$	-0.963	$3.95 \times 10^3$
10 <sub>1</sub>	$1.37 \times 10^{-4}$	$1.2 \times 10^{-4}$	$1.18 \times 10^{-4}$	-3.93	$7.05 \times 10^{-1}$	-0.152	$8.78 \times 10^2$
5 <sub>1</sub>	$1.038 \times 10^{-3}$	$5.6 \times 10^{-4}$	$5.6 \times 10^{-4}$	-3.25	$1.02 \times 10^{-2}$	-1.992	$1.31 \times 10^4$
6 <sub>1</sub>	$9.80 \times 10^{-3}$	$2.2 \times 10^{-3}$	$2.2 \times 10^{-3}$	-2.65	$3.36 \times 10^{-1}$	-0.474	$1.69 \times 10^4$
7 <sub>1</sub>	$9.89 \times 10^{-2}$	$9.6 \times 10^{-3}$	$6.8 \times 10^{-3}$	-2.17	5.42	0.734	$1.68 \times 10^4$
8 <sub>1</sub>	1.020	$6.6 \times 10^{-2}$	$1.45 \times 10^{-2}$	-1.84	1.53	0.184	$1.58 \times 10^4$
9 <sub>1</sub>	5.36	$3.3 \times 10^{-1}$	$1.74 \times 10^{-2}$	-1.76	$6.96 \times 10^{-2}$	-1.158	$1.97 \times 10^4$

Table 2. Tetraphenylarsonium chloride extraction data.

Run I, series 2 (Ta)  $\leq 5 \times 10^{-7}$  M (TPA Cl) =  $6.6 \times 10^{-5}$  M  
 $C_{HF}$ ,  $(H^+)_{calc}$ ,  $(F^-)_{calc}$  and  $\log(F^-)$  same as Table 1

Sample #	$\phi$	$\log \phi$	Total count rate, cpm
1B <sub>2</sub>	$2.51 \times 10^{-1}$	-0.601	$3.21 \times 10^3$
10 <sub>2</sub>	1.72	0.235	$1.30 \times 10^3$
5 <sub>2</sub>	$6.71 \times 10^{-2}$	-1.174	$8.87 \times 10^3$
6 <sub>2</sub>	1.85	0.267	$1.66 \times 10^4$
7 <sub>2</sub>	$1.52 \times 10^1$	1.181	$1.63 \times 10^4$
8 <sub>2</sub>	$1.16 \times 10^1$	1.064	$1.62 \times 10^4$
9 <sub>2</sub>	$5.21 \times 10^{-1}$	-0.284	$1.86 \times 10^4$

Table 3. Tetraphenylarsonium chloride extraction data.

Run I, series 3 (Ta)  $\leq 5 \times 10^{-7}$  M (TPA Cl) =  $1.9 \times 10^{-4}$  M  
 $C_{HF}$ ,  $(H^+)_{calc}$ ,  $(F^-)_{calc}$  and  $\log(F^-)$  same as Table 1

Sample #	$\phi$	$\log \phi$	Total count rate, cpm
1B <sub>3</sub>	3.70	0.568	$3.39 \times 10^3$
10 <sub>3</sub>	7.55	0.878	$1.29 \times 10^3$
5 <sub>3</sub>	$9.03 \times 10^{-2}$	-1.045	$8.70 \times 10^3$
6 <sub>3</sub>	3.46	0.538	$2.02 \times 10^4$
7 <sub>3</sub>	$5.16 \times 10^1$	1.712	$1.95 \times 10^4$
8 <sub>3</sub>	$3.81 \times 10^1$	1.581	$2.05 \times 10^4$
9 <sub>3</sub>	1.78	0.250	$2.29 \times 10^4$

Table 4. Crystal violet extraction data.

Series 1 (Ta) $\leq 5 \times 10^{-7}$ M		(CVCl) = $2.5 \times 10^{-5}$ M					
Sample #	$C_{HF}$ , M	$(H^+)_{calc}$ , M	$(F^-)_{calc}$ , M	$\log (F^-)_{calc}$	$\phi$	$\log \phi$	Total count rate cpm
11 <sub>1</sub>	$6.5 \times 10^{-5}$	$6.0 \times 10^{-5}$	$6.0 \times 10^{-5}$	-4.22	$7.20 \times 10^{-2}$	-1.143	$3.41 \times 10^3$
12 <sub>1</sub>	$7.5 \times 10^{-5}$	$6.9 \times 10^{-5}$	$6.9 \times 10^{-5}$	-4.16	2.78	0.444	$1.15 \times 10^4$
13 <sub>1</sub>	$1.62 \times 10^{-4}$	$1.4 \times 10^{-4}$	$1.35 \times 10^{-4}$	-3.87	$5.44 \times 10^{-2}$	-1.265	$7.76 \times 10^3$
14 <sub>1</sub>	$1.04 \times 10^{-3}$	$5.6 \times 10^{-4}$	$5.6 \times 10^{-4}$	-3.25	$6.39 \times 10^{-1}$	-0.195	$1.05 \times 10^4$
15 <sub>1</sub>	$9.80 \times 10^{-3}$	$2.2 \times 10^{-3}$	$2.2 \times 10^{-3}$	-2.65	9.24	0.965	$1.34 \times 10^4$
16 <sub>1</sub>	$9.89 \times 10^{-2}$	$9.3 \times 10^{-3}$	$6.6 \times 10^{-3}$	-2.18	$5.98 \times 10^1$	1.776	$1.36 \times 10^4$
17 <sub>1</sub>	1.02	$6.5 \times 10^{-2}$	$1.45 \times 10^{-2}$	-1.84	3.62	0.558	$1.43 \times 10^4$
18 <sub>1</sub>	5.36	$3.3 \times 10^{-1}$	$1.74 \times 10^{-2}$	-1.76	$6.86 \times 10^{-2}$	-1.164	$1.26 \times 10^4$

Table 5. Crystal violet extraction data.

Series 2 (Ta) $\leq 5 \times 10^{-7}$ M		(CVCl) = $1.9 \times 10^{-4}$ M					
Sample #	$C_{HF}$ , M	$(H^+)_{calc}$ , M	$(F^-)_{calc}$ , M	$\log (F^-)_{calc}$	$\phi$	$\log \phi$	Total count rate cpm
11 <sub>2</sub>	$6.4 \times 10^{-5}$	$6.0 \times 10^{-5}$	$6.0 \times 10^{-5}$	-4.22	$2.82 \times 10^{-1}$	-0.550	$2.15 \times 10^3$
12 <sub>2</sub>	$7.3 \times 10^{-5}$	$6.8 \times 10^{-5}$	$6.8 \times 10^{-5}$	-4.17	$1.66 \times 10^1$	1.220	$1.13 \times 10^4$
13 <sub>2</sub>	$1.58 \times 10^{-4}$	$1.3 \times 10^{-4}$	$1.32 \times 10^{-4}$	-3.88	$9.46 \times 10^{-2}$	-1.024	$3.61 \times 10^3$
14 <sub>2</sub>	$1.02 \times 10^{-3}$	$5.5 \times 10^{-4}$	$5.5 \times 10^{-4}$	-3.26	2.99	0.476	$9.93 \times 10^3$
15 <sub>2</sub>	$9.59 \times 10^{-3}$	$2.2 \times 10^{-3}$	$2.2 \times 10^{-3}$	-2.65	$4.93 \times 10^1$	1.693	$1.36 \times 10^4$
16 <sub>2</sub>	$9.58 \times 10^{-2}$	$9.1 \times 10^{-3}$	$6.6 \times 10^{-3}$	-2.18	$2.6 \times 10^2$	2.416	$1.33 \times 10^4$
17 <sub>2</sub>	1.00	$6.3 \times 10^{-2}$	$1.45 \times 10^{-2}$	-1.84	$4.7 \times 10^1$	1.67	$1.47 \times 10^4$
18 <sub>2</sub>	5.24	$3.2 \times 10^{-1}$	$1.74 \times 10^{-2}$	-1.76	$7.50 \times 10^{-1}$	-0.126	$1.17 \times 10^4$

Table 6. Crystal violet extraction data.

Sample #	Series 3 (Ta) $\leq 1.01 \times 10^{-6}$ M		(CV Cl) = $1.9 \times 10^{-4}$ M			$\phi$	log $\phi$	Total count rate cpm
	C <sub>HF</sub> , M	(H <sup>+</sup> ) <sub>calc</sub> , M	(F <sup>-</sup> ) <sub>calc</sub> , M	log(F <sup>-</sup> ) <sub>calc</sub>				
11 <sub>3</sub>	$1.43 \times 10^{-4}$	$1.2 \times 10^{-4}$	$1.2 \times 10^{-4}$	-3.92	$1.14 \times 10^{-1}$	-0.943	$7.23 \times 10^3$	
12 <sub>3</sub>	$1.52 \times 10^{-4}$	$1.3 \times 10^{-4}$	$1.26 \times 10^{-4}$	-3.90	5.83	0.767	$3.74 \times 10^4$	
13 <sub>3</sub>	$2.37 \times 10^{-4}$	$1.8 \times 10^{-4}$	$1.82 \times 10^{-4}$	-3.74	$1.20 \times 10^{-1}$	-0.921	$1.64 \times 10^4$	
14 <sub>3</sub>	$1.09 \times 10^{-3}$	$5.8 \times 10^{-4}$	$5.8 \times 10^{-4}$	-3.24	2.18	0.338	$3.25 \times 10^4$	
15 <sub>3</sub>	$9.67 \times 10^{-3}$	$2.2 \times 10^{-3}$	$2.2 \times 10^{-3}$	-2.65	$3.90 \times 10^1$	1.591	$4.40 \times 10^4$	
16 <sub>3</sub>	$9.59 \times 10^{-2}$	$9.1 \times 10^{-3}$	$6.6 \times 10^{-3}$	-2.18	$9.40 \times 10^1$	1.973	$4.19 \times 10^4$	
17 <sub>3</sub>	1.00	$6.3 \times 10^{-2}$	$1.45 \times 10^{-2}$	-1.84	$4.88 \times 10^1$	1.688	$4.51 \times 10^4$	
18 <sub>3</sub>	5.24	$3.2 \times 10^{-1}$	$1.74 \times 10^{-2}$	-1.76	$5.34 \times 10^{-1}$	-0.273	$3.39 \times 10^4$	

Table 7. Tetraphenylarsonium chloride extraction data.

Sample #	Run II, series 1 (Ta) $\leq 5 \times 10^{-7}$ M,		(TPA Cl) = $5 \times 10^{-4}$ M			$\phi$	log $\phi$	Total count rate, cpm
	C <sub>HF</sub> , M	(H <sup>+</sup> ) <sub>calc</sub> , M	(F <sup>-</sup> ) <sub>calc</sub> , M	log(F <sup>-</sup> ) <sub>calc</sub>				
5 <sub>1</sub>	5.36	$3.3 \times 10^{-1}$	$1.7 \times 10^{-2}$	-1.76	1.88	0.274	$1.51 \times 10^4$	
6 <sub>1</sub>	1.02	$6.5 \times 10^{-2}$	$1.4 \times 10^{-2}$	-1.84	$2.72 \times 10^1$	1.434	$1.73 \times 10^4$	
7 <sub>1</sub>	$9.88 \times 10^{-2}$	$9.3 \times 10^{-3}$	$6.6 \times 10^{-3}$	-2.18	$5.85 \times 10^1$	1.767	$1.1 \times 10^4$	
8 <sub>1</sub>	$9.77 \times 10^{-3}$	$2.2 \times 10^{-3}$	$2.2 \times 10^{-3}$	-2.65	6.36	0.803	$1.1 \times 10^3$	
9 <sub>1</sub>	$1.01 \times 10^{-3}$	$5.5 \times 10^{-4}$	$5.5 \times 10^{-4}$	-3.26	$6.94 \times 10^{-2}$	-1.159	$4.0 \times 10^3$	

Table 8. Tetraphenylarsonium chloride extraction data.

Run II, series 2 ( $Ta \leq 1.06 \times 10^{-6}$ M, (TPACl) = $5 \times 10^{-4}$ M							
Sample #	$C_{HF}$ , M	$(H^+)_{calc}$ , M	$(F^-)_{calc}$ , M	$\log (F^-)_{calc}$	$\phi$	$\log \phi$	Total count rate cpm
5 <sub>2</sub>	5.36	$3.3 \times 10^{-1}$	$1.7 \times 10^{-2}$	-1.757	2.62	0.418	$2.97 \times 10^4$
6 <sub>2</sub>	1.02	$6.5 \times 10^{-2}$	$1.4 \times 10^{-2}$	-1.84	$4.73 \times 10^1$	1.674	$3.25 \times 10^4$
7 <sub>2</sub>	$9.89 \times 10^{-2}$	$9.3 \times 10^{-3}$	$6.6 \times 10^{-3}$	-2.18	$5.87 \times 10^1$	1.768	$3.49 \times 10^4$
8 <sub>2</sub>	$9.81 \times 10^{-3}$	$2.2 \times 10^{-3}$	$2.2 \times 10^{-3}$	-2.65	5.34	0.727	$2.45 \times 10^4$
9 <sub>2</sub>	$1.06 \times 10^{-3}$	$5.6 \times 10^{-4}$	$5.6 \times 10^{-4}$	-3.25	$6.65 \times 10^{-2}$	-1.178	$5.63 \times 10^3$

Table 9. Tetraphenylarsonium chloride extraction data.

Run II, series 3 ( $Ta \leq 2.3 \times 10^{-6}$ M, (TPACl) = $5 \times 10^{-4}$ M							
Sample #	$C_{HF}$ , M	$(H^+)_{calc}$ , M	$(F^-)_{calc}$ , M	$\log (F^-)_{calc}$	$\phi$	$\log \phi$	Total count rate cpm
5 <sub>3</sub>	5.36	$3.3 \times 10^{-1}$	$1.7 \times 10^{-2}$	-1.76	3.43	0.535	$5.93 \times 10^4$
6 <sub>3</sub>	1.02	$6.5 \times 10^{-2}$	$1.4 \times 10^{-2}$	-1.84	$4.77 \times 10^1$	1.678	$6.67 \times 10^4$
7 <sub>3</sub>	$9.90 \times 10^{-2}$	$9.3 \times 10^{-3}$	$6.6 \times 10^{-3}$	-2.18	$5.52 \times 10^1$	1.742	$6.64 \times 10^4$
8 <sub>3</sub>	$9.91 \times 10^{-3}$	$2.3 \times 10^{-3}$	$2.3 \times 10^{-3}$	-2.64	5.63	0.750	$5.21 \times 10^4$
9 <sub>3</sub>	$1.16 \times 10^{-3}$	$6.0 \times 10^{-4}$	$6.0 \times 10^{-4}$	-3.22	$7.9 \times 10^{-2}$	-1.10	$1.3 \times 10^4$

( $F^-$ ) and ( $H^+$ ) values, distribution ratios ( $\phi = \text{cpm}/1.5 \text{ ml org} \div \text{cpm}/1.5 \text{ ml aq}$ ) and total count rates ( $\text{cpm}/1.5 \text{ ml org} + \text{cpm}/1.5 \text{ ml aq}$ ). Distribution curves ( $\log \phi$  vs  $\log [F^-]$ ) are shown in Figures 2 to 5.

## Discussion

### Comparison of TPA Chloride and Crystal Violet Extractions

Comparison of Figures 2 and 3 reveals that the two extractants tetraphenylarsonium chloride and crystal violet exhibit essentially the same behavior toward tantalum fluoride complexes. Both sets of curves have two maxima, one at approximately  $10^{-4}$  M ( $F^-$ ) and the other, more prominent and precise, at  $1 \times 10^{-2}$  M ( $F^-$ ). Crystal violet is the better extractant; at the same extractant concentration of about  $1.9 \times 10^{-4}$  M the distribution ratio reaches a high of  $2.6 \times 10^2$  for crystal violet extraction compared to a maximum of  $5.2 \times 10^1$  for TPA chloride.

The slopes of the curves upon approaching the  $10^{-2}$  M ( $F^-$ ) distribution maximum should be an indication of the number of fluoride ions being added to already existing tantalum complexes to form the extractable species; however, since activity coefficients are expected to vary with increasing fluoride concentration in these runs, the implications of the slopes cannot be taken very seriously. Curves for the two extractants differ in this regard; TPA chloride graphs exhibit slopes in this region of approximately three, while slopes for

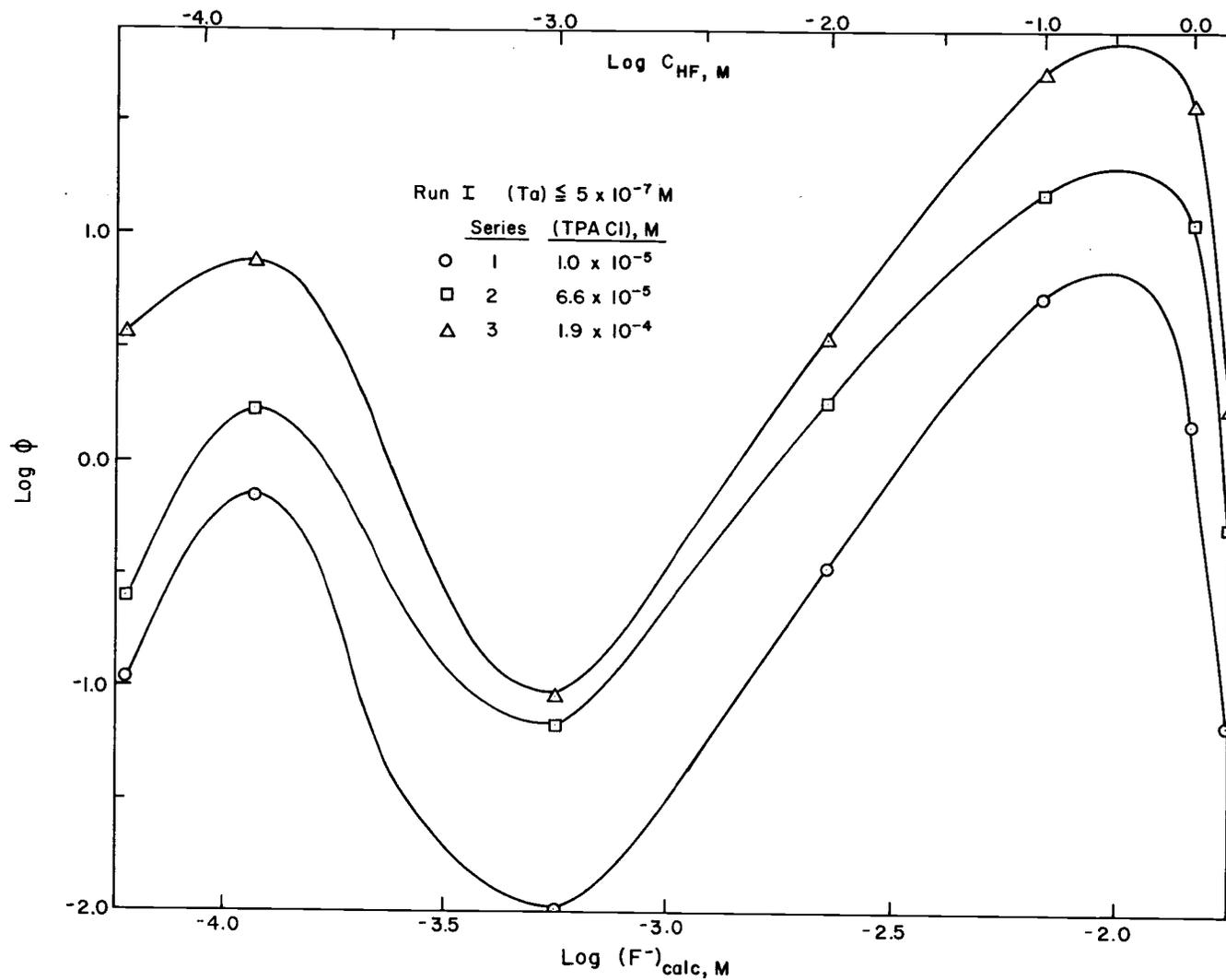


Figure 2.— Distribution of  $^{182}Ta$  between  $CHCl_3$  and aqueous HF solutions containing TPA chloride.

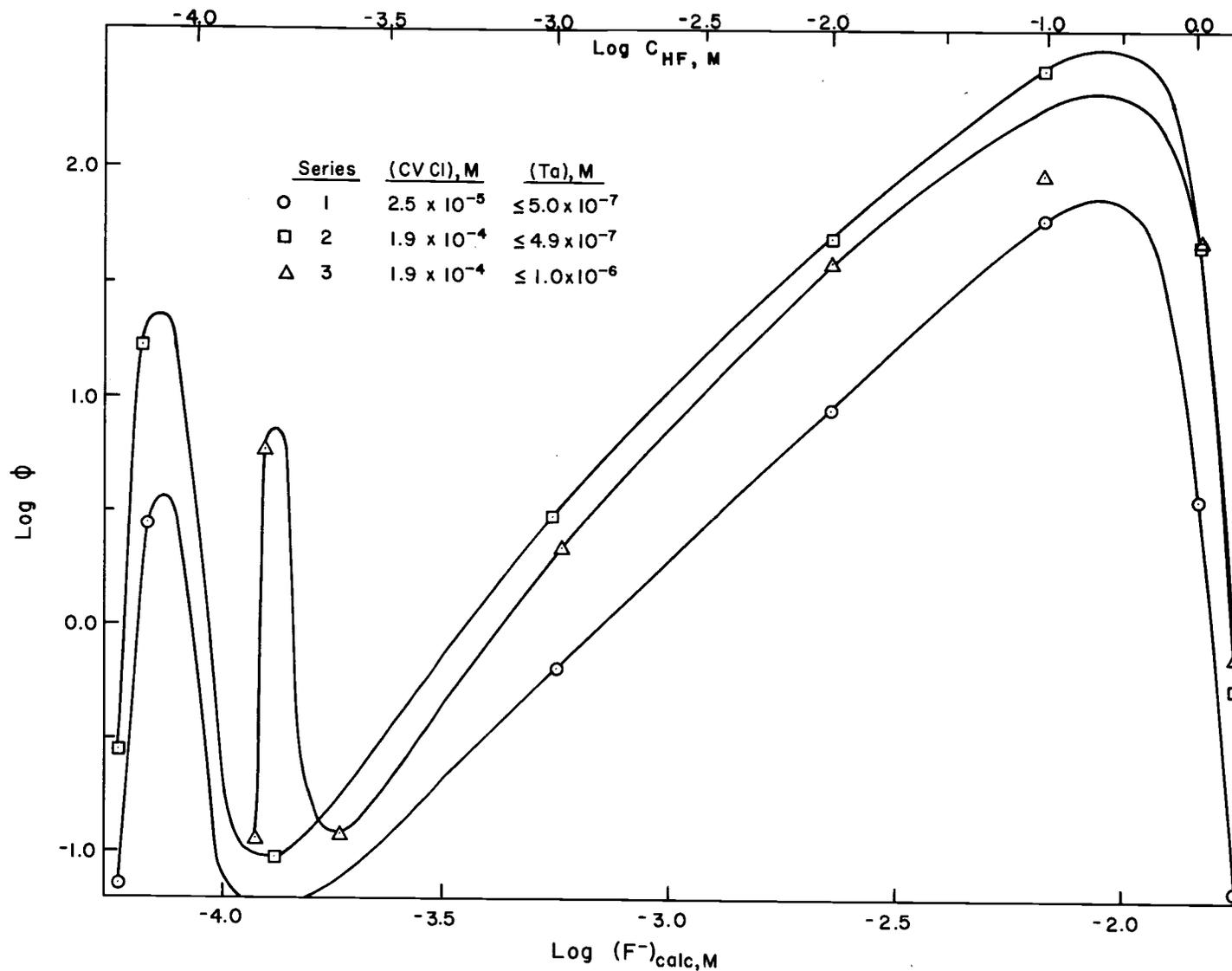


Figure 3.— Distribution of  $^{182}\text{To}$  between  $\text{CHCl}_3$  and aqueous HF solutions containing crystal violet.

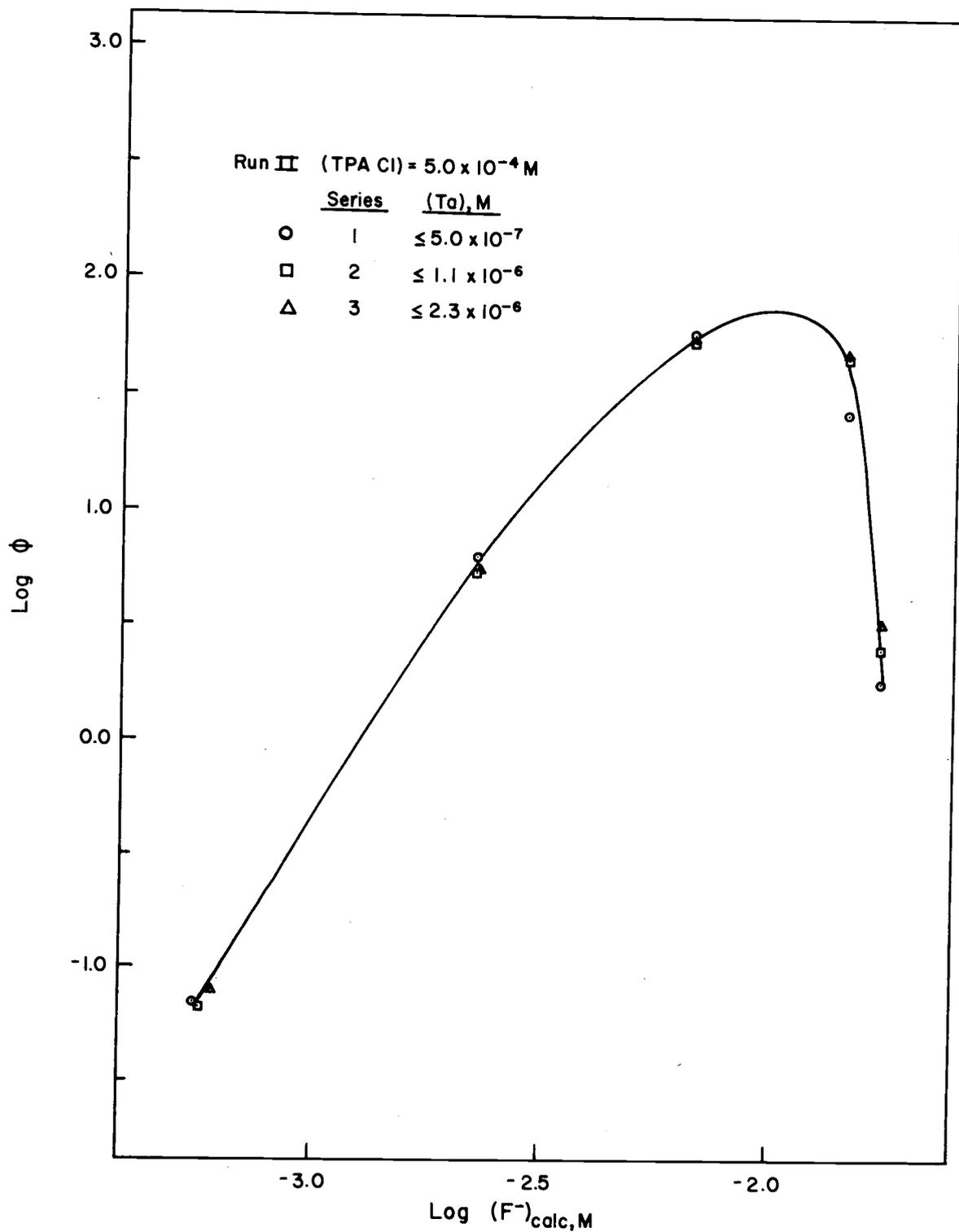


Figure 4.— TPA chloride extraction of  $^{182}\text{Ta}$  from aqueous HF into  $\text{CHCl}_3$  at various levels of (Ta).

crystal violet extraction are closer to two. It is possible that equilibria involving hydrogen ion and different forms of crystal violet in the aqueous phase may affect the crystal violet extraction.

On the high fluoride side of the  $10^{-2}$  M ( $F^-$ ) distribution maximum, however, both extraction systems exhibit the same sharp drop in distribution, indicating the wholesale replacement of the extractable complex by another complex of greater stability in that ( $F^-$ ) region.

Although the data are not precise in this respect, an examination of the dependence of extraction upon extractant concentration shows it to be approximately linear for both extractants; thus one cation is involved in each extractable compound or ion pair.

It is also fairly certain that in both cases the extracted cation (and therefore anion) each bear a single charge. While the crystal violet cation may have a positive charge of from one to three according to the pH (69, p. 701), Makorova and Alimarin (58) found that extracts of fluorotantalate with triphenylmethane dyes give the same infrared spectrum as do solutions of dyes present in the form of singly charged cations. That the extracted crystal violet ion carries a unit charge is also supported by the results given here, in that crystal violet shows the same extraction maxima as the TPA cation of known single charge.

## Nature of Fluo-Tantalum Species at Higher C<sub>HF</sub>

It has been established that the anions extracted by crystal violet and tetraphenylarsonium chloride are singly charged; the question of their identity, however, remains. The species responsible for the  $10^{-2}$  M ( $F^-$ ) distribution maximum will be discussed first.

Alimarin and Makorova (3, 4, 58) assumed  $TaF_6^-$  to be the species extracted by both TPA and crystal violet. This assumption is supported by the work of Keller and Chetham-Strode (54), whose Raman studies of  $HF-NH_4F$  solutions containing about one molar tantalum indicated that  $TaF_6^-$  and  $TaF_7^{2-}$  were the only tantalum complexes present in most of their solutions, and that  $TaF_7^{2-}$  completely replaces  $TaF_6^-$  with increasing fluoride concentration. Such a replacement is demonstrated by the sharp drop in distribution above  $10^{-2}$  M ( $F^-$ ) in the present studies.

It must be pointed out, however, that most of the solutions of Keller and Chetham-Strode were of relatively high acidity, containing from 2.0 to 24 M HF. In another series of solutions, whose only source of acidity was from 0 to 0.5 M HF (a considerable range of uncertainty),  $TaF_6^-$  and  $TaF_7^{2-}$  were still the predominant species but evidence was found for the presence of two other complexes. An additional peak which appeared in the spectrum at low fluoride concentration was thought to be due to a fluoride complex of different

ligand number, although in the opinion of this writer it may have been a mixed hydroxy-fluoro complex. At high  $\text{NH}_4\text{F}$  concentration a band appeared in the tantalum-oxygen stretching region and was attributed to  $\text{TaOF}_5^{2-}$  or  $\text{TaOF}_6^{3-}$ .

Since the hydrofluoric acid concentration at the TPA and crystal violet distribution maxima is only about 0.4 M, it follows from the above considerations that mixed hydroxy-fluoro complexes and/or oxyfluoro species may be present in the aqueous phase. One such complex,  $\text{TaOF}_4^-$ , was reported by Djordjević and Sevdic (26) to extract well from 0.04 M HF into chloroform containing di-n-octylaminoethanol; the distribution ratio was said to decrease upon increasing the HF concentration to 0.4 M.

While it does not necessarily follow that  $\text{TaOF}_4^-$  would be extracted by TPA and crystal violet if it were present, it seems reasonable to assume that it would be. It can further be assumed that  $\text{TaF}_6^-$  and  $\text{TaOF}_4^-$  do not extract at the same fluoride concentration. However, the shapes of the main TPA and crystal violet distribution maxima are not consistent with the extraction of two species but rather suggest a single extracting species at  $C_{\text{HF}}$  above  $10^{-3}$  M. Since  $\text{TaF}_6^-$  is expected to extract if present, and since the data of Keller and Chetham-Strode in this HF concentration range indicate that  $\text{TaF}_6^-$  is indeed present even if accompanied by hydrolytic species, the probable extracting species is  $\text{TaF}_6^-$ .

The possibility of existence of polynuclear tantalum complexes in the higher fluoride range was tested by studying the effect of tantalum concentration upon extraction by tetraphenylarsonium chloride. The results for three different tantalum concentrations, two of them greater than the metal concentration usually employed, are shown in Tables 7-9 and are plotted in Figure 4. All of the points fell on or near a single curve indicating that no appreciable amount of polymerization occurs within this range of metal concentration ( $10^{-7}$  to  $10^{-6}$  M) and  $C_{\text{HF}}$  ( $10^{-3}$  M to 5 M). Crystal violet distribution curves at two different Ta concentrations (Figure 3) differed at intermediate fluoride concentrations possibly because of experimental error. Evidence from the literature for the predominance of mononuclear complexes of tantalum in fluoride solutions has already been discussed (7, 66, 24).

In conclusion, then, in solutions of hydrofluoric acid greater than  $10^{-3}$  M the complex extracted by TPA and crystal violet is probably  $\text{TaF}_6^-$ . This species is likely formed by stepwise addition of fluoride ion to the complexes  $\text{TaF}_3^{2+}$  and  $\text{TaF}_4^+$ , although hydrolytic complexes may also be involved at the lower fluoride concentrations. At  $C_{\text{HF}}$  greater than 0.4 M the distribution drops sharply due to replacement of  $\text{TaF}_6^-$  by  $\text{TaF}_7^{2-}$ .

### Nature of Fluo-Tantalum Species at Lower $C_{HF}$

In addition to the main extraction maximum at  $10^{-2}$  M ( $F^-$ ), the TPA chloride and crystal violet distribution curves also show a maximum at low fluoride concentration, approximately  $10^{-4}$  M ( $F^-$ ). Since the concentration of chloride present in the aqueous phase from the extractant was comparable to the free fluoride concentration in this range, the possibility existed that mixed chloro-fluoro tantalum species might be formed and might extract. To determine whether this was likely, additional runs were made in the absence of chloride using tetraphenylarsonium perchlorate as extractant. The data are given in Tables 10 and 11 and the results plotted in Figure 5.

Distribution ratios for tantalum fluoride using TPA perchlorate were considerably lower than those obtained with TPA chloride, due to the high extractability of perchlorate; nonetheless, the tantalum species was able to compete for a share of the TPA cations. The first series of the run showed no maximum at low ( $F^-$ ), with very little tantalum being extracted. However, after additional  $^{182}\text{Ta}$  was added for the second series and several hours allowed for equilibration, the distribution ratio of the lowest fluoride samples increased markedly while the higher fluoride samples ( $C_{HF} > 2 \times 10^{-3}$  M) were scarcely affected. Since an extraction maximum of sorts was demonstrated in the absence of chloride, it is unlikely that the

Table 10. Tetraphenylarsonium perchlorate extraction data.

Sample #	$C_{HF}, M$	Series 1 (Ta) $\leq 5 \times 10^{-7} M$ (TPA C10 = $10^{-5} M$ in $CHCl_3$ for samples 1-8 (TPA C10 <sub>4</sub> ) = $10^{-4} M$ in $CHCl_3$ for samples 9-16		$\log(F^-)$	$\phi$	$\log \phi$	Total count rate cpm
		$(H^+)_{calc}, M$	$(F^-)_{calc}, M$				
1 <sub>1</sub>	$6.5 \times 10^{-5}$	$6.0 \times 10^{-5}$	$6.0 \times 10^{-5}$	-4.22	$\sim 1.5 \times 10^{-3}$	-2.8	$9.9 \times 10^3$
2 <sub>1</sub>	$7.5 \times 10^{-5}$	$6.9 \times 10^{-5}$	$6.9 \times 10^{-5}$	-4.16	$\sim 1.5 \times 10^{-3}$	-2.8	$1.08 \times 10^4$
3 <sub>1</sub>	$1.62 \times 10^{-4}$	$1.4 \times 10^{-4}$	$1.35 \times 10^{-4}$	-3.87	$\sim 9.6 \times 10^{-4}$	-3.0	$1.45 \times 10^4$
4 <sub>1</sub>	$1.04 \times 10^{-3}$	$5.6 \times 10^{-4}$	$5.6 \times 10^{-4}$	-3.25	$3.4 \times 10^{-3}$	-2.47	$1.52 \times 10^4$
5 <sub>1</sub>	$9.80 \times 10^{-3}$	$2.2 \times 10^{-3}$	$2.2 \times 10^{-3}$	-2.65	$1.89 \times 10^{-1}$	-0.724	$1.57 \times 10^4$
6 <sub>1</sub>	$9.89 \times 10^{-2}$	$9.3 \times 10^{-3}$	$6.8 \times 10^{-3}$	-2.17	2.13	0.328	$1.65 \times 10^4$
7 <sub>1</sub>	1.02	$6.5 \times 10^{-2}$	$1.45 \times 10^{-2}$	-1.84	1.26	0.100	$1.68 \times 10^4$
8 <sub>1</sub>	5.36	$3.3 \times 10^{-1}$	$1.74 \times 10^{-2}$	-1.76	$6.3 \times 10^{-2}$	-1.20	$1.46 \times 10^4$
9 <sub>1</sub>	$6.5 \times 10^{-5}$	$6.0 \times 10^{-5}$	$6.0 \times 10^{-5}$	-4.22	$5.4 \times 10^{-3}$	-2.27	$1.01 \times 10^4$
10 <sub>1</sub>	$7.5 \times 10^{-5}$	$6.9 \times 10^{-5}$	$6.9 \times 10^{-5}$	-4.16	$8.8 \times 10^{-3}$	-2.06	$1.04 \times 10^4$
11 <sub>1</sub>	$1.62 \times 10^{-4}$	$1.35 \times 10^{-4}$	$1.35 \times 10^{-4}$	-3.87	$7.0 \times 10^{-3}$	-2.16	$6.62 \times 10^3$
12 <sub>1</sub>	$1.04 \times 10^{-3}$	$5.6 \times 10^{-4}$	$5.6 \times 10^{-4}$	-3.25	$2.35 \times 10^{-1}$	-0.629	$1.51 \times 10^4$
13 <sub>1</sub>	$9.80 \times 10^{-3}$	$2.2 \times 10^{-3}$	$2.2 \times 10^{-3}$	-2.65	$9.67 \times 10^{-1}$	-0.015	$1.61 \times 10^4$
14 <sub>1</sub>	$9.89 \times 10^{-2}$	$9.3 \times 10^{-3}$	$6.8 \times 10^{-3}$	-2.17	$1.06 \times 10^1$	1.025	$1.74 \times 10^4$
15 <sub>1</sub>	1.02	$6.5 \times 10^{-2}$	$1.45 \times 10^{-2}$	-1.84	6.87	0.837	$1.74 \times 10^4$
16 <sub>1</sub>	5.36	$3.3 \times 10^{-1}$	$1.74 \times 10^{-2}$	-1.76	$5.48 \times 10^{-1}$	-0.262	$1.61 \times 10^4$

Table 11. Tetraphenylarsonium perchlorate extraction data.

Sample #	$C_{HF}$ , M	Series 2 (Ta) $\leq 1.06 \times 10^{-6}$ M (TPA ClO <sub>4</sub> ) = $10^{-5}$ M in CHCl <sub>3</sub> for samples 1-8					Total count rate cpm
		(H <sup>+</sup> ) <sub>calc</sub> , M	(F <sup>-</sup> ) <sub>calc</sub> , M	log(F <sup>-</sup> ) <sub>calc</sub>	$\phi$	log $\phi$	
1 <sub>2</sub>	$1.37 \times 10^{-4}$	$1.2 \times 10^{-4}$	$1.2 \times 10^{-4}$	-3.93	$8.53 \times 10^{-2}$	-1.069	$1.33 \times 10^4$
2 <sub>2</sub>	$1.47 \times 10^{-4}$	$1.3 \times 10^{-4}$	$1.26 \times 10^{-4}$	-3.90	$2.66 \times 10^{-1}$	-0.576	$1.41 \times 10^4$
3 <sub>2</sub>	$2.34 \times 10^{-4}$	$1.8 \times 10^{-4}$	$1.82 \times 10^{-4}$	-3.74	$8.01 \times 10^{-2}$	-1.097	$2.01 \times 10^4$
4 <sub>2</sub>	$1.12 \times 10^{-3}$	$5.9 \times 10^{-4}$	$5.9 \times 10^{-4}$	-3.23	$9.46 \times 10^{-3}$	-2.024	$3.21 \times 10^4$
5 <sub>2</sub>	$9.87 \times 10^{-3}$	$2.2 \times 10^{-3}$	$2.2 \times 10^{-3}$	-2.65	$1.65 \times 10^{-1}$	-0.783	$3.32 \times 10^4$
6 <sub>2</sub>	$9.90 \times 10^{-2}$	$9.6 \times 10^{-3}$	$6.8 \times 10^{-3}$	-2.17	1.80	0.255	$3.64 \times 10^4$
7 <sub>2</sub>	1.02	$6.6 \times 10^{-2}$	$1.45 \times 10^{-2}$	-1.84	1.26	0.100	$3.70 \times 10^4$
8 <sub>2</sub>	5.36	$3.3 \times 10^{-1}$	$1.74 \times 10^{-2}$	-1.76	$7.04 \times 10^{-2}$	-1.153	$3.30 \times 10^4$
9 <sub>2</sub>	$1.37 \times 10^{-4}$	$1.2 \times 10^{-4}$	$1.2 \times 10^{-4}$	-3.93	$2.51 \times 10^{-1}$	-0.601	$6.62 \times 10^3$
10 <sub>2</sub>	$1.47 \times 10^{-4}$	$1.3 \times 10^{-4}$	$1.26 \times 10^{-4}$	-3.90	$1.70 \times 10^{-1}$	-0.770	$6.89 \times 10^3$
11 <sub>2</sub>	$2.34 \times 10^{-4}$	$1.8 \times 10^{-4}$	$1.82 \times 10^{-4}$	-3.74	$1.46 \times 10^{-1}$	-0.836	$1.44 \times 10^4$
12 <sub>2</sub>	$1.11 \times 10^{-3}$	$5.8 \times 10^{-4}$	$5.8 \times 10^{-4}$	-3.24	$1.85 \times 10^{-1}$	-0.733	$3.13 \times 10^4$
13 <sub>2</sub>	$9.87 \times 10^{-3}$	$2.2 \times 10^{-3}$	$2.2 \times 10^{-3}$	-2.65	$7.99 \times 10^{-1}$	-0.098	$3.58 \times 10^4$
14 <sub>2</sub>	$9.90 \times 10^{-2}$	$9.6 \times 10^{-3}$	$6.8 \times 10^{-3}$	-2.17	$1.04 \times 10^1$	1.017	$3.89 \times 10^4$
15 <sub>2</sub>	1.02	$6.6 \times 10^{-2}$	$1.45 \times 10^{-2}$	-1.84	7.13	0.853	$3.96 \times 10^4$
16 <sub>2</sub>	5.36	$3.3 \times 10^{-1}$	$1.74 \times 10^{-2}$	-1.76	$6.05 \times 10^{-1}$	-0.219	$3.58 \times 10^4$

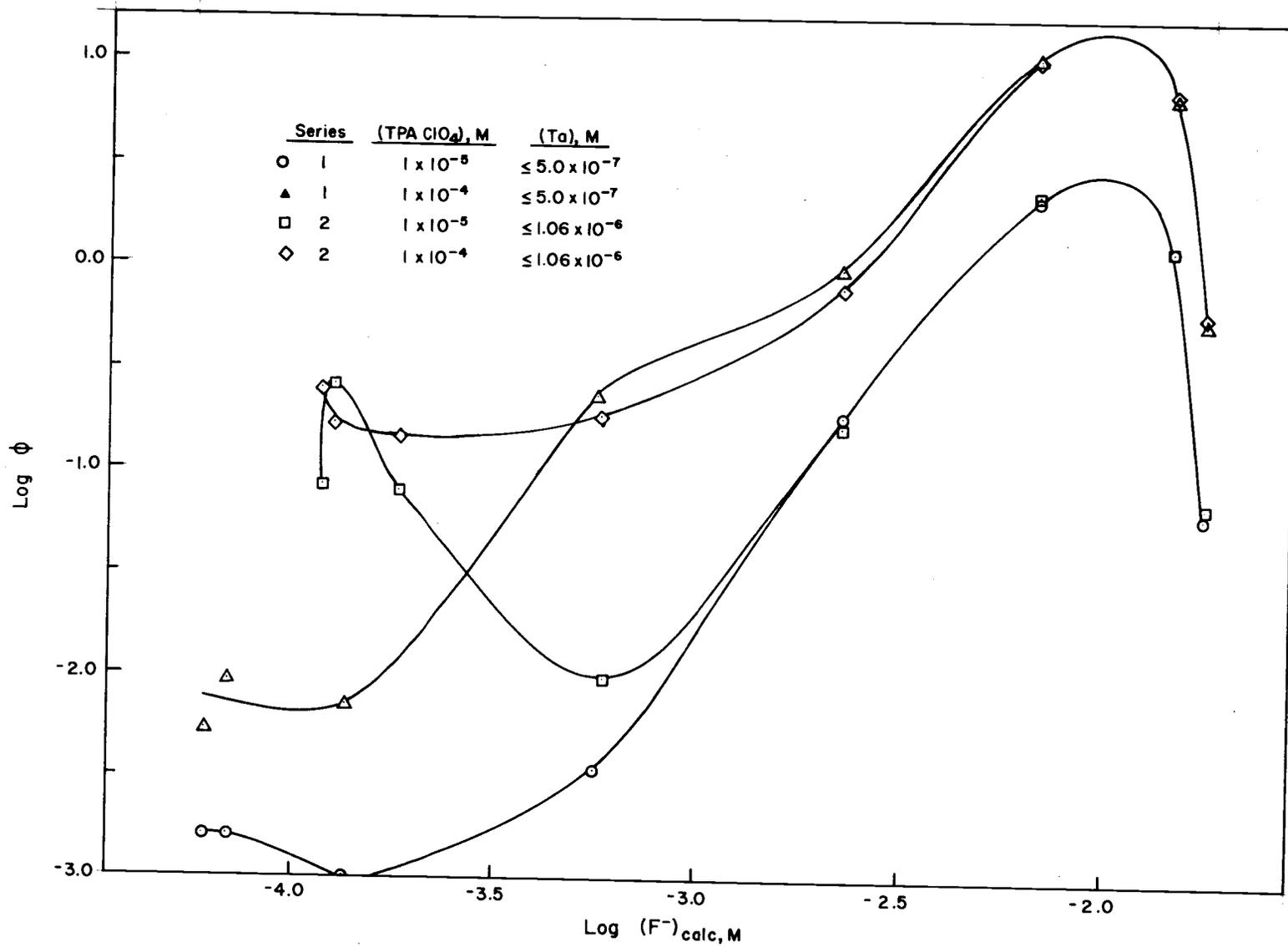


Figure 5.— TPA perchlorate extraction of <sup>182</sup>Ta from aqueous HF solutions into CHCl<sub>3</sub>.

maxima at low ( $F^-$ ) in the TPA chloride and crystal violet extraction curves were due to mixed chloro-fluoro complexes.

The most likely alternative explanation for the distribution at low ( $F^-$ ) involves the formation of hydrolytic and polynuclear species of tantalum at these low fluoride and low acid concentrations. Hydrolysis and polymerization are rather slow processes, which may help to explain the growth of the TPA perchlorate distribution curves at low ( $F^-$ ); the fact that the tantalum concentration had been increased points to polymerization in this region.

An examination of the total count rate (cpm/1.5 ml org + cpm/1.5 ml aq) for the samples in various runs shows that they are significantly less than average for samples of aqueous  $C_{HF}$  of  $10^{-3}$  M or less. Some of the total count rates decreased from one series to another of the same run. The only plausible explanation for the reduced count rates is the occurrence of hydrolysis and polymerization to such an extent that some of the tantalum, even at the low metal concentration of  $5 \times 10^{-7}$  M, drops out of solution.

The extraction maximum near  $10^{-4}$  M ( $F^-$ ) is probably due to one of the intermediates in these processes which possesses a single charge. While  $TaOF_4^-$  is apparently the only anion of this type which has been specifically mentioned in the literature, other possibilities, such as  $TaO_2F^-$  or various polynuclear species, could be proposed. Although it is also possible that water-insoluble, electrically neutral

tantalum compounds could extract into chloroform, this would be inconsistent with the increase of tantalum distribution upon increasing the TPA concentration (Figure 2).

### Summary

Solvents of low dipole moment such as cyclohexane, benzene and chloroform failed to extract the electrically neutral tantalum fluoride complex  $TaF_5$ . This failure is not, however, to be interpreted as a certain indication that the species is not present in aqueous solution.

Studies of extraction of tantalum fluorides by the large cationic extractants tetraphenylarsonium ion and crystal violet were carried out from aqueous HF solution into chloroform, using  $^{182}Ta$  as tracer. Concentration ranges investigated were:  $C_{HF}$ ,  $5 \times 10^{-5}$  to 5.36 M;  $(Ta) \leq 5 \times 10^{-7}$  to  $2 \times 10^{-6}$  M; extractant concentration,  $1 \times 10^{-5}$  to  $1.9 \times 10^{-4}$  M. Use of a constant ionic medium to control activity coefficients was not possible because of the high extractability of perchlorate. Crystal violet gave higher distribution ratios than did tetraphenylarsonium chloride. Approximate free fluoride concentrations were calculated for solutions of various  $C_{HF}$  and distribution curves ( $\log \phi$  vs  $\log [F^-]$ ) prepared.

At  $(F^-) > 6 \times 10^{-4}$  M or  $C_{HF} > 10^{-3}$  M the distribution was independent of metal concentration, indicating absence of polymerization.

All curves showed a definite maximum at  $10^{-2}$  M ( $F^-$ ) or 0.4 M  $C_{HF}$  with the distribution sharply decreasing at higher fluoride concentrations. This maximum is most likely due to extraction of  $TaF_6^-$  by the singly charged large cations, through formation of ion pairs. Slopes of the curves indicated that two or three fluoride ions may be involved in the formation of the extractable complex from already existing complexes.

In samples of  $C_{HF} \cong 10^{-3}$  M, total count rates were reduced indicating partial hydrolysis and polymerization of tantalum. Distribution ratios in this area showed some anomalous behavior and appeared to be somewhat dependent upon equilibration time and metal concentration. A maximum in the distribution curves near  $10^{-4}$  M  $C_{HF}$  is probably due to the extraction of an intermediate hydrolysis or polymerization product.

MUTUAL SOLUBILITIES IN (H, Na)ClO<sub>4</sub>-MIBK  
AND HF-MIBK SYSTEMS

General

Prior to a study of the distribution of tantalum fluoride complexes into methyl isobutyl ketone (MIBK), investigations of the solubility of MIBK in the aqueous phase and of HClO<sub>4</sub>, NaClO<sub>4</sub> and HF in the MIBK phase was deemed important. This was undertaken for three reasons: to determine amounts of MIBK to be added to aqueous phases, to determine how many pre-equilibrations of the MIBK phase with fresh aqueous phase would be required to achieve essentially complete saturation, and to provide a check upon the assumption of constant activity coefficients within the systems to be studied.

The general procedure was as follows: HClO<sub>4</sub>, NaClO<sub>4</sub>, HClO<sub>4</sub>-NaClO<sub>4</sub> or HF solutions of known concentration were saturated with MIBK and their concentrations redetermined; the approximate volume percent solubility was figured from the loss in concentration. Each MIBK-saturated solution was then equilibrated with an equal volume of MIBK. Following equilibration the concentration of HClO<sub>4</sub>, NaClO<sub>4</sub> or HF in the organic phase was determined and that in the aqueous phase calculated by difference, taking into account any change in volume. Distribution ratios  $\phi$  were obtained and from these, for the extraction of HClO<sub>4</sub> and HF, distribution coefficients  $\lambda$  were derived in terms of the most likely mechanism

and extracting species.

## MIBK-Aqueous Perchlorate Equilibria

### Experimental

#### Stock Solutions

All solutions in these experiments were made up with distilled water, boiled to eliminate  $\text{CO}_2$ . Dilutions to volume and measurements of solutions were carried out at  $25 \pm 0.2^\circ\text{C}$  using recalibrated glassware.

#### Sodium Perchlorate Stock Solution

A 4.64 M  $\text{NaClO}_4$  solution was prepared by neutralization of 2 l of 5 M  $\text{HClO}_4$  (made up from Baker and Adamson reagent grade 70% perchloric acid) with 510 g of anhydrous sodium carbonate (Baker and Adamson reagent grade). A rough adjustment of the pH was made by checking with pH paper and adding either sodium carbonate or concentrated perchloric acid until the reaction was slightly acidic. The solution was then heated until evolution of  $\text{CO}_2$  ceased, and after cooling to room temperature final adjustment to pH 7 was made with the aid of a pH meter and dropwise addition of concentrated  $\text{HClO}_4$  and concentrated  $\text{NaOH}$ . A slight suspension of hydrous ferric oxide was removed by filtration; later a white gelatinous precipitate,

probably hydrous aluminum oxide, appeared requiring repeated filtrations. To forestall the possibility that aluminum could be introduced by leaching of the glass container, the solution was transferred to a new polyethylene bottle for long storage.

The concentration of the stock solution was determined by drying 10.00-ml aliquots in porcelain crucibles and weighing as  $\text{NaClO}_4$ .

#### Perchloric Acid Stock Solutions

An approximately 5 M  $\text{HClO}_4$  solution was prepared by addition of 840 ml Baker and Adamson reagent grade 70% perchloric acid to 1100 ml water. The concentration was determined periodically by titration against 1 N carbonate-free sodium hydroxide solution (standardized against potassium biphthalate) using phenolphthalein as indicator.

Upon depletion of the above solution a second was prepared in the same manner from Mallinckrodt analytical reagent 70%  $\text{HClO}_4$ .

#### Solutions for Equilibration

The following solutions were made up by volume from the above described  $\text{HClO}_4$  and  $\text{NaClO}_4$  stock solutions: 1.000, 2.000 and 3.000 N  $\text{HClO}_4$  and 1.00 and 2.00 M  $\text{NaClO}_4$ . From the 2.00 M  $\text{NaClO}_4$  and  $\text{HClO}_4$  solutions thus obtained, the mixtures 0.400 N  $\text{HClO}_4$ -0.60 M  $\text{NaClO}_4$  and 0.700 N  $\text{HClO}_4$ -0.30 M  $\text{NaClO}_4$  were also prepared.

## Solubility of MIBK in Perchlorate Solutions

### Procedure

To determine the approximate solubility of MIBK in 1.00 M  $\text{NaClO}_4$ , 1.00, 2.00 and 3.00 N  $\text{HClO}_4$  and the two perchlorate mixtures, Mallinckrodt analytical reagent grade methyl isobutyl ketone was added to each solution in small amounts with shaking until a slight amount of undissolved MIBK was present. The solutions were then brought to 25°C and any excess MIBK was evaporated with the aid of a stream of air.

The concentrations of the MIBK-saturated solutions were then determined. The  $\text{HClO}_4$  and  $\text{HClO}_4$ - $\text{NaClO}_4$  solutions were titrated against 1 N NaOH and aliquots of the  $\text{NaClO}_4$  solution were dried and weighed.

Assuming additive volumes, the absolute value of the percent loss in concentration is equal to the percent gain in volume, and the volume percent solubility of MIBK in the final solution is

$$\text{Solubility (vol \%)} = \frac{\% \text{ gain in volume}}{100 + \% \text{ gain in volume}}$$

### Data

Concentrations of solutions before and after addition of MIBK, and solubilities of MIBK in the saturated solutions according to the

above equation are given in the following table.

Table 12. Solubility of MIBK in perchlorate solutions.

Concentration of solution before saturation	Concentration of solution after saturation	MIBK solubility vol %
1.00 M NaClO <sub>4</sub>	0.994 M	0.6
0.400 N HClO <sub>4</sub> (-0.60 M NaClO <sub>4</sub> )	0.3916 N HClO <sub>4</sub>	2.1
0.700 N HClO <sub>4</sub> (-0.30 M NaClO <sub>4</sub> )	0.6834 N HClO <sub>4</sub>	2.32
1.000 N HClO <sub>4</sub>	0.9638 N	3.49
2.000 N HClO <sub>4</sub>	1.902 N	4.7
3.000 N HClO <sub>4</sub>	2.797 N	6.34

### Discussion

These data indicate that MIBK is more soluble in HClO<sub>4</sub> than in NaClO<sub>4</sub> solution and that its solubility increases with acid concentration. However, the value of 0.6% solubility of MIBK in 1 M NaClO<sub>4</sub> is probably too low as indicated by the solubility of MIBK in water at 25°C reported by Marsden (61, p. 253) which is 1.7% wt/wt or approximately 2.1% vol/vol.

The solubility of MIBK in HClO<sub>4</sub> solutions is plotted against the HClO<sub>4</sub> concentration of saturated solutions in Figure 6 and shows an approximately linear dependence. This plot was used to determine amounts of MIBK to be dissolved in aqueous phases for tantalum fluoride extractions.

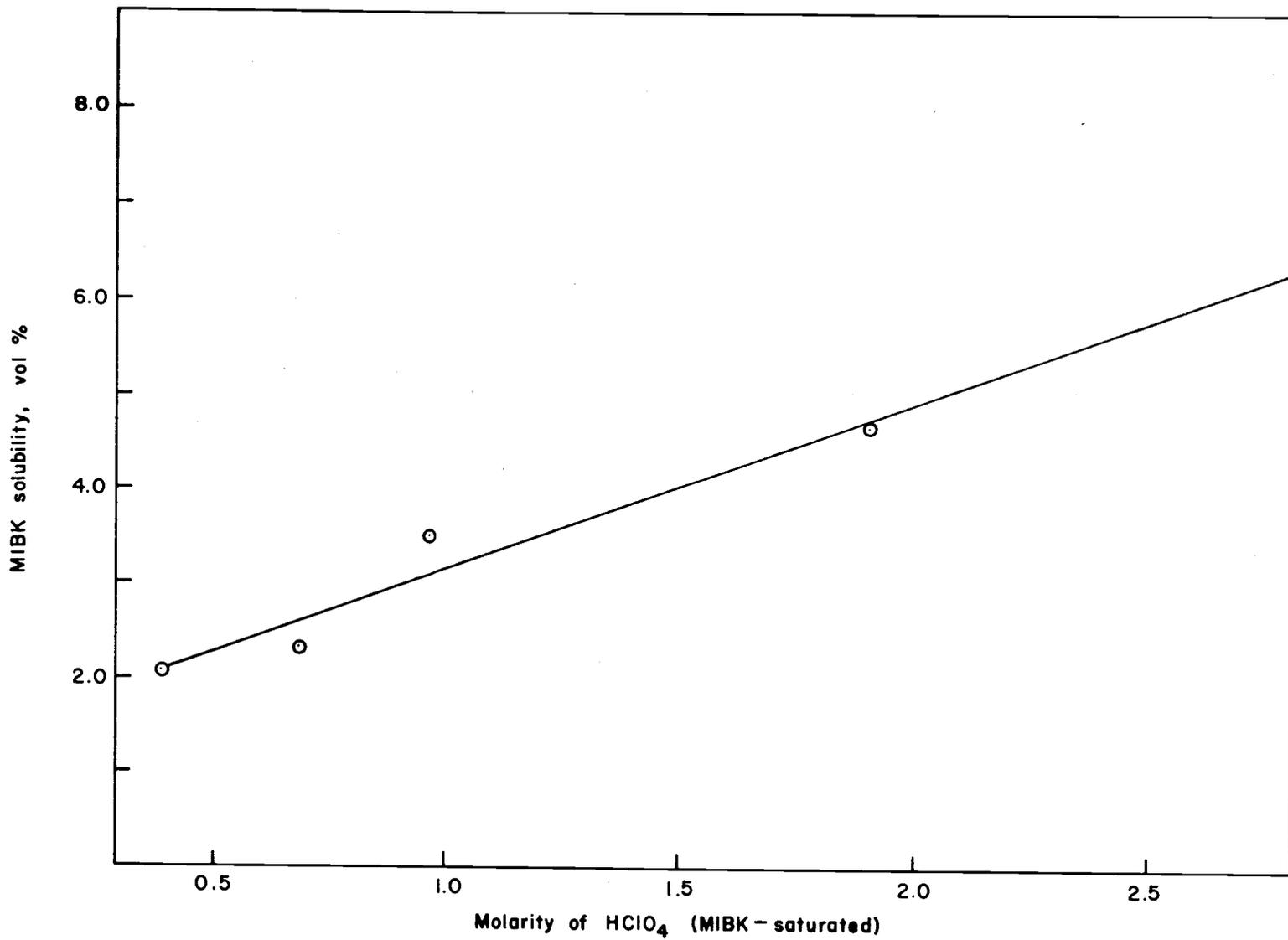


Figure 6.— Solubility of MIBK in aqueous HClO<sub>4</sub> solutions.

## Extraction of $\text{HClO}_4$ and $\text{NaClO}_4$ into MIBK

### Procedure

Preparation of Equilibration Samples. In the manner described above, solutions of 1.00 M  $\text{NaClO}_4$ , 1.00, 2.00 and 2.792 N  $\text{HClO}_4$  and the mixtures 0.400 N  $\text{HClO}_4$ -0.60 M  $\text{NaClO}_4$  and 0.700 N  $\text{HClO}_4$ -0.30 M  $\text{NaClO}_4$  were saturated with MIBK and their concentrations redetermined. Duplicate equilibration samples were then prepared from each solution; for each sample 25.00 ml of the MIBK-saturated perchlorate solution and 25.00 ml of MIBK were pipetted into a 4-oz Teflon bottle. Samples were placed in a water bath at  $25 \pm 0.2^\circ\text{C}$ ; total equilibration times varied from two to four days.

Change in Volume of Phases. The changes occurring in volumes of phases were independently determined by pipetting equal volumes (25.00 ml) of MIBK and MIBK-saturated perchlorate solution into Teflon bottles, allowing to equilibrate at  $25^\circ\text{C}$  for about 24 hours and then carefully transferring the contents into a 50-ml graduated cylinder. After allowing a few moments for separation, the total volume and the volume of the lower (aqueous) phase were recorded and the volume of the MIBK phase found by difference. Average final volumes of phases of duplicate samples are shown in Table 13.

Determination of Extracted  $\text{HClO}_4$ . In order to determine the

equilibrium concentration of  $\text{HClO}_4$  in the MIBK phases of those samples containing perchloric acid, each equilibrated sample was transferred to a separatory funnel. The aqueous phase was rejected and duplicate 10.00-ml aliquots of the MIBK phase were pipetted into Erlenmeyer flasks for titration against standard sodium hydroxide solution of the appropriate concentration, using phenolphthalein as indicator. The presence of immiscible MIBK was found to interfere with indicator action and proper mixing; thus about 20 ml water was added to the flask and the solvent evaporated by gentle heating before titration was carried out. Corrections were made for indicator blanks where appropriate and the average of four values of  $(\text{HClO}_4)_{\text{MIBK}}$  for each aqueous solution was recorded in Table 13.

Calculation of Aqueous  $\text{HClO}_4$  Concentrations. Having thus determined the change in volumes and the equilibrium  $\text{HClO}_4$  concentrations of the MIBK phases, those of the aqueous phases were calculated using the principle of milliequivalents:

$$(\text{HClO}_4)_{\text{aq}} = \frac{[25.0 \text{ ml} \times \text{original } (\text{HClO}_4)_{\text{aq}}] - [(\text{HClO}_4)_{\text{MIBK}} \times \text{final MIBK vol in ml}]}{[\text{final aqueous vol in ml}]}$$

Distribution ratios could then be calculated:

$$\phi_{\text{HClO}_4} = \frac{(\text{HClO}_4)_{\text{MIBK}}}{(\text{HClO}_4)_{\text{aq}}}$$

Values of  $(\text{HClO}_4)_{\text{aq}}$  and  $\phi_{\text{HClO}_4}$  are entered in Table 13.

Figure 7 shows the dependence of  $(\text{HClO}_4)_{\text{MIBK}}$  upon  $(\text{HClO}_4)_{\text{aq}}$  and permits estimation of expected concentrations of  $\text{HClO}_4$  in MIBK phases of equilibration samples to be used in the study of tantalum fluoride extraction.

Extraction of  $\text{NaClO}_4$  into MIBK. Determination of  $\text{NaClO}_4$   
 extracted into MIBK from the solvent-saturated 0.994 M  $\text{NaClO}_4$  solution was attempted by drying 10.00-ml aliquots of the separated MIBK phase in porcelain crucibles. A brown residue resulted indicating reaction of perchlorate with the solvent. Equilibrations were repeated and this time aliquots of the MIBK phase were transferred to Erlenmeyer flasks containing water. By heating the MIBK was evaporated and then most of the water; drying was completed in a  $110^\circ\text{C}$  oven. The white residue was weighed as  $\text{NaClO}_4$ . Since little  $\text{NaClO}_4$  was extracted phase volumes were assumed equal and the final aqueous  $\text{NaClO}_4$  concentration was taken to be the difference between the original concentration and that extracted into MIBK; the distribution ratio  $\phi_{\text{NaClO}_4}$  was calculated as for  $\text{HClO}_4$ .

Determination of  $\text{NaClO}_4$  Co-Extracted with  $\text{HClO}_4$ . To ascertain if the distribution of  $\text{NaClO}_4$  is significantly affected by the presence of  $\text{HClO}_4$ , the amounts of  $\text{NaClO}_4$  co-extracted with  $\text{HClO}_4$  from the MIBK-saturated solutions 0.393 N  $\text{HClO}_4$ -0.59 M  $\text{NaClO}_4$  and 0.684 N  $\text{HClO}_4$ -0.29 M  $\text{NaClO}_4$  were determined. This was accomplished by weighing the Erlenmeyer flasks prior to titration of aliquots

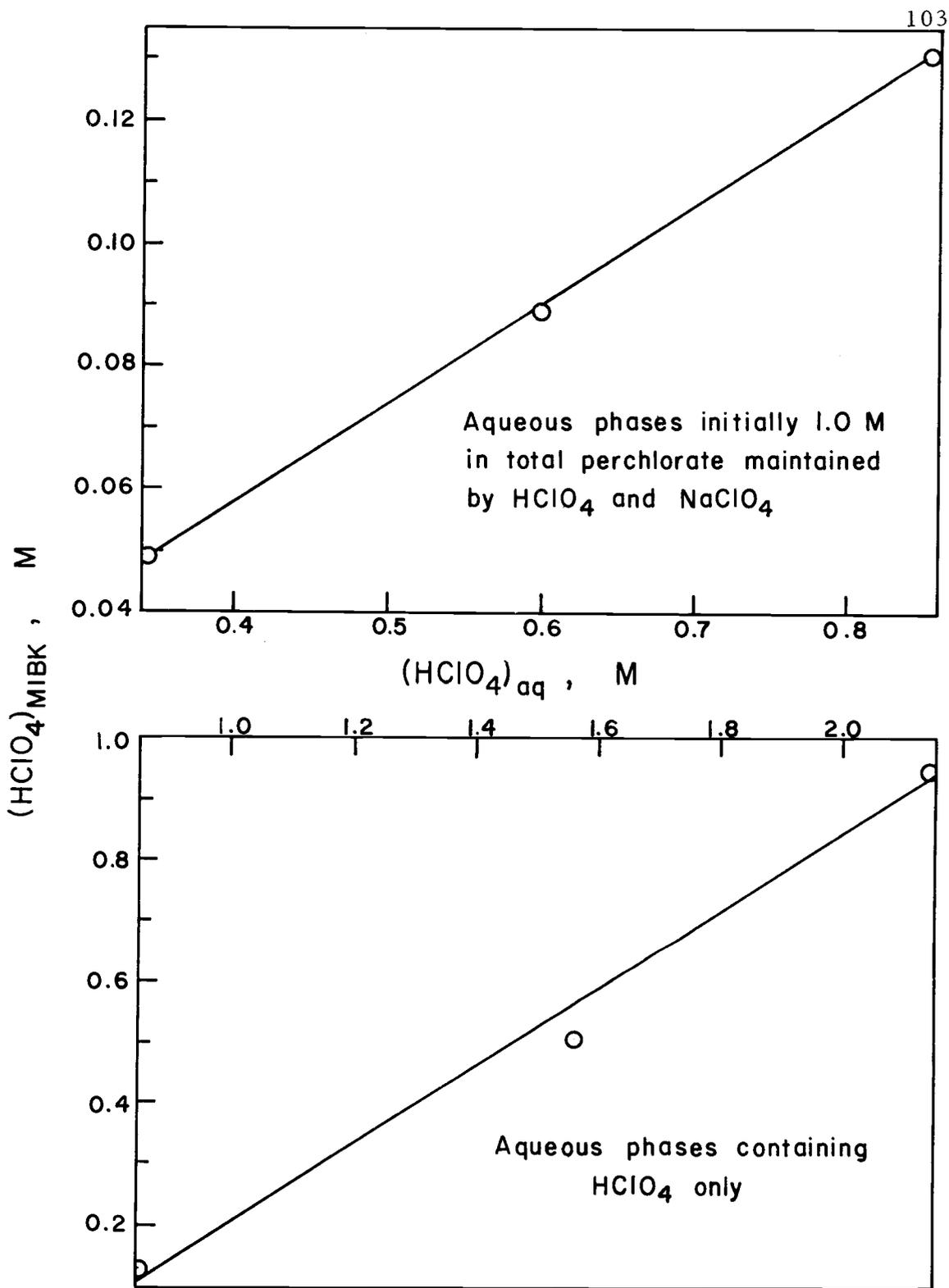


Figure 7.—Distribution of  $\text{HClO}_4$  between MIBK and aqueous perchlorate solutions.

of MIBK phases of these samples with NaOH, drying the titrated samples and weighing to find the total perchlorate extracted. In each case the weight of sodium perchlorate was corrected for the weight of phenolphthalein added and also for the indicator blank, or excess NaOH required to obtain a visible endpoint, as well as for the extracted  $\text{HClO}_4$ . The remaining weight was that of the extracted  $\text{NaClO}_4$ . The average  $(\text{NaClO}_4)_{\text{MIBK}}$  and  $\phi_{\text{NaClO}_4}$  values (taking into account any change in volume) for the two mixtures are given in Table 13.

## Discussion

### $\text{NaClO}_4$ Extraction

The data of Table 13 show at a glance that sodium perchlorate is much less extractable than perchloric acid, as expected. While the distribution ratios appear to be somewhat greater for  $\text{NaClO}_4$  in the presence of  $\text{HClO}_4$  than for  $\text{NaClO}_4$  alone, the values of co-extracted  $\text{NaClO}_4$  concentrations are the result of a procedure experimentally involving several operations and mathematically involving the difference of two numbers of similar magnitude; hence their accuracy should be viewed with some skepticism. No further treatment of the  $\text{NaClO}_4$  data was felt to be justified.

Table 13. Extraction of  $\text{HClO}_4$  and  $\text{NaClO}_4$  into MIBK.

Composition of MIBK-satd. aq phase prior to extraction	Total vol of phases at equilibrium, ml	Final vol MIBK phase, ml	$(\text{HClO}_4)_{\text{MIBK}}$ N	Final vol aq phase, ml	$(\text{HClO}_4)_{\text{aq}}$ N	$\phi_{\text{HClO}_4}$	$(\text{NaClO}_4)_{\text{MIBK}}$ M	$(\text{NaClO}_4)_{\text{aq}}$ M	$\phi_{\text{NaClO}_4}$
(A) 0.994 M $\text{NaClO}_4$	-	-	-	-	-	-	$5.5 \times 10^{-3}$	0.989	$5.6 \times 10^{-3}$
(B) 0.393 N $\text{HClO}_4$ - 0.587 M $\text{NaClO}_4$	50.15	25.1	0.0496	25.05	0.343	0.145	$5.0 \times 10^{-3}$	0.581	$8.6 \times 10^{-3}$
(C) 0.684 N $\text{HClO}_4$ - 0.293 M $\text{NaClO}_4$	50.2	25.45	0.0891	24.75	0.599	0.149	$4.3 \times 10^{-3}$	0.292	$1.5 \times 10^{-2}$
(D) 0.9746 N $\text{HClO}_4$	50.15	25.55	0.1310	24.6	0.854	0.153	-	-	-
(E) 1.944 N $\text{HClO}_4$	49.8	27.5	0.506	22.3	1.56	0.324	-	-	-
(F) 2.792 N $\text{HClO}_4$	50.5	32.1	0.950	18.4	2.14	0.444	-	-	-

## HClO<sub>4</sub> Extraction

Inspection of Table 13 reveals a significant increase in the distribution ratio of HClO<sub>4</sub> with increasing aqueous phase HClO<sub>4</sub> concentration, along with a shift in volume from the aqueous to the organic phase.

Vinarov and Byk (95) also reported an increasing distribution of HClO<sub>4</sub> between MIBK and water with increasing HClO<sub>4</sub> concentration. However, their observation that in HClO<sub>4</sub>-NaClO<sub>4</sub> mixtures of constant ionic strength, the distribution ratio of HClO<sub>4</sub> is greatest at the greatest concentration of NaClO<sub>4</sub>, is not borne out by the present data.

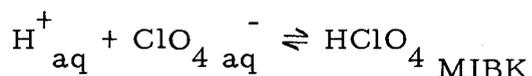
It is expected that water should accompany the extraction of perchloric acid; however, the amount of water extracted from ~3 N HClO<sub>4</sub> seems to exceed the 4:1 mole ratio of water to perchloric acid reported by Tuck and Diamond (88) for extraction into diisopropyl ketone.

Considering that each aqueous phase was presaturated with MIBK, but not vice versa, and that according to Marsden (61, p. 253) water is soluble in MIBK to the extent of 1.9% wt/wt or approximately 1.5% vol/vol, it is surprising that the equilibrium organic phase volumes are not greater than those of the aqueous phases from the very lowest acid concentration. The fact that they are not may indicate

that the MIBK had absorbed some water from the air prior to equilibration.

#### Distribution Coefficients for $\text{HClO}_4$

Concentration Distribution Coefficients. The extraction of  $\text{HClO}_4$  into MIBK via the hydrate-solvate mechanism may be represented:



The equilibrium constant for the extraction reaction is considered here to be a special case of the distribution coefficient, thus

$$\lambda = \frac{(\text{HClO}_4)_{\text{MIBK}}}{(\text{H}^+)_{\text{aq}} (\text{ClO}_4^-)_{\text{aq}}}$$

Concentration distribution coefficients were calculated from the data of Table 13 using the above formula and are recorded in Table 14. They show a slight increase over the range of increasing acid concentration.

Activity Distribution Coefficients. In order to further elucidate the extraction of  $\text{HClO}_4$ , it was thought desirable to make corrections for activity coefficients in the aqueous phase. Although the necessary data is not available to estimate activity coefficients of  $\text{HClO}_4$  in the

two perchlorate mixtures, activity coefficients for solutions of  $\text{HClO}_4$  reported by Robinson and Stokes (71) show substantial increases with acid concentration. Ignoring the presence of MIBK, approximate activity coefficients for the three equilibrated aqueous phases not containing  $\text{NaClO}_4$  were obtained by conversion of the  $\text{HClO}_4$  molarity to molality from knowledge of densities (43, p. 54) and by interpolation of the activity coefficient values given by Robinson and Stokes for various molalities.

Since little is known of the significance or magnitude of activity coefficients in the organic phase, the numerator of the formula for the concentration distribution coefficient was left unchanged in the expression for the activity distribution coefficient.

$$\lambda_{\text{act}} = \frac{(\text{HClO}_4)_{\text{MIBK}}}{(\gamma_{\pm})^2 (\text{H}^+)_{\text{aq}} (\text{ClO}_4^-)_{\text{aq}}}$$

Approximate aqueous phase activity coefficients and the values of  $\lambda_{\text{act}}$  derived from them are given in Table 14.

Table 14. Distribution coefficients of  $\text{HClO}_4$ .

Aqueous phase	$(\text{HClO}_4)_{\text{MIBK}}$ N	$(\text{H}^+)_{\text{aq}}$ N	$(\text{ClO}_4^-)_{\text{aq}}$ M	$\lambda_{\text{HClO}_4}$	$\gamma_{\pm}$	$\lambda_{\text{act}}$
B	0.0496	0.343	0.924	0.156	--	--
C	0.0891	0.599	0.891	0.167	--	--
D	0.1310	0.854	0.854	0.180	0.808	0.275
E	0.506	1.56	1.56	0.208	0.972	0.220
F	0.950	2.14	2.14	0.207	1.196	0.145

Dissociation of  $\text{HClO}_4$  in MIBK. In contrast to the concentration coefficients, the activity distribution coefficients decrease markedly with increasing aqueous acid concentration. This decrease indicates that perchloric acid dissociates upon dilution in MIBK, as suggested by other results. Tribalat (86) reported on the basis of studies with the bromothymol blue diacid that strong acids exist in water-saturated MIBK as hydronium salts which dissociate upon dilution. It was found by Turner and Diamond (89) that perchloric acid extracted by 1-decanol into 1,2-dichloroethane, a solvent having a dielectric constant of 10.36, is predominantly dissociated at concentrations below 0.001 M. Since MIBK has a higher dielectric constant, equal to 13.11 at 20°C according to Marsden (61, p. 253) the dissociation of  $\text{HClO}_4$  in MIBK should be greater than in 1,2-dichloroethane. Dissociation of acids occurs in solvents of dielectric constant greater than about 10, according to Dulova and co-workers (27).

No calculation of the dissociation constant of  $\text{HClO}_4$  in MIBK was attempted because of uncertainties arising from different aqueous phase MIBK solubilities and different concentrations of  $\text{HClO}_4$  and  $\text{H}_2\text{O}$  in the MIBK phases of the equilibration samples involved.

MIBK - Aqueous HF Equilibria

Experimental

Hydrofluoric Acid Solutions

The following HF solutions were diluted from Baker and Adamson or Mallinckrodt reagent grade 48% hydrofluoric acid and their concentrations determined by titration against standard sodium hydroxide solution using phenolphthalein as indicator: 0.05225, 1.027 and 5.367 N.

Solubility of MIBK in HF Solutions

Procedure was the same as for  $\text{HClO}_4$  solutions; the three HF solutions were saturated with MIBK and then were again titrated with sodium hydroxide solution to determine the new concentrations, permitting calculation of the volume percent solubility of MIBK. Data are given in the following table.

Table 15. Solubility of MIBK in HF solutions.

HF concentration prior to saturation, N	HF concentration after saturation, N	MIBK solubility in sat. solution, vol %
0.05225	0.0511	2.2
1.027	0.999	2.7
5.367	5.202	3.0

As may be seen, the solubility of MIBK increases with HF concentration but is significantly less than the solubility in  $\text{HClO}_4$  solutions.

#### Extraction of HF

Again the same procedure was followed as for  $\text{HClO}_4$  solutions. Duplicate equilibration samples were prepared from each of the HF solutions using 25.00 ml of MIBK-saturated HF and 25.00 ml MIBK in Teflon bottles. The samples were allowed to equilibrate in a 25°C water bath for 19-20 days; aliquots of the MIBK phase were mixed with water and the MIBK was evaporated by heating before titrating with NaOH to find the HF concentration of the organic phase. The phase volume ratio was checked independently for the  $\sim 1$  M and  $\sim 5$  M HF samples; there was a slight change in that of the latter sample upon equilibration, so that for this sample the equilibrium HF concentration of the aqueous phase was found using the principle of milliequivalents rather than by taking the simple difference. Data and distribution ratios  $\phi_{\text{HF}} = \frac{C_{\text{HF MIBK}}}{C_{\text{HF aq}}}$  are shown in Table 16.

Table 16. Extraction of HF by MIBK.

Original HF concentration of MIBK-satd. solution, N	Volume Ratio MIBK:aq	$C_{\text{HF MIBK}}, \text{N}$	$C_{\text{HF aq}}, \text{N}$	$\phi_{\text{HF}}$
0.0511	25.0:25.0	0.0114	0.0397	0.287
0.999	25.0:25.0	0.230	0.769	0.299
5.202	26.55:23.45	1.304	4.070	0.320

## Discussion

### Other Results

The  $\phi$  values for extraction of HF into MIBK from  $\sim 1$  M and  $\sim 5$  M solutions of HF are reasonably consistent with those given by Bock and Herrmann (12) considering that these authors used a lower temperature, 20°C. Distribution ratios (denoted  $\alpha$ ) were reported to be 0.315 for extraction from 1 N HF and 0.332 for extraction from 5 N HF. The distribution ratio increased to a value of 0.414 for extraction from 20 N HF.

The present data on mutual solubilities of HF solutions and MIBK cover only a limited range of lower HF concentrations; Cockbill and Magid (20) have presented a diagram for the ternary system H<sub>2</sub>O-HF-MIBK showing that as the HF concentration is increased MIBK and water increase in miscibility until the system becomes homogeneous.

### Distribution Coefficients for HF Extraction

Since HF is a weak acid it is probably extracted essentially as molecular HF, although limited hydration and solvation of the proton is no doubt involved.

The distribution coefficient for HF extraction may then be

expressed:

$$\lambda = \frac{(\text{HF})_{\text{MIBK}}}{(\text{HF})_{\text{aq}}}$$

Assuming that monomers of HF predominate in the organic phase, then

$$\lambda = \frac{C_{\text{HF MIBK}}}{(\text{HF})_{\text{aq}}}$$

To calculate values of  $\lambda$  requires a knowledge of the concentrations of molecular HF in the aqueous phases. These were determined using the HF dissociation constants and procedure described in the previous section for calculation of free fluoride concentration in HF solutions. First the  $(\text{F}^-)$  value for each aqueous phase, neglecting the presence of MIBK, was found by trial and error from equation (15), making successive approximations until both sides of the equation were equal; the  $(\text{HF})$  value was then found by equation (16).

Calculated values of  $(\text{HF})_{\text{aq}}$  and of the distribution coefficient for each equilibration sample are shown in Table 17.

Table 17. Distribution coefficients for HF.

$C_{\text{HF aq, N}}$	$(\text{HF})_{\text{aq, M}}$	$C_{\text{HF MIBK, N}}$	$\lambda$
0.0397	0.0340	0.0114	0.336
0.769	0.675	0.230	0.336
4.07	3.58	1.304	0.354

Identical values for  $\lambda$  in the two lower fluoride samples indicate that HF is extracted as molecular HF and that monomers of HF predominate in the MIBK phase in the lower fluoride range. The greater  $\lambda$  value for the most concentrated fluoride sample indicates that dimerization of HF begins to occur in the  $\sim 1 \text{ N } C_{\text{HF MIBK}}$  range.

### Summary and Conclusions

To summarize the results of this section a table may be presented showing expected aqueous phase MIBK solubilities and organic phase  $\text{HClO}_4$  concentrations for systems to be used in the study of tantalum fluoride complexes.

Table 18. Mutual solubility data for MIBK-aqueous perchlorate systems.

Aqueous phase composition	Aqueous phase MIBK solubility, vol %	$(\text{HClO}_4)_{\text{MIBK}}, \text{N}$
0.400 N $\text{HClO}_4$ - 0.60 M $\text{NaClO}_4$	2.1	0.058
0.700 N $\text{HClO}_4$ - 0.30 M $\text{NaClO}_4$	2.6	0.107
1.00 N $\text{HClO}_4$	3.15	0.20
2.00 N $\text{HClO}_4$	4.9	0.85

These data show that caution should be taken in comparing distribution curves even within the 1.0 M perchlorate system; some of the differences in distribution behavior may be attributable to activity coefficient changes. In addition, assuming a range of aqueous hydrofluoric acid concentration of  $10^{-3}$  to 2.0 M within a given extraction

run, the MIBK phase hydrofluoric acid concentration will range from about  $3 \times 10^{-4}$  to  $7 \times 10^{-1}$  M; the aqueous phase solubility of MIBK may also increase slightly at the high fluoride end of the run. Thus the assumption of constant activity coefficients in both phases may not hold strictly true even within a given run.

The greatest concentration of solute in the MIBK phase occurs in the 2.0 M  $\text{HClO}_4$  extraction system where the expected MIBK phase  $\text{HClO}_4$  concentration is 0.85 M. In calculating the number of pre-equilibrations with fresh aqueous phase required to attain this concentration in the MIBK phase, it was found that after four pre-equilibrations the value of  $(\text{HClO}_4)_{\text{MIBK}}$  is about 0.842 M or within 1% of saturation; this should be close enough. For systems of lower acid concentration, four pre-equilibrations result in virtually complete saturation of the MIBK phase.

EXTRACTION OF FLUO-TANTALUM SPECIES BY  
METHYL ISOBUTYL KETONE

General

Studies of the distribution of  $^{182}\text{Ta}$  fluoride between MIBK and aqueous perchlorate media were planned so as to investigate the dependence of the extraction upon the hydrogen ion concentration and to ascertain whether distribution data obtained from the 1.0 M perchlorate system would be consistent with formation constants of tantalum fluoride complexes obtained by Varga and Freund (92) using other methods. Runs were made at constant hydrogen ion concentrations of 0.4, 0.7 and 1.0 M each in a constant ionic medium of 1.0 M perchlorate maintained by  $\text{HClO}_4$  and  $\text{NaClO}_4$ . A fourth run at  $(\text{H}^+) = 2.0 \text{ M}$  and  $(\text{ClO}_4^-) = 2.0 \text{ M}$  was added to furnish a bridge between the 1.0 M extraction results and the 3 M  $\text{HClO}_4$ -MIBK data of Varga and co-workers (94), and to help establish whether the combined data are consistent with the extraction of  $\text{TaF}_6^-$  as a complex metal acid and with the increasing stability of tantalum fluoride complexes with ionic strength, as observed by Varga. The aqueous phase tantalum concentration was less than  $5.2 \times 10^{-7} \text{ M}$  and the free fluoride concentration ranged from  $1.6 \times 10^{-6}$  to  $8 \times 10^{-3} \text{ M}$  in these studies.

Planning of Aqueous Phase Composition

In order to maintain a constant hydrogen ion concentration throughout each run, careful advance planning of the composition of aqueous phases was necessary, so that as the ( $H^+$ ) contributed by HF became significant at higher fluoride levels the amount of added  $HClO_4$  could be reduced correspondingly and supplemented by  $NaClO_4$  to maintain the required concentration of hydrogen ion and of perchlorate. The success of such a procedure depends primarily upon the accuracy of the weak acid dissociation constants used.

HF Dissociation Constants for 1.0 M  $NaClO_4$

Dissociation constants  $Ka_1$  and  $Ka_2$  were obtained by taking the reciprocals of the association constants  $K_{11}$  and  $K_{12}$  given by Farrer and Rossotti (33) for 1.0 M  $NaClO_4$  at 25°C.

$$Ka_1 = \frac{(H^+)(F^-)}{(HF)} = (1.12 \pm 0.025) \times 10^{-3}$$

$$Ka_2 = \frac{(HF)(F^-)}{(HF_2^-)} = 0.26 \pm 0.06$$

## HF Dissociation Constants for 2.0 Perchlorate

Ka<sub>1</sub>

Although Farrer and Rossotti gave association constants for only 1.0 and 3.0 M sodium perchlorate media at 25°C, they stated that their values of K<sub>11</sub> conformed (within experimental error) to the Debye-Hückel equation

$$\log K_{11} = 3.17 - \frac{1.022 I^{\frac{1}{2}}}{1 + 1.322 I^{\frac{1}{2}}} + 0.218 I = -\log Ka_1$$

where I is the ionic strength. For I=2.0 the value of Ka<sub>1</sub> calculated from this equation is  $(7.68 \pm 0.18) \times 10^{-4}$ .

Ka<sub>2</sub>

It was suggested by Farrer and Rossotti that log K<sub>12</sub> increases approximately linearly with the electrolyte concentration. On this basis the value for 2.0 M NaClO<sub>4</sub> was taken as the mean of log K<sub>12</sub> values for 1.0 and 3.0 M NaClO<sub>4</sub> media:

$$\log K_{12} = 0.72 \pm 0.06 = -\log Ka_2$$

and Ka<sub>2</sub> = 0.19 ± 0.03.

### Calculation of Aqueous Phase Concentrations

The first step was the selection of representative free fluoride concentrations within the expected range for each run. Each sample, then, had fixed  $(\text{H}^+)$  and  $(\text{F}^-)$  values from which the concentrations of other fluoride species  $(\text{HF})$  and  $(\text{HF}_2^-)$  were easily obtained:

$$(\text{HF}) = \frac{(\text{H}^+)(\text{F}^-)}{K_{a_1}} \quad \text{and} \quad (\text{HF}_2^-) = \frac{(\text{HF})(\text{F}^-)}{K_{a_2}}$$

The total fluoride concentration of the aqueous phase, to be added as HF, was the sum of the various fluoride species according to conservation of mass:

$$C_{\text{HF}} = (\text{F}^-) + (\text{HF}) + 2 (\text{HF}_2^-)$$

Likewise the total acid concentration was given:

$$C_{\text{H}} = (\text{H}^+) + (\text{HF}) + (\text{HF}_2^-)$$

From  $C_{\text{H}}$  the concentration of  $\text{HClO}_4$  to be added was derived:

$$C_{\text{HClO}_4} = C_{\text{H}} - C_{\text{HF}}$$

Then  $C_{\text{NaClO}_4} = I - C_{\text{HClO}_4}$ , where  $I$  is the strength of the constant ionic medium used in the run.

In this way the concentrations of  $\text{HF}$ ,  $\text{HClO}_4$  and  $\text{NaClO}_4$  to

be added to obtain the desired ( $H^+$ ) and ( $F^-$ ) concentrations of the aqueous phases were calculated.

Approximately  $1.36 \times 10^{-3}$  M HF was added to each aqueous phase as a constituent of 0.025 ml of radioactive tantalum stock solution; since this  $C_{FTa}$  was greater than originally anticipated, readjustment of ( $F^-$ ) values were required at the lower end of the free fluoride scale, although the hydrogen ion concentrations were not affected.

#### Readjustment of ( $F^-$ ) Values

The radiotantalum aliquots were added following pre-equilibrations, hence some of the  $C_{FTa}$  was expected to extract into the MIBK phase. The amount remaining in the aqueous phase was calculated using  $\lambda = 0.336$  for HF (as given in the previous section for lower fluoride concentrations) and assuming that in the media containing 0.4 to 2.0 M ( $H^+$ ) the added  $1.36 \times 10^{-3}$  M fluoride is present as molecular HF. Then

$$C_{FTa \text{ aq}} = \frac{1.36 \times 10^{-3} \text{ M}}{1.336} = 1.02 \times 10^{-3} \text{ M}$$

This amount was added to the  $C_{HF}$  value and the new ( $F^-$ ) value for the sample was found by successive approximation from the expression for  $Ka_1$ , using the adjusted value of  $C_{HF}$ .

Readjustments of the ( $F^-$ ) values were also made in cases where

amounts used in making up aqueous phases deviated from those planned.

The amount of fluoride involved in complexation of tantalum was negligible with respect to the total fluoride at all levels.

### Hydrogen Ion Concentrations

In aqueous phases of less than about  $10^{-4}$  M ( $F^-$ ) or  $10^{-2}$  M  $C_{HF}$ , the hydrogen ion concentration contributed through the ionization of HF was negligible relative to  $C_{HClO_4}$ . In samples of higher fluoride concentration the hydrogen ion concentration was maintained by slight reduction of  $C_{HClO_4}$  according to the calculations; the ( $H^+$ ) contributed by HF was less than 0.04 M in all but two samples. A quinhydrone-saturated calomel cell was prepared for the purpose of checking the ( $H^+$ ) values in aqueous phases of  $C_{HF} > 10^{-2}$  M, but did not function properly; therefore the hydrogen ion concentrations of these samples were assumed to be as calculated.

## Experimental

### Reagents

### General

All solutions were prepared with distilled water, and were brought to 25°C previous to standardization. Pipets and burets used

in measurement of solutions were recalibrated; final dilution of solutions prepared by volume was made at 25°C.

#### Hydrofluoric Acid Stock Solutions

The following stock solutions were prepared by dilution from Mallinckrodt analytical reagent grade 48% hydrofluoric acid and their concentrations determined by titration against standard 0.01, 0.1 or 1 N sodium hydroxide solution, using phenolphthalein as an indicator:  $5.38 \times 10^{-3}$ ,  $1.081 \times 10^{-2}$ ,  $4.68 \times 10^{-2}$ , 0.1174, 0.5053, 0.838 and 5.364 N. These solutions were stored in polyethylene bottles.

#### Perchloric Acid Stock Solutions

Solutions of 4.659 N and 0.9612 N  $\text{HClO}_4$  were prepared by dilution from Mallinckrodt analytical reagent grade 70% perchloric acid. Their concentrations were determined through titration against standard 1 N sodium hydroxide, using phenolphthalein as indicator. For convenience in the preparation of aqueous phases, two more solutions, 3.00 and 4.00 N, were made up by volume from the 4.659 N stock solution.

#### Sodium Perchlorate Stock Solution

A 3.00 M sodium perchlorate solution was prepared by diluting 323.25 ml of the 4.64 M  $\text{NaClO}_4$  solution (whose preparation was

described in the previous section ) to 500 ml in a volumetric flask.

### Methyl Isobutyl Ketone

Mallinckrodt analytical reagent grade methyl isobutyl ketone was used in these studies and was pre-equilibrated with aqueous phase.

### $^{182}\text{Ta}$ Stock Solution

$^{182}\text{Ta}$  radioisotope was received from Oak Ridge National Laboratory in the form of tantalate in 1.18 N KOH solution. At the time of shipping the tantalum concentration was 0.26 mg/ml and the specific activity 11,808 mc/g, but the isotope was not used for these equilibrations until a year later when the specific activity had decreased to approximately  $1.11 \times 10^3$  mc/g. During this time a precipitate developed in the tantalate solution which was not entirely dissolved by the addition of hydrofluoric acid. Therefore the tantalum concentration of the stock solution can be given only as an upper limit,  $3.1 \times 10^{-4}$  M. The total fluoride concentration was calculated from the known amount of HF added to the Oak Ridge tantalate solution assuming additive volumes and was 0.814 M. Concentrations resulting from addition of 0.025 ml stock  $^{182}\text{Ta}$  solution to 15.0 ml aqueous phase were  $1.36 \times 10^{-3}$  M fluoride and  $< 5.2 \times 10^{-7}$  M Ta.

### Makeup of Aqueous Phases

The calculated volumes of the  $\text{HClO}_4$ ,  $\text{NaClO}_4$  and HF stock solutions required to prepare 100 ml of each aqueous phase were measured out at 25°C using recalibrated pipets and burets. Hydrofluoric acid solutions less concentrated than  $10^{-2}$  N were handled with Pyrex glassware while the more concentrated HF solutions were measured via polystyrene buret and polypropylene graduated pipet.

Aqueous phases of less than  $10^{-2}$  M total fluoride were diluted to volume in 100-ml Pyrex volumetric flasks; higher fluoride phases were diluted in a 100-ml graduated cylinder of polyethylene or polypropylene. After transfer of the required amounts of  $\text{HClO}_4$ ,  $\text{NaClO}_4$  and HF to the container, an amount of MIBK equal to the solubility indicated by the graph in Figure 6 for the particular  $\text{HClO}_4$  concentration, plus 0.1 ml, was added and the solution was diluted nearly to volume with distilled water and mixed well. The container was then placed in the 25°C water bath for at least 20 minutes before final dilution of the solution to volume.

### Pre-Equilibration of MIBK Phases

After preparation of each aqueous phase, four pre-equilibrations of the corresponding MIBK phase were carried out. For the first pre-equilibration 20 ml of aqueous phase and 20 ml of MIBK

were brought together in a polypropylene separatory funnel, shaken vigorously and allowed to separate. The lower, aqueous phase was then rejected. For samples of higher acidity involving a change in the phase volume ratio, it was necessary to again measure 20 ml of MIBK phase after each pre-equilibration and discard the excess. 20 ml of fresh aqueous phase was then added to the MIBK phase in the separatory funnel for the second pre-equilibration and the procedure repeated. After the fourth addition and rejection of aqueous phase, 15.0 ml of the pre-equilibrated MIBK and 15.0 ml of fresh aqueous phase were pipetted into a one-ounce polyethylene bottle.

#### Addition of $^{182}\text{Ta}$ Stock Solution

Following completion of the above procedure, 0.025 ml of  $^{182}\text{Ta}$  stock solution was added to each equilibration sample. Glass micropipets used for this purpose in previous experiments were felt to be unsatisfactory for these reasons: they were calibrated to contain instead of deliver and were subject to some adsorption of tantalum causing decreased reproducibility, and they would be unsuitable at the higher fluoride concentration of this solution (0.814 M). Therefore, for the measurement of  $^{182}\text{Ta}$  stock solution in these studies a micropipet was used which was drawn from polypropylene tubing and was calibrated to deliver 0.025 ml with a precision of within 1%.

## Equilibration

After addition of the  $^{182}\text{Ta}$  spike each sample was shaken manually and then allowed to equilibrate for a period of from two to seven days. Samples were kept at  $25^{\circ}\text{C}$  for several hours or longer before 1.50-ml aliquots were taken of both phases using the procedure described for the TPA and crystal violet extraction experiments. These aliquots were transferred to 12 x 75 mm high-temperature polyethylene tubes for counting.

## Radioactive Counting

### General

Radioactive tantalum is produced at Oak Ridge National Laboratory through thermal neutron irradiation of natural tantalum (99.988%  $^{181}\text{Ta}$ , 0.0123%  $^{180}\text{Ta}$ ) followed by processing to improve the specific activity. Although the major activity resulting is due to the 115-day  $^{182}\text{Ta}$ , small contributions are made by the shorter-lived  $^{182\text{m}}\text{Ta}$  (16.5 min.) and  $^{183}\text{Ta}$  (5.2 days). Each of these isotopes is a mixed beta-gamma emitter decaying to an inactive tungsten isotope. The  $^{182}\text{Ta}$  radioisotope used in these studies had been allowed to decay for over a year, so that the  $^{182\text{m}}\text{Ta}$  and  $^{183}\text{Ta}$  activities were virtually extinct.

The decay scheme for  $^{182}\text{Ta}$  has been described by Strominger, Hollander and Seaborg (83, p. 755). The maximum energy for beta radiation is 0.51 Mev, while the three most intense gammas have energies of 0.106, 1.122 and 1.222 Mev.

### Counting Equipment

A single-channel differential pulse height analysis unit, the Nuclear-Chicago model 1810 Radiation Analyzer, was used in conjunction with a shielded, well-type scintillation detector of thallium-activated sodium iodide, and with a Nuclear-Chicago model 151A scaler. The coincidence resolving time for this setup is approximately 5  $\mu\text{sec}$ .

The gamma energy spectrum of the Oak Ridge  $^{182}\text{Ta}$  was run as well as a background curve to determine optimum operating conditions. For measurement of the counting rate of aqueous and organic phase aliquots, differential counting with a wide window, including the 1.12 and 1.22 Mev gammas, was utilized. Count rates were corrected for background, which under these conditions averaged less than 20 cpm; coincidence corrections were unnecessary.

### Data

Aqueous phase concentrations, distribution ratios ( $\phi = \text{cpm}/1.50 \text{ ml org} \div \text{cpm}/1.50 \text{ ml aq}$ ) and logarithms of ( $F^-$ ) and of  $\phi$  for

samples of the four runs are given in Tables 19 through 22. Distribution curves are shown in Figure 8. The main features of the extraction behavior include a shift in the distribution maximum from higher to lower ( $F^-$ ) values with an increase in hydrogen ion concentration, and an increasing distribution of  $^{182}\text{Ta}$  as ( $H^+$ ) increases within the 1.0 M perchlorate medium. Upon a change in the constant ionic medium from 1.0 to 2.0 M  $\text{HClO}_4$ , however, the distribution ratio significantly increases at lower ( $F^-$ ) values while the maximum distribution is somewhat decreased. Limiting slopes of the distribution curves at low ( $F^-$ ) are: Run I, 1.80; Run II, 1.76; Run III, 1.73; and Run IV, 1.4.

## Discussion

### Errors

#### Free Fluoride Concentration

Experimental error in making up aqueous phases should be of minor significance since all measuring equipment was recalibrated and dilutions were made at  $25^\circ\text{C}$ .

Some error may have been introduced at the high end of the fluoride scale by regarding the solubility of MIBK in aqueous phases as a function of the concentration of  $\text{HClO}_4$  only; thus aqueous phases containing higher HF concentrations may not have been completely

Table 19. Methyl isobutyl ketone extraction data.

Run I ( $H^+$ ) = 1.00 M ( $ClO_4^-$ ) = 1.00 M ( $Ta \cong 5.2 \times 10^{-7}$ M)								
Sample #	$C_{HF}, M$	$C_H, M$	$C_{HClO_4}, M$	$C_{NaClO_4}, M$	$(F^-), M$	$\log (F^-)$	$\phi$	$\log \phi$
1	$1.63 \times 10^{-3}$	1.001	1.000	--	$1.82 \times 10^{-6}$	-5.740	$1.33 \times 10^{-2}$	-1.876
2	$1.97 \times 10^{-3}$	1.003	1.000	--	$2.20 \times 10^{-6}$	-5.658	$2.02 \times 10^{-2}$	-1.692
3	$4.75 \times 10^{-3}$	1.004	1.000	--	$5.31 \times 10^{-6}$	-5.275	$1.20 \times 10^{-1}$	-0.922
4	$7.45 \times 10^{-3}$	1.007	1.000	--	$8.33 \times 10^{-6}$	-5.079	$2.96 \times 10^{-1}$	-0.529
5	$1.37 \times 10^{-2}$	1.013	1.000	--	$1.54 \times 10^{-5}$	-4.813	$8.51 \times 10^{-1}$	-0.070
6	$2.71 \times 10^{-2}$	1.027	1.000	--	$3.04 \times 10^{-5}$	-4.517	2.61	0.417
7	$4.50 \times 10^{-2}$	1.045	1.000	--	$5.03 \times 10^{-5}$	-4.299	4.85	0.685
8	$7.18 \times 10^{-2}$	1.071	1.000	--	$8.03 \times 10^{-5}$	-4.096	7.90	0.897
9	$1.34 \times 10^{-1}$	1.134	1.000	--	$1.50 \times 10^{-4}$	-3.824	$1.44 \times 10^1$	1.157
10	$2.69 \times 10^{-1}$	1.268	0.999	.001	$3.00 \times 10^{-4}$	-3.523	$1.93 \times 10^1$	1.286
11*	$4.43 \times 10^{-1}$	1.43	0.99	.001	$4.98 \times 10^{-4}$	-3.303	$1.93 \times 10^1$	1.285
12	$7.19 \times 10^{-1}$	1.716	0.997	.003	$8.00 \times 10^{-4}$	-3.097	$1.84 \times 10^1$	1.266
14	2.74	3.71	0.970	0.030	$3.00 \times 10^{-3}$	-2.523	$1.05 \times 10^1$	1.019

\* ( $H^+$ )  $\cong$  0.99 M, = 0.99 M.

Table 20. Methyl isobutyl ketone extraction data.

Run II $(H^+) = 0.70 \text{ M}$ $(ClO_4^-) = 1.00 \text{ M}$ $(Ta) \leq 5.2 \times 10^{-7} \text{ M}$								
Sample #	$C_{HF}, \text{ M}$	$C_H, \text{ M}$	$C_{HClO_4}, \text{ M}$	$C_{NaClO_4}, \text{ M}$	$(F^-), \text{ M}$	$\log (F^-)$	$\phi$	$\log \phi$
15	$1.23 \times 10^{-3}$	0.701	0.700	0.300	$1.96 \times 10^{-6}$	-5.708	$4.86 \times 10^{-3}$	-2.314
16	$2.17 \times 10^{-3}$	0.702	0.700	0.300	$3.46 \times 10^{-6}$	-5.461	$1.88 \times 10^{-2}$	-1.726
17	$3.43 \times 10^{-3}$	0.703	0.700	0.300	$5.47 \times 10^{-6}$	-5.262	$3.30 \times 10^{-2}$	-1.482
18	$5.33 \times 10^{-3}$	0.705	0.700	0.300	$8.68 \times 10^{-6}$	-5.062	$9.92 \times 10^{-2}$	-1.004
19	$9.68 \times 10^{-3}$	0.709	0.700	0.300	$1.55 \times 10^{-5}$	-4.810	$2.67 \times 10^{-1}$	-0.573
20	$1.91 \times 10^{-2}$	0.719	0.700	0.300	$3.06 \times 10^{-5}$	-4.515	$8.70 \times 10^{-1}$	-0.061
21	$3.17 \times 10^{-2}$	0.731	0.700	0.300	$5.06 \times 10^{-5}$	-4.296	1.99	0.299
22	$5.04 \times 10^{-2}$	0.750	0.700	0.300	$8.05 \times 10^{-5}$	-4.094	3.28	0.516
23	$9.42 \times 10^{-2}$	0.794	0.700	0.300	$1.50 \times 10^{-4}$	-3.824	7.26	0.861
24	0.189	0.888	0.699	0.301	$3.01 \times 10^{-4}$	-3.522	$1.16 \times 10^1$	1.064
25	0.315	1.014	0.699	0.301	$5.01 \times 10^{-4}$	-3.301	$1.29 \times 10^1$	1.110
26	0.504	1.202	0.698	0.302	$8.00 \times 10^{-4}$	-3.097	$1.34 \times 10^1$	1.128
27	0.949	1.642	0.693	0.307	$1.50 \times 10^{-3}$	-2.824	$1.18 \times 10^1$	1.073
28	1.93	2.60	0.670	0.330	$3.00 \times 10^{-3}$	-2.523	8.29	0.918
29	3.26	3.89	0.630	0.370	$5.00 \times 10^{-3}$	-2.301	5.22	0.718

Table 21. Methyl isobutyl ketone extraction data.

Run III $(H^+) = 0.40 \text{ M}$ $(ClO_4^-) = 1.00 \text{ M}$ $(Ta) \leq 5.2 \times 10^{-7} \text{ M}$								
Sample #	$C_{HF}, \text{ M}$	$C_H, \text{ M}$	$C_{HClO_4}, \text{ M}$	$C_{NaClO_4}, \text{ M}$	$(F^-), \text{ M}$	$\log(F^-)$	$\phi$	$\log \phi$
30	$1.02 \times 10^{-3}$	0.401	0.400	0.600	$2.84 \times 10^{-6}$	-5.547	$2.80 \times 10^{-3}$	-2.553
31	$1.36 \times 10^{-3}$	0.401	0.400	0.600	$3.80 \times 10^{-6}$	-5.421	$4.16 \times 10^{-3}$	-2.381
32	$2.08 \times 10^{-3}$	0.402	0.400	0.600	$5.80 \times 10^{-6}$	-5.237	$7.75 \times 10^{-3}$	-2.111
33	$3.16 \times 10^{-3}$	0.403	0.400	0.600	$8.82 \times 10^{-6}$	-5.065	$1.98 \times 10^{-2}$	-1.704
34	$5.67 \times 10^{-3}$	0.405	0.400	0.600	$1.58 \times 10^{-5}$	-4.801	$5.27 \times 10^{-2}$	-1.278
35	$1.10 \times 10^{-2}$	0.411	0.400	0.600	$3.08 \times 10^{-5}$	-4.512	$1.60 \times 10^{-1}$	-0.796
36	$1.83 \times 10^{-2}$	0.418	0.400	0.600	$5.12 \times 10^{-5}$	-4.291	$4.34 \times 10^{-1}$	-0.362
37	$2.90 \times 10^{-2}$	0.429	0.400	0.600	$8.10 \times 10^{-5}$	-4.092	$7.96 \times 10^{-1}$	-0.099
38	$5.41 \times 10^{-2}$	0.454	0.400	0.600	$1.51 \times 10^{-4}$	-3.822	1.97	0.294
39	$1.08 \times 10^{-1}$	0.507	0.399	0.601	$3.00 \times 10^{-4}$	-3.523	4.12	0.615
40	$1.80 \times 10^{-1}$	0.579	0.399	0.601	$5.00 \times 10^{-4}$	-3.301	5.79	0.763
41	$2.89 \times 10^{-1}$	0.687	0.398	0.602	$8.00 \times 10^{-4}$	-3.097	6.45	0.809
42	$5.44 \times 10^{-1}$	0.939	0.395	0.605	$1.50 \times 10^{-3}$	-2.824	6.48	0.811
43	1.10	1.48	0.380	0.620	$3.00 \times 10^{-3}$	-2.523	4.74	0.676
44	1.86	2.22	0.360	0.640	$5.00 \times 10^{-3}$	-2.301	3.48	0.541
45	3.04	3.35	0.310	0.690	$8.00 \times 10^{-3}$	-2.097	2.37	0.375

Table 22. Methyl isobutyl ketone extraction data.

Run IV ( $H^+$ ) = 2.00 M ( $ClO_4^-$ ) = 2.00 M ( $Ta$ ) $\leq 5.2 \times 10^{-7}$ M								
Sample #	$C_{HF}, M$	$C_H, M$	$C_{HClO_4}, M$	$C_{NaClO_4}, M$	$(F^-), M$	$\log(F^-)$	$\phi$	$\log \phi$
46	$4.19 \times 10^{-3}$	2.004	2.000	--	$1.61 \times 10^{-5}$	-5.793	$2.93 \times 10^{-1}$	-0.533
47	$8.09 \times 10^{-3}$	2.008	2.000	--	$3.11 \times 10^{-6}$	-5.507	$7.87 \times 10^{-1}$	-0.103
48	$1.33 \times 10^{-2}$	2.013	2.000	--	$5.12 \times 10^{-6}$	-5.291	1.42	0.152
49	$2.11 \times 10^{-2}$	2.021	2.000	--	$8.10 \times 10^{-6}$	-5.092	2.93	0.533
50	$3.93 \times 10^{-2}$	2.039	2.000	--	$1.51 \times 10^{-5}$	-4.821	5.99	0.777
51	$7.84 \times 10^{-2}$	2.078	2.000	--	$3.01 \times 10^{-5}$	-4.522	$1.03 \times 10^1$	1.011
52	$1.30 \times 10^{-1}$	2.130	2.000	--	$5.00 \times 10^{-5}$	-4.301	$1.27 \times 10^1$	1.104
53	$2.08 \times 10^{-1}$	2.208	2.000	--	$8.00 \times 10^{-5}$	-4.097	$1.46 \times 10^1$	1.166
54	$3.91 \times 10^{-1}$	2.390	1.999	0.001	$1.50 \times 10^{-4}$	-3.824	$1.60 \times 10^1$	1.204
55	$7.83 \times 10^{-1}$	2.781	1.998	0.002	$3.00 \times 10^{-4}$	-3.523	$1.56 \times 10^1$	1.192
56	1.36	3.30	1.990	0.010	$5.22 \times 10^{-4}$	-3.282	$1.26 \times 10^1$	1.100

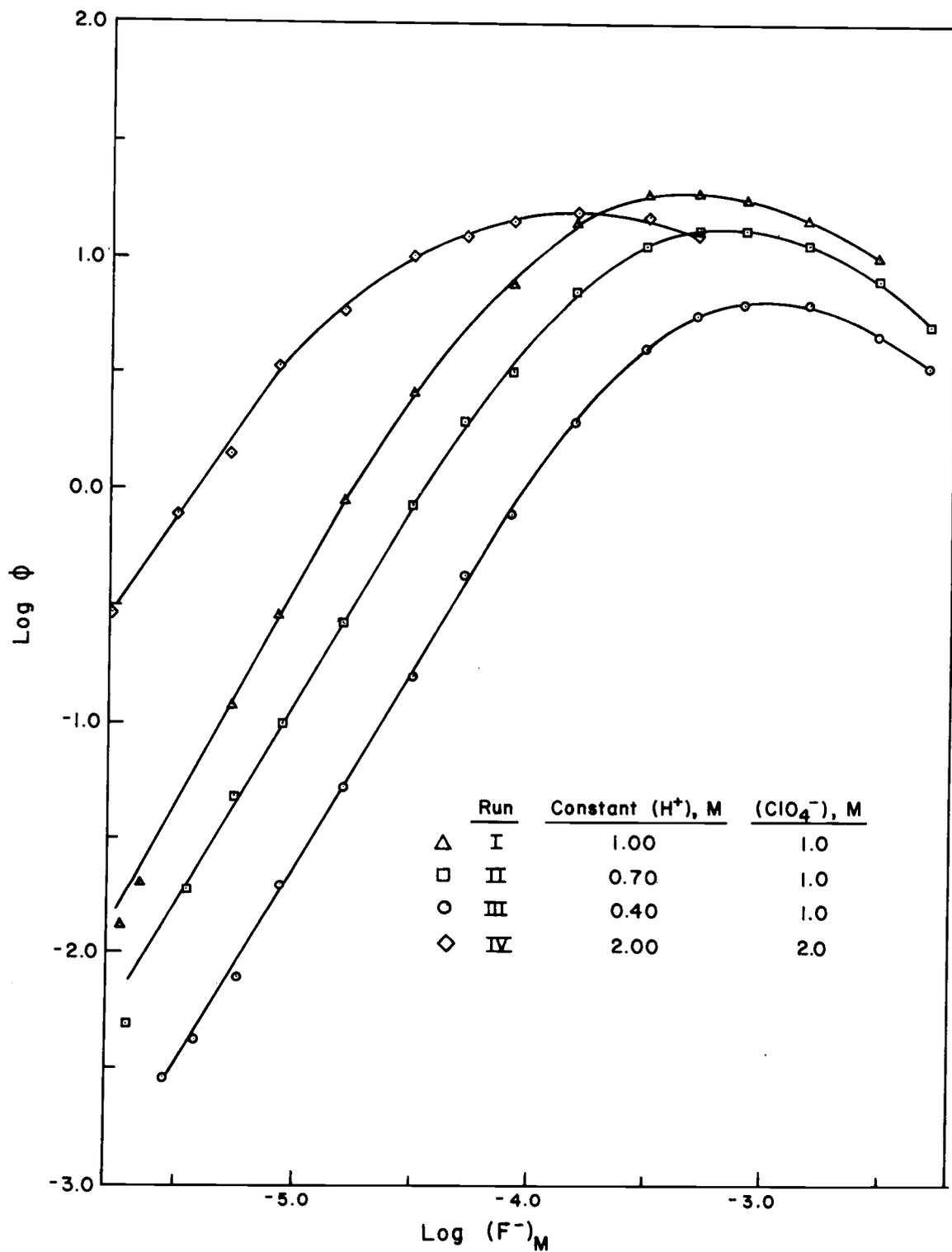


Figure 8.— Distribution of  $^{182}\text{Ta}$  between MIBK and aqueous perchlorate media at varying  $(F^-)$ .

saturated with MIBK when made up. At the low end of the free fluoride scale the uncertainty in the value of  $C_{FTa}$  may have caused some deviation.

The assumption that actual ( $H^+$ ) values in higher fluoride samples are the same as those calculated is probably no more significant as a source of error than other factors, among which is the uncertainty in the HF dissociation constants. It should be noted at this point that the constants of Farrer and Rossotti (33) were determined for sodium perchlorate media, whereas the aqueous phases of the present investigation were either  $HClO_4$  or mixed  $HClO_4$ - $NaClO_4$  solutions and were saturated with MIBK. Changes occurring in the HF dissociation constants as the sodium ion of the background electrolyte is replaced by hydrogen ion are doubtless significant, and especially so at the higher ionic strengths. These factors are expected to cause some errors in the calculated free fluoride concentrations.

#### Distribution Ratio

The standard deviation in the distribution ratio  $\phi$  due to statistical counting error is approximately 1.4%. The average overall error, as indicated by the scatter of points from the distribution curve of Run III, is in the neighborhood of 4%.

## Comparison of Results with Published Data of Varga

3 M HClO<sub>4</sub> Data of Varga and Co-Workers

Logarithms were taken of the  $\phi$  and ( $F^-$ ) values given by Varga and co-workers (94) for MIBK extraction from 3 M HClO<sub>4</sub> medium, and the distribution curve was plotted in Figure 9 along with the curves for 1.0 M and 2.0 M HClO<sub>4</sub> from this investigation.

A difference between the conditions of this work and of Varga's should be noted. Varga did not maintain a constant ( $H^+$ ) throughout the extraction run; the fluoride concentration was varied by the addition of solid sodium fluoride to 3 M HClO<sub>4</sub> solution, resulting in a reduction of ( $H^+$ ) in the three highest fluoride samples to as low as 2.36 M.

The 2.0 M HClO<sub>4</sub> distribution curve differs considerably from the 1.0 M HClO<sub>4</sub> plot, but closely resembles Varga's curve for 3 M HClO<sub>4</sub>, in fact coinciding with it at lower ( $F^-$ ) values within the experimental error. Such behavior would, in the case of an extraction system where the mechanism is independent of hydrogen ion, indicate that hydrolysis occurs at lower ( $H^+$ ) and ceases at higher ( $H^+$ ) values where coincidence of distribution curves is observed. In this case, however, the best evidence available points to the extraction of TaF<sub>6</sub><sup>-</sup> as a complex metal acid from 3 M HClO<sub>4</sub>. This type of extraction

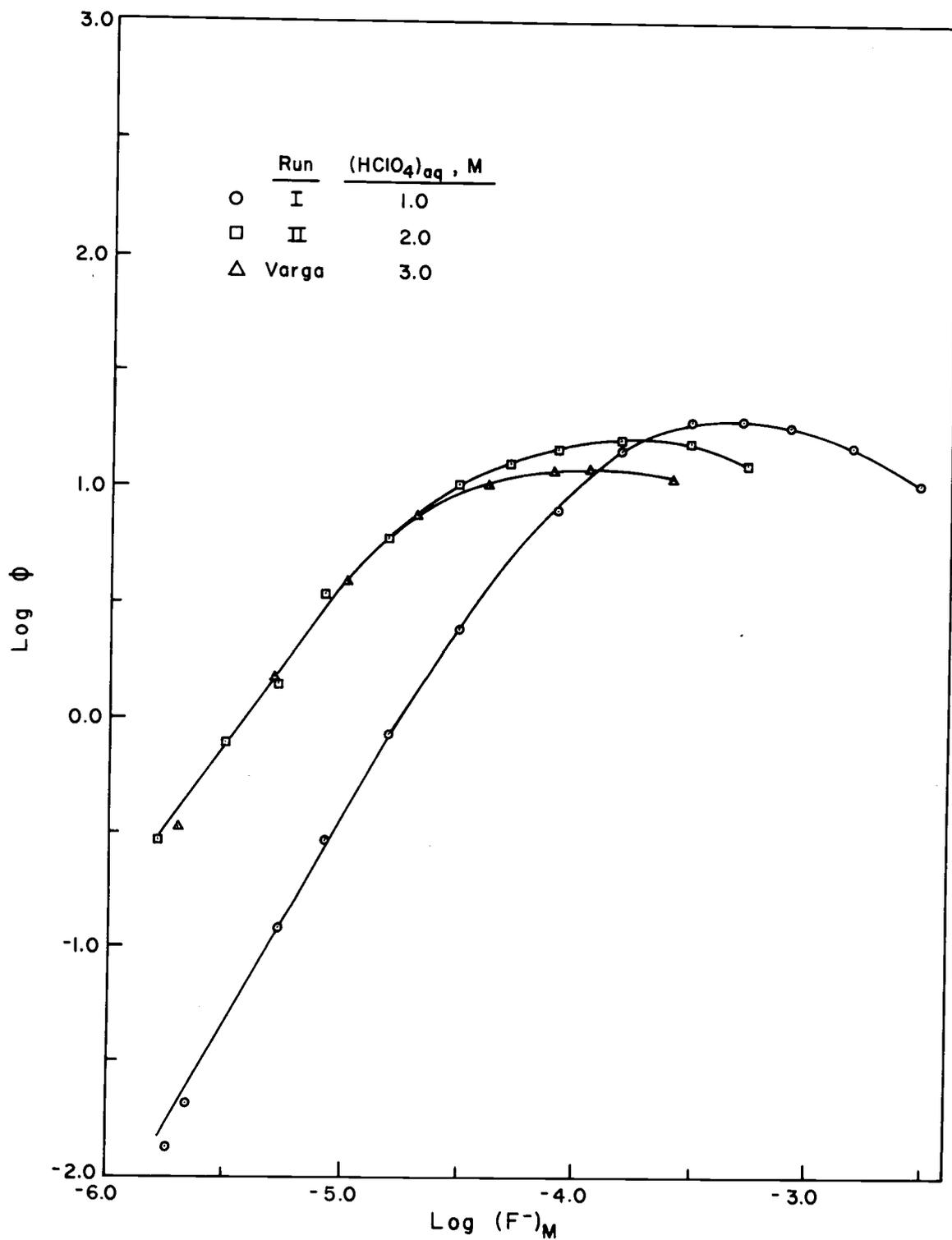
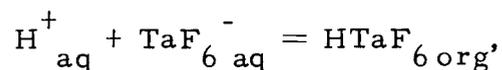


Figure 9.—Distribution of  $^{182}\text{Ta}$  between MIBK and aqueous 1, 2 and 3 M  $\text{HClO}_4$  media at varying  $(F^-)$ .

should continue to depend on the hydrogen ion concentration whether or not hydrolysis occurs at lower acid concentrations.

Contrary to expectation of an approximately linear increase in distribution ratio with hydrogen ion concentration, the maximum distribution undergoes slight decreases in the series 1, 2 and 3 M  $\text{HClO}_4$ . If the extraction of tantalum in these systems indeed occurs according to the suggested equilibrium:



the decreasing distribution must be attributed to other phenomena, which could cause a fortuitous coincidence of parts of the 2 and 3 M extraction curves.

Possible explanations for such a decrease in distribution may include common ion effects due to addition of perchloric acid, or marked changes in activity coefficients in the organic phase as well as in the aqueous phase with increasing ionic strength; changes in the activity of water and of the solvent may cause the hydration and solvation numbers to change. These possibilities may be examined in greater detail.

### Common Ion Effect

The common ion effect, as explained by Diamond and Tuck (23, p. 168) and Zolotov (102) may occur when perchloric acid is added to an extraction system in which the complex metal acid is completely dissociated in the organic phase. The extracted perchloric acid furnishes excess hydrogen ions, forcing some of the complex metal acid to associate again and to be driven back into the aqueous phase; thus the distribution ratio of the metal decreases.

Since perchloric acid has been shown to dissociate upon dilution in MIBK, it is reasonable to expect that  $\text{HTaF}_6$  may do the same. However, the greatest dissociation will occur when the organic phase contains the least concentration of  $\text{HTaF}_6$  and of  $\text{HClO}_4$ ; that is, in the 0.4 M  $\text{HClO}_4$ --0.6 M  $\text{NaClO}_4$  extraction system. If enough dissociation occurs for the common ion effect to be demonstrated, the distribution ratio should decrease upon further addition of  $\text{HClO}_4$  to this system. This is not the effect observed; the 0.7 M  $\text{HClO}_4$ --0.3 M  $\text{NaClO}_4$  and 1.0 M  $\text{HClO}_4$  systems, which show increased extraction of  $\text{HClO}_4$ , also exhibit a marked increase in extraction of tantalum (Figure 8). Since the decrease in tantalum distribution does not occur until the aqueous phase  $\text{HClO}_4$  concentration has increased to 2.0 M, it is unlikely that common ion effects are responsible.

## Activity Coefficient Changes

Activity coefficients for 1.0, 2.0 and 3.0 M  $\text{HClO}_4$  (neglecting the presence of MIBK) were obtained by converting molarities to molalities with the aid of density data (43, p 54) and finding the coefficients by interpolation from the tables of Robinson and Stokes (71). The resulting values are given in the following table, along with the MIBK solubility for each aqueous phase and the concentration of  $\text{HClO}_4$  in the MIBK phase (from the data of the previous section).

Table 23. Activity and solubility data for MIBK--aqueous  $\text{HClO}_4$  systems.

$(\text{HClO}_4)_{\text{aq}}$ , M	$\gamma_{\pm\text{aq}}$	MIBK solubility vol %	$(\text{HClO}_4)_{\text{MIBK}}$ , M
1.0	0.834	3.1	0.20
2.0	1.13	4.9	0.85
3.0	1.72	6.7	1.5

The marked increases in aqueous activity coefficients and MIBK solubilities and in the concentration of MIBK phase  $\text{HClO}_4$  in the series 1.0, 2.0 and 3.0 M  $\text{HClO}_4$  are certain to affect the value of the distribution ratio. However, the direction and magnitude of the effects cannot be estimated; therefore it cannot be concluded with certainty that activity coefficient changes are responsible for the decrease in maximum extraction.

Another factor which may be involved at higher acid concentrations is a possible change in the hydration and solvation configuration of the extracted complex metal acid. Such a change would be expected to result in a different value for the distribution coefficient of the extracted species.

### 1 M Perchlorate Results of Varga and Freund

#### Differences in Conditions

In the present work the hydrogen ion concentration was held constant in each of the three runs in the 1.0 M perchlorate medium and aqueous phases were saturated with MIBK. The aqueous phases in the 1 M perchlorate studies of Varga and Freund (92) contained no solvent; those for anion exchange measurements had a constant background of 1 M  $\text{HClO}_4$ , so that with addition of increasing amounts of hydrofluoric acid the hydrogen ion concentration exceeded 1 M. On the other hand, the potentiometric  $\text{H}^+$  ion runs were carried out at different, constant total acid concentrations  $C_{\text{H}}$  ranging from 0.100 to 0.350 M, so that these aqueous phases contained high proportions of  $\text{NaClO}_4$ . The slightly imperfect alignment observed when data from the two methods were combined may well have been a consequence of the different acid concentrations involved.

An additional discrepancy between the present investigation and

that of Varga and Freund is the use of somewhat different values of the HF dissociation constants. Varga utilized the constants given by Ahrland (1) for the 1 M sodium perchlorate medium at 20°C and applied a temperature correction to obtain the approximate value of  $Ka_1$  at 25°C =  $1.07 \times 10^{-3}$ . Due to its low reliability, Ahrland's value of  $Ka_2 = 0.32$  was used without further correction.

The constants used in this work, determined by Farrer and Rossotti (33) for 1.0 M  $NaClO_4$  at 25°C, were  $Ka_1 = 1.12 \times 10^{-3}$  and  $Ka_2 = 0.26$ ; the use of these constants results in  $(F^-)$  values which are approximately 5% greater than those calculated from the same  $C_{HF}$  and  $(H^+)$  using Ahrland's constants.

#### Calculation of $TaF_6^-$ Distribution Curve from Formation Constants

For comparison of the 1.0 M  $HClO_4$  distribution curve with the results of Varga and Freund, the formation constants of tantalum fluoride complexes given by these authors were used to calculate the expected distribution curve assuming that  $TaF_6^-$  is extracted as in the 3 M  $HClO_4$  system.

The distribution of  $TaF_6^-$  is described by the two expressions

$$\lambda = \frac{(HTaF_6)_{org}}{(H^+)_{aq} (TaF_6^-)_{aq}}$$

and

$$\phi = \frac{(\text{HTaF}_6)_{\text{org}}}{C_{\text{Ta}_{\text{aq}}}}$$

According to the results of Varga and Freund the lowest species of tantalum present is  $\text{TaF}_4^+$  and the highest  $\text{TaF}_9^{4-}$ . Then

$$\phi = \frac{(\text{HTaF}_6)_{\text{org}}}{\sum_{j=4} (\text{TaF}_j)_{\text{aq}}} = \frac{\lambda(\text{H}^+)(\text{TaF}_6^-)}{\sum_{j=4} (\text{TaF}_j)} \quad (\text{all aqueous concentrations})$$

Introducing the overall formation constants based on  $\text{TaF}_4^+$ ,

$$\phi = \frac{\lambda(\text{H}^+) (\text{TaF}_4^+) \beta_6 (\text{F}^-)^2}{(\text{TaF}_4^+) (1 + \sum_{j=5} \beta_j (\text{F}^-)^{j-4})}$$

$$\text{or } \phi = \frac{\lambda(\text{H}^+) \beta_6 (\text{F}^-)^2}{1 + \sum_{j=5} \beta_j (\text{F}^-)^{j-4}}$$

To obtain the theoretical distribution curve, the overall formation constants were first calculated from the stepwise formation constants given by Varga and Freund:  $\beta_5 = k_5$ ,  $\beta_6 = k_5 k_6$ ,  $\beta_7 = k_5 k_6 k_7$ ,  $\beta_8 = k_5 k_6 k_7 k_8$  and  $\beta_9 = k_5 k_6 k_7 k_8 k_9$ . Then for representative  $(\text{F}^-)$  values over the range covered by the experimental MIBK distribution curve, values were computed of the quantity

$$\frac{\phi}{\lambda(\text{H}^+)} = \frac{\beta_6 (\text{F}^-)^2}{1 + \sum_{j=5}^9 \beta_j (\text{F}^-)^{j-4}}$$

When  $\frac{\phi}{\lambda(\text{H}^+)}$  had been obtained as a function of  $(\text{F}^-)$ , comparison of  $\frac{\phi}{\lambda(\text{H}^+)}$  values with experimental distribution ratios permitted the assignment of the value of  $\lambda = 3.49 \times 10^1$  which provided best agreement of the theoretical and experimental distribution ratios. This is considerably greater than the value of the equivalent coefficient reported by Varga and co-workers (94) for the 3.0 M  $\text{HClO}_4$  system,  $K_{\text{MIBK}} = 5.00 \pm 0.21$ .

Using  $\lambda = 3.49 \times 10^1$  and  $(\text{H}^+) = 1.0 \text{ M}$ ,  $\phi$  values were obtained and the theoretical distribution curve for  $\text{TaF}_6^-$  was plotted in comparison with the experimental 1.0 M  $\text{HClO}_4$  distribution curve (Figure 10). At lower free fluoride concentrations the experimental distribution curve follows the theoretical distribution fairly closely and the maximum distribution of both curves occurs at approximately  $3.0 \times 10^{-4} \text{ M}(\text{F}^-)$ , corresponding to the greatest concentration of  $\text{TaF}_6^-$  in the aqueous phase. Thus up to this point the MIBK extraction data appear to confirm the formation of  $\text{TaF}_5$  and  $\text{TaF}_6^-$  from  $\text{TaF}_4^+$  as described by Varga and Freund. As the free fluoride concentration increases, however, the experimental distribution remains high while the theoretical distribution of  $\text{TaF}_6^-$  drops off rather sharply.

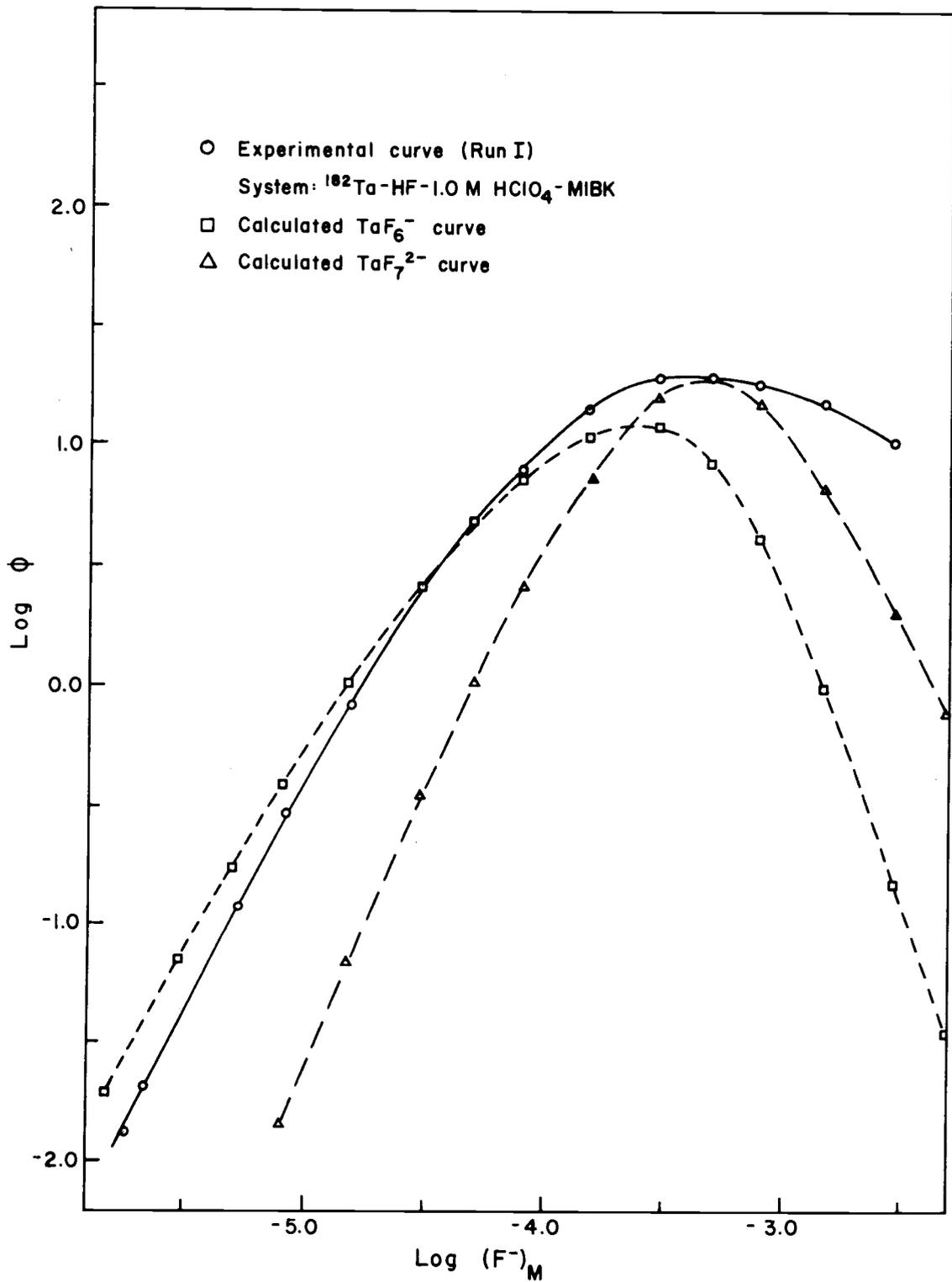
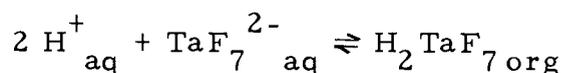


Figure 10.— Calculated distribution curves for  $\text{TaF}_6^-$  and  $\text{TaF}_7^{2-}$  compared with experimental curve.

### Possibility of $\text{TaF}_7^{2-}$ Extraction

The enhanced experimental distribution at higher ( $\text{F}^-$ ) suggests the possibility of the extraction of  $\text{TaF}_7^{2-}$ , either alone or in addition to the extraction of  $\text{TaF}_6^-$ . To examine this possibility the theoretical distribution for  $\text{TaF}_7^{2-}$  was also calculated from the formation constants of Varga and Freund. The equilibrium for the extraction of  $\text{TaF}_7^{2-}$  may be expressed:



with 
$$\lambda = \frac{(\text{H}_2 \text{TaF}_7)_{\text{org}}}{(\text{H}^+)_{\text{aq}}^2 (\text{TaF}_7^{2-})_{\text{aq}}}$$

and 
$$\phi = \frac{\lambda (\text{H})^2 \beta_7 (\text{F}^-)^3}{9 \left( 1 + \sum_{j=5} \beta_j (\text{F}^-)^{j-4} \right)}$$

The theoretical distribution curve for the extraction of  $\text{TaF}_7^{2-}$  was calculated in the same manner as that for  $\text{TaF}_6^-$ , with  $(\text{H}^+) = 1.0 \text{ M}$  and  $\lambda$  assigned the value of  $7.16 \times 10^1$ . The result is shown in Figure 10 along with the other curves.

The  $\text{TaF}_7^{2-}$  distribution curve represents the experimental distribution maximum somewhat better than does the  $\text{TaF}_6^-$  plot, but is less broad and the agreement at lower fluoride concentrations is

poor; again, the distribution at higher ( $F^-$ ) drops more steeply than the experimental curve. Therefore, taken alone, the  $TaF_6^-$  curve is regarded as a better description of the experimental distribution.

Attempts to describe the experimental curve through a combination of the theoretical  $TaF_6^-$  and  $TaF_7^{2-}$  curves were not generally satisfactory; to enhance the distribution at higher ( $F^-$ ) values required a low  $\lambda$  for  $TaF_6^-$  and a high  $\lambda$  for  $TaF_7^{2-}$  (which is not reasonable since the singly charged anion should be much better extracted than the doubly charged) and destroyed the agreement at lower fluoride concentrations.

As a final check upon the likelihood of  $TaF_7^{2-}$  extracting, the dependence of  $\phi$  upon ( $H^+$ ) within the 1.0 M perchlorate system was investigated. As may be seen from the expressions given for the extraction equilibria, the distribution of  $TaF_6^-$  as a complex metal acid should have a linear dependence upon the hydrogen ion concentration while the distribution of  $TaF_7^{2-}$  should depend upon the square of ( $H^+$ ). Thus for two different hydrogen concentrations at the same ( $F^-$ ), the quotient of the distribution ratios would be  $\phi_1/\phi_2 = (H^+)_1 / (H^+)_2$  for the extraction of  $TaF_6^-$ , but  $\phi_1/\phi_2 = (H^+)_1^2 / (H^+)_2^2$  for  $TaF_7^{2-}$  extraction.

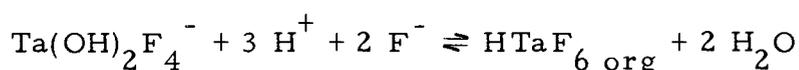
A comparison of distribution ratios in Runs I, II and III showed the dependence of  $\phi$  on ( $H^+$ ) to change with increasing free fluoride concentration. At ( $F^-$ ) =  $10^{-5}$  M, the extraction depends on more

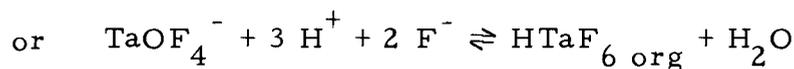
than the square, in fact on approximately the cube of  $(H^+)$ . The dependence decreases to the square of  $(H^+)$  at approximately  $1.5 \times 10^{-4}$  M  $(F^-)$  and finally to an approximately linear dependence at fluoride concentrations above the distribution maximum.

This situation cannot reasonably be interpreted to mean that a triply charged anion such as  $TaF_8^{3-}$  is extracted at low  $(F^-)$  and a doubly charged anion, perhaps  $TaF_7^{2-}$ , at moderate  $(F^-)$ , while a singly charged anion, probably  $TaF_6^-$ , extracts at high  $(F^-)$ . If  $TaF_7^{2-}$  is extracted at all, its distribution should be reflected by a dependence of  $\phi$  upon the square of  $(H^+)$  at and above the fluoride concentration of maximum distribution. The linear dependence of  $\phi$  upon  $(H^+)$  in the high  $(F^-)$  region implies that if there is any validity to the observed dependence, the actual extracting species is probably singly charged.

Reasons for Changing Dependence of  $\phi$  upon  $(H^+)$

Possibility of Hydrolysis. At low  $(F^-)$  three hydrogen ions appear to be involved in the formation of the extractable species as well as up to two fluoride ions. Then, assuming  $TaF_6^-$  is extracted as  $HTaF_6$ , the overall reaction occurring within the 1.0 M perchlorate system to form this species could be represented:





$$\text{with } \lambda = \frac{(\text{HTaF}_6)_{\text{org}}}{(\text{TaOF}_4^-) (\text{H}^+)^3 (\text{F}^-)^2}$$

for the second equilibrium, ignoring the concentration of water.

Since it may take a higher concentration of fluoride ion to displace the hydroxy group or oxygen from  $\text{Ta}(\text{OH})_2\text{F}_4^-$  or  $\text{TaOF}_4^-$  than to displace water of hydration from the hydrated  $\text{TaF}_4^+$  ion, the free fluoride ion concentration of maximum extraction may shift to lower ( $\text{F}^-$ ) values as the hydrogen ion concentration increases. In addition, if one of the intermediate hydrolysis products extracts in addition to  $\text{TaF}_6^-$  at lower hydrogen ion concentrations, an explanation is furnished not only for the shift in distribution maximum as ( $\text{H}^+$ ) increases but also for the decrease in distribution of 2 and 3 M  $\text{HClO}_4$  as the extractable hydrolysis product disappears.

There are, however, several objections and inconsistencies relative to such an explanation.

To explain the shift of distribution maximum and decrease of  $\phi$  by the extraction of two different species, one of them hydrolytic, requires (assuming that  $\text{TaF}_6^-$  is the species extracting from 3 M  $\text{HClO}_4$ ) the hydrolytic species to be formed at a higher fluoride concentration than  $\text{TaF}_6^-$ . It is improbable that a complex such as  $\text{Ta}(\text{OH})_2\text{F}_4^-$ ,  $\text{TaOF}_4^-$  or  $\text{Ta}(\text{OH})\text{F}_5^-$  (all possible candidates for extraction) would require a greater fluoride concentration for its formation than that required to form  $\text{TaF}_6^-$ . In fact, the hydrolysis

equilibrium mentioned above indicates that  $\text{Ta}(\text{OH})_2\text{F}_4^-$  or  $\text{TaOF}_4^-$ , if present at all, exists at the lowest ( $\text{F}^-$ ) and ( $\text{H}^+$ ) values covered in the investigation. The TPA and crystal violet extraction results reported in a previous section indicated that  $\text{TaF}_6^-$ , rather than  $\text{TaOF}_4^-$ , is extracted from 0.4 MHF solution containing no additional acid and may be considered as evidence against the extraction of hydrolysis products from higher acid media.

Secondly, regardless of whether hydrolytic species are extracted, the occurrence of hydrolysis at lower ( $\text{H}^+$ ) should significantly disturb the equilibrium of fluorotantalum complexes and cause a change in shape of the distribution curves with increasing ( $\text{H}^+$ ). As Figure 8 shows, such a change is not observed within the 1.0 M perchlorate system; the positive slope of the distribution curve remains almost constant as ( $\text{H}^+$ ) increases from 0.4 to 1.0 M and is in fair agreement with the slope of the theoretical  $\text{TaF}_6^-$  distribution curve calculated from the formation constants of Varga and Freund (92). These authors found that hydrolytic species of tantalum are probably absent in fluoride solutions of  $C_{\text{H}}/C_{\text{M}} > 150$ .

Finally, other available data are consistent with the findings of Varga and Freund; there is no reliable evidence for the existence of hydroxy or oxyfluoro species of tantalum even in solutions of the lowest  $\text{H}^+$  concentration used, 0.4 M. To make hydrolysis the explanation for the overall distribution behavior would require the

presence of hydrolytic species in higher acid media of up to 2.0 M  $\text{HClO}_4$ , which is even more improbable.

On the basis of these considerations hydrolysis may be rejected as a plausible explanation for the shift in distribution maximum or for the decrease in maximum distribution at 2 and 3 M  $\text{HClO}_4$ .

Activity Effects within 1.0 M Perchlorate . If the shift in distribution maximum within the 1.0 M perchlorate system is a consequence of changing activity coefficients as  $\text{Na}^+$  is replaced by  $\text{H}^+$  in the background electrolyte, then the comparison of distribution curves to determine the dependence of  $\phi$  upon  $(\text{H}^+)$  as described above will lead to erroneous results. A more accurate estimate of the dependence of  $\phi$  upon  $(\text{H}^+)$  would be obtained if rough corrections for activity changes were applied. A simple way to do this would be to shift the curves along the horizontal axis until the distribution maxima all occur at the same free fluoride concentration, and then compare distribution ratios. When this procedure was followed for the 1.0 M perchlorate runs by shifting curves for Runs II and III along the  $\log(\text{F}^-)$  axis, the three curves were found to be approximately parallel. The average ratio of Run I distribution ratios to those of Run III was 3.6, compared to expected values of 2.5 for linear dependence on  $(\text{H}^+)$  and of 6.25 for dependence on  $(\text{H}^+)^2$ . Changes in activity coefficients of both phases occurring upon increase of  $(\text{H}^+)$  create some uncertainty in the comparison of distribution ratios;

the implication is, however, that  $\text{TaF}_7^{2-}$  is extracted only slightly if at all and that  $\text{TaF}_6^-$  is the species primarily extracted from 1.0 M perchlorate by MIBK.

The fact that the 1.0 M perchlorate distribution curves are approximately parallel upon rearrangement and that the dependence of  $\phi$  upon  $(\text{H}^+)$  with the curves in this position is consistent with the extraction primarily of  $\text{TaF}_6^-$  throughout the range of free fluoride concentration lends weight to the contention that the shift in distribution maximum is an activity effect. This likelihood may be examined somewhat further by considering the possible direction of activity coefficient changes within the aqueous phase.

Activity coefficients of microcomponents present in a solution containing an excess of background electrolyte are considered to be affected primarily by changes in the activity coefficient of the background electrolyte. In the present case we have a series of three media: 0.4 M  $\text{HClO}_4$ -0.6 M  $\text{NaClO}_4$ , 0.7 M  $\text{HClO}_4$ -0.3 M  $\text{NaClO}_4$ , and 1.0 M  $\text{HClO}_4$ . Although information on activity coefficients in mixed  $\text{HClO}_4$ - $\text{NaClO}_4$  solutions is not available, an estimate of the overall mean ionic activity coefficient of the mixed electrolyte background may be obtained by taking the geometric mean of the activity coefficients of the two components:

$$\gamma \cong (\gamma_{\text{HClO}_4})^x (\gamma_{\text{NaClO}_4})^y$$

where  $\gamma_{\text{HClO}_4}$  and  $\gamma_{\text{NaClO}_4}$  are the activity coefficients of each electrolyte at the total perchlorate concentration,  $x$  is the fraction of the perchlorate present as  $\text{HClO}_4$  and  $y$  is the fraction present as  $\text{NaClO}_4$ .

Activity coefficients for  $\text{HClO}_4$  and  $\text{NaClO}_4$  in the tables of Robinson and Stokes (71) were given according to molality, thus total perchlorate molalities were estimated from the individual  $\text{HClO}_4$  and  $\text{NaClO}_4$  molarities with the aid of published density data (43, p. 54, 80) and the quantities  $x$  and  $y$  were fractions of total molality. Resulting activity coefficients were 0.70 for 0.4 M  $\text{HClO}_4$ -0.6 M  $\text{NaClO}_4$  (Run III) and 0.76 for 0.7 M  $\text{HClO}_4$ -0.3 M  $\text{NaClO}_4$  (Run II). The activity coefficient of 1.0 M  $\text{HClO}_4$  (Run I) is 0.834. These values reveal a rising activity coefficient of the background electrolyte as  $\text{Na}^+$  is replaced by  $\text{H}^+$ . Assuming that the presence of MIBK decreases the activity of water thus in effect increasing the activity of ionic solutes, the effect of MIBK solubility (increasing with hydrogen ion concentration) should be to accentuate the discrepancies in activity coefficients.

Since the concentration of the perchlorate anion is kept constant while ( $\text{H}^+$ ) and ( $\text{Na}^+$ ) vary, the activity coefficients of micro-component anions should be affected more than those of cations, according to Fomin (35) and Tobias (85).

It has been pointed out already that some error is expected in

the calculated free fluoride concentration as sodium perchlorate is replaced by perchloric acid. If the activity of free fluoride ion increases out of proportion to concentration as the activity coefficient of the background electrolyte increases,  $\text{TaF}_6^-$  will be formed and extracted at lower ( $\text{F}^-$ ), as observed. If, in addition, the activity coefficients of  $\text{TaF}_6^-$  and of higher anionic complexes are increased over those of  $\text{TaF}_4^+$  and  $\text{TaF}_5$ , the stability of anionic fluorotantalum species is enhanced, which, again, is reflected by a shift in distribution to lower ( $\text{F}^-$ ) values.

#### Reason for Breadth of MIBK Distribution Curves

The possibility of extraction of a second species, such as  $\text{TaF}_7^{2-}$  or  $\text{TaOF}_4^-$ , in addition to  $\text{TaF}_6^-$  has been discussed and rejected as a likely cause for the enhanced distribution at higher ( $\text{F}^-$ ) over that expected from the formation constants of Varga and Freund (92).

The distribution curves of tetraphenylarsonium chloride and crystal violet (Figures 2-4) cannot be closely compared to the MIBK distribution curves since no constant ionic medium was involved, but it is clear that they drop off more sharply at high fluoride concentrations than do the MIBK curves, although  $\text{TaF}_6^-$  is the probable extracting species in each case. This comparison, as well as the comparison between the 1.0 M  $\text{HClO}_4$  MIBK extraction curve and

the theoretical  $\text{TaF}_6^-$  distribution curve, suggests that the exaggerated breadth of the MIBK curves at high ( $\text{F}^-$ ) may not be linked directly to the identity and stability of aqueous phase fluo-tantalum species but may instead be a characteristic of the solvent. Crystal violet and TPA were diluted by chloroform, whose miscibility with water is slight and does not appear to be affected by HF concentration. In contrast, the miscibility of MIBK with aqueous phases is significant and increases with acid concentration. A greater distribution at higher ( $\text{F}^-$ ) may be at least partially due to activity changes occurring as a consequence of increasing miscibility with HF concentration. Under these conditions the distribution could also be affected by changes in hydration and solvation numbers of the extracting species.

### Conclusions

Taken as a whole, the present MIBK extraction data are reasonably consistent with the results of Varga (92, 94) and support his observation of increasing stability of tantalum fluoride complexes with increasing background  $\text{HClO}_4$  concentration. The reasons for the rising stability have received some attention here. Changing mutual solubilities of constituents of phases in the MIBK extraction system may help to explain irregularities in distribution behavior but cannot be a major factor in the changing stability which has been

demonstrated by Varga in systems not involving MIBK.

The shift in distribution maximum to lower ( $F^-$ ) as the hydrogen ion concentration increases within the 1.0 M perchlorate system is most likely a consequence of activity effects instead of hydrolysis equilibria; the probable extracting species is  $TaF_6^-$ , paired with the hydrated and solvated hydronium ion. A surprising decrease in maximum tantalum fluoride distribution upon changing the concentration of the background electrolyte to 2 and 3 M  $HClO_4$  cannot be satisfactorily explained by common ion effects; changes in activity coefficients of both phases and changes in the hydration and solvation of the extracted species may contribute to this behavior.

#### Suggestions for Further Research

The recently introduced fluoride ion activity electrode could help to eliminate one source of error, the inadequacy of available HF dissociation constants. This electrode was used by Hall and Slater (45) in the determination of stability constants of tin (II) fluoride complexes. Vanderborgh (90) studied the response of the electrode in media of 0.05-0.5  $\mu$  maintained by  $NaClO_4$  and  $HClO_4$  and concluded that it functions as an indicator of fluoride ion activity in acidic solutions.

Much more information regarding activity coefficients, especially of individual ions, in solutions of electrolytes, mixed

electrolytes, non-aqueous solvents, and solvent mixtures must be obtained before a complex extraction system of the kind studied here can be fully elucidated.

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