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Distribution, Rate of Extraction, and Complexing Action of Thenoyltrifluoroacetone in the Synergistic System Kerosine/Thenoyltrifluoroacetone/Tributylphosphate/Dilute HNO_3*

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Summary

A study of the variation of the distribution coefficients of thenoyltrifluorotone (HTTA) and Sm with time has been made in the synergistic system kerosine/HTTA/tributylphosphate (TBP)/dilute HNO_3. The results indicate that the phenomena of antagonism or antisynergism which takes place at TBP concentrations above 0.1 *M* is due to the large reduction of the free HTTA-enol in the organic phase and to a much lesser extent to the reduction of the free TBP concentration in the same phase through the formation of $HTTA \cdot H_2O$ and $HTTA \cdot H_2O \cdot TBP$, respectively. Equations which allow calculation of the free HTTA-enol and free TBP are developed.

INTRODUCTION

Since thenoyltrifluoroacetone (HTTA) was synthesized by Reid and Calvin (*1*), a formidable amount of work in the field of solvent extraction using HTTA as a chelating agent has followed. It has become one

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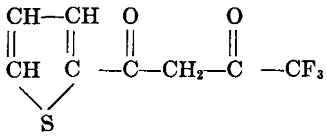
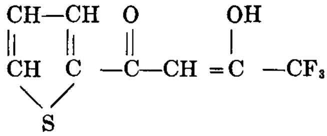
of the most widely used of the β-diketones in the solvent extraction of metal ions, particularly for analytical purposes. It is used alone, dissolved in organic solvents to form chelates that are extractable in the organic phase, or in combination with a neutral ligand extractant to form a synergistic system which gives greatly enhanced extraction in the organic phase.

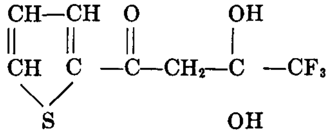
HTTA can exist in the following forms:



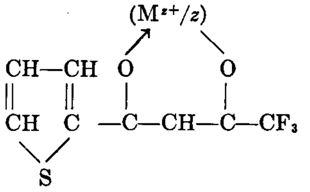
keto



enol



ketohydrate



metal enolate extractable
in organic phases

Behavior of HTTA in Solvent Extraction Systems

According to several investigators (*1*, *2*), HTTA is 11% in the ketohydrate form and the rest is in the enol form in a benzene–dilute nitric acid system in the benzene phase. In the dilute acid phase about 1.6% of the HTTA is in the enol form and the rest is in the ketohydrate. The distribution coefficient of HTTA for the system benzene/HTTA/dilute acid is 40. Thus, using benzene as a diluent, no more than 2½% of the HTTA is in an aqueous phase at low pH values.

Almost no data of this kind on the behavior of systems involving HTTA and neutral ligands, such as tributylphosphate (TBP), has been reported.

On the other hand, it has been a rule in metal extraction process studies to use rather simple treatments under the mass-action law to obtain correlations among the different variables affecting the extraction.

As is common knowledge in the field, the synergistic extraction of a metal ion involving HTTA and TBP can be summarized in a general form as follows:

$$M^{n+}{}_{(aq)} + m\mathrm{TBP}_{(org)} + n\mathrm{HTTA}_{(org)} \overset{K_{eq}}{\rightleftharpoons} \mathrm{M(TTA)}_n(\mathrm{TBP})_{m(org)} + n\mathrm{H}^+{}_{(aq)} \quad (1)$$

$$K_{eq} = \frac{(\mathrm{M(TTA)}_n(\mathrm{TBP})_m)_{(org)}(\mathrm{H}^+)^n{}_{(aq)}}{(\mathrm{M}^{n+})_{(aq)}(\mathrm{TBP})^m{}_{(org)}(\mathrm{HTTA})^n{}_{(org)}} \quad (2)$$

with a defined distribution coefficient of the metal

$$q^{o/a} = \frac{(\mathrm{M(TTA)}_n(\mathrm{TBP})_m)_{(org)}}{(\mathrm{M}^{n+})_{(aq)}} = K_{eq}\frac{(\mathrm{TBP})^m{}_{(org)}(\mathrm{HTTA})^n{}_{(org)}}{(\mathrm{H}^+)^n{}_{(aq)}} \quad (3)$$

At a constant $(\mathrm{HTTA})_{(org)}$ and $(\mathrm{H}^+)_{(aq)}$

$$\log q^{o/a} = m \log (\mathrm{TBP})_{(org)} + \mathrm{const} \quad (4)$$

The slope of the $\log q^{o/a}$ vs. $\log (\mathrm{TBP})_{(org)}$ at infinite dilution, therefore, gives the number of molecules of TBP in the extracted complex. Similar treatments can be used to find the (HTTA) and (H^+) dependence. This technique assumes that there is only one metal complex extracted into the organic phase and no organometal complexes in the aqueous phase. It has been used by most previous investigators to determine the number of molecules of HTTA and TBP in the metal complex.

In a rigorous treatment all terms in brackets are activities of the free complexing species in each phase.

Generally, to simplify the study, low concentrations of the species are used in order not to have complicated thermodynamic factors affecting the activity coefficients of the solutes.

However, in some cases a mass-action law treatment of the distribution data becomes difficult because of the relatively high loss of the reagents to the aqueous phase. Another complicating factor has been the actual inability to find real free concentrations of the different complexing agents, mainly when it is suspected that strong interactions between them produce association products. As we will argue later, this inability to find free concentrations gives rise to the phenomena first called "antisynergism" (*3*) and later "antagonism" (*4*).

Synergism and Destruction of Synergism

The extraction of samarium from the aqueous phase, in this work, was carried out in the synergistic system kerosine/HTTA/TBP/dilute HNO_3.

Cuninghame and co-workers (*5*) found in 1954 that the addition of TBP increased the extraction of praseodymium and neodymium by solutions of HTTA in kerosine. Much work followed after that (*6–10*).

Healy et al. (*3*) found that if an excess of neutral ester is added to a synergistic system, a decrease of the extraction coefficient of the metal occurs. He called this destruction of synergism "antisynergism," later called "antagonism" (*4*). The degree of antagonism depends on the quantity and nature of the neutral ester. Healy concluded that the cause of the antagonistic effect is bound up with the solubility of water in the mixture of the neutral additive and the diluent. There is UV spectral evidence that the anhydrous species is destroyed with the formation of a hydrated HTTA species when most neutral additives are present in excess.

Healy (*11*) also found that the so-called "inert" diluents produced a large effect on the distribution coefficients.

Ferraro and Peppard (*12*) proposed that the mechanism of antagonism was due to a direct interaction between the acid and the ester, with the formation of an association product, thereby effectively removing these reagents from the extraction system.

Healy et al. (*3*) later speculated that water in the organic phase has an appreciable effect on the breakdown of the anhydrous synergistic complex, and that the organic phase water content is responsible for the reduction of the activity of HTTA-enol form and for the formation of the HTTA-ketohydrate species.

Newman and Klotz (*13*, *14*) concluded that in the case of synergism with TBP and HTTA to form complexes of the form, i.e., $M(TTA)_3 \cdot 2TBP$, where two molecules of TBP are involved, one molecule is bound to the TTA^- and the second to the metal.

Scruggs et al. (*15*) have demonstrated that the interaction between HTTA in the enol form and TBP is slight. They applied the results to the extraction of Zn(II) by HTTA and TBP or tri-*n*-butoxiethyl phosphate (TBEP). In order to evaluate the mixed equilibrium constant K' for the reaction that leads to the formation of $Zn(TTA)_2 \cdot TBP$, it must be determined that HTTA and TBP or TBEP do not react with one another; otherwise the associated equilibrium must be known so that the concentrations of free HTTA and free TBP or TBEP can be evaluated. They made proton magnetic resonance (PMR) measurements of solutions of HTTA and TBP or TBEP in dry CCl_4 and found the equilibrium constant for the interaction of HTTA and TBP or TBEP to be of the order of 0.2. They conclude that the concentrations of free HTTA and free TBP or TBEP are not affected by the very weak hydrogen bonding between them. However, they did not take into account the losses of complexing agents in the aqueous phase or the affect that water can have in the organic phase.

Wang et al. (*16*) reported PMR evidence of the formation of ketohydrate of the β-diketones in the destruction of synergism. In their studies they used hexafluoroacetylacetone (HFA) and tri-*n*-octyl phosphine oxide (TOPO) that extract Zn(II) synergistically as $Zn(HFA)_2(TOPO)_2$. These investigators proposed the following over-all reaction for the destruction of the Zn complex in the presence of excess TOPO and acid:

$$Zn(HFA)_2(TOPO)_2 + 2TOPO + 2H^+ + 4H_2O \rightleftarrows Zn^{2+} + 2HFA\cdot 2H_2O(TOPO)_2$$

where the last molecule is formed by $HFA\cdot 2H_2O$ is hydrogen-bonded to TOPO. Similar PMR evidence for the formation of the ketohydrates of HTTA and BTA (benzoyltrifluoroacetone) have been observed. Several metal complexes of HTTA and BTA with TOPO have been prepared and similar PMR measurements were carried out as has been reported for $Zn(HFA)_2(TOPO)_2$. The appearance of new peaks due to the ketohydrate species has been observed in the presence of acid in the aqueous phase. The formation of ketohydrate occurs more readily for the HTTA complex than for the BTA.

Contact Time between Phases

Generally, the rate of extraction of one species from one phase to the other can be governed by several factors:

(a) Diffusion and convection of the products through the bulk of the phases.
(b) Diffusion through the boundary layers.
(c) The crossing of the interface.
(d) Chemical reactions.

These processes may depend on the temperature, viscosity of the two solvents, rate of agitation, and concentration of the various species.

A system where slow kinetics has been observed is that involving HTTA. It has been mentioned in the literature (*2*) that anomalous or unexpected extraction behavior occurs when HTTA is involved in short contact time extraction experiments, i.e., contact times of up to 10 min. In order to avoid these problems, almost all the distribution data reported in the literature and involving HTTA were run as two-phase systems shaken for periods of time ranging from 1 to 24 hr.

The rate of enolization of HTTA (keto-enol equilibrium) can be the controlling factor (*17*) when using HTTA alone as extracting agent.

On the other hand, extractions of metal ions involving TBP alone are generally fast, reaching equilibrium in a matter of seconds (*18*).

Very little has been published on the extraction of metal ions as a function of the contact time between phases. Several authors (*19–21*) have reported the appearance of maxima when the distribution coefficients of some metals were plotted as a function of phase contact time in synergistic systems using HTTA as one of the complexing agents.

Healy (*20*) reports the times to reach equilibrium as being a few minutes for TBP alone (no HTTA) and 1 to 3 hr with HTTA alone (no TBP). He reports that when working with both in the synergistic system, the distribution coefficient gradually increases with time, reaching a maximum within a few hours, but in many instances this figure decreased again, sometimes by a factor of up to five, with final equilibrium being reached within 4 hr. After establishment of equilibrium in a diluent/HTTA/metal/aqueous mixture (1–3 hr), addition of the neutral ester caused a synergistic effect on the distribution coefficient of the metal by a factor up to 10^5 in a few minutes, i.e., upon establishment of the new equilibrium. According to Healy, this indicates that the rate-determining step in the synergistic reaction of the metal/HTTA/ester system is the usual slow keto–enol equilibrium, and that the synergistic reaction must be caused by the action of the neutral ester on the metal-TTA complex, but he does not suggest any explanation for the maxima noticed.

Finston and Inoue (*21*) investigated the effect of hexone on the extraction rate of iron by HTTA in the presence of 0.1 *M* ammonium thiocyanate at various pH's and HTTA concentrations. The addition of hexone promotes the extraction rate remarkably, but the extraction curve starts to show a maximum. No maximum appears in the absence of hexone, but in its presence a definite peak appears. When the hexone concentration is increased, the position of the peak increases and shifts to shorter contact times. Finston and Inoue consider that iron is overextracted beyond the equilibrium point because of the very fast rate of Fe-SCN extraction, in contrast with the slow rate for attaining Fe-TTA extraction equilibrium. They also point out that the gradual decrease in distribution coefficient after the maximum may reflect the recovery from over-extraction. Another anomalous fact not explained by these investigators is that at higher hexone concentrations extraction and stripping curves do not appear to converge.

Poskanzer and Foreman (*22*) have proposed that the rate of approach to equilibrium for HTTA chelation depends on the degree of contact between the phases. They found wrist-action shaking to be more efficient than mechanical shaking, and if the proper technique is employed, only a few minutes may be required to reach equilibrium.

Davis et al. (*19*) noticed an overshoot in the rate of extraction of metal ions with the synergistic system kerosine/HTTA/TBP/dilute nitric acid, but had not completed work intended to clarify the mechanism.

The present work deals mostly with the behavior of HTTA in a two-phase system where the organic phase is kerosine/HTTA or kerosine/HTTA/TBP and the aqueous phase is dilute HNO_3. Some data involving the behavior of HTTA in systems using organic diluents other than kerosine are also included, as well as distribution and rate of extraction data for the synergistic extraction of Sm^{3+} in the kerosine/HTTA/dilute HNO_3 system.

EXPERIMENTAL

Materials, Apparatus, and Procedures

The HTTA used in this work was obtained from Columbia Organic Company, Columbia, South Carolina. It was purified by recrystallization from spectroquality hexane. The purified HTTA showed a melting point of 42.5–43°C, and it was stored in the dark in a dessicator.

The TBP was obtained from Matheson Coleman and Bell, Norwood, Ohio, and it was purified by the method outlined by Irving and Edgington (*23*).

The kerosine (normal paraffin mixture) was obtained from Continental Oil Company, Baltimore, Maryland, as "N-C_{12}-C_{14} Paraffin" with the following distribution:

C_{12}	9.5 wt-%	C_{14}	33.3 wt-%
C_{13}	55.1 wt-%	C_{16}	0.1 wt-%

This kerosine is that presently used now by the Savannah River Plant, Aiken, South Carolina, in their solvent extraction process, and it was used without further purification.

Samarium nitrate was obtained from K and K Laboratories, Plainview, New York, as the hexahydrate, 99.9% pure.

All the other reagents were analytical grade or better.

The distribution of the HTTA between phases was followed by measuring the concentration of HTTA in the aqueous phase by means of a Beckman Spectrophotometer DB. Since equal volumes of the two phases were contacted and no volume change noticed, the HTTA concentration in the organic phase was measured by difference from the initial known concentration in the organic less the final concentration in the aqueous phase. The measurements with the spectrophotometer were carried out at 30°C (cell compartment), slit width 23, and the absorption peak at 267 mμ used. High dilutions were used to measure the HTTA concentration in the aqueous phase due to the strong absorption of the HTTA. When Sm^{+3} was present, it was present in such low concentrations that it did not interfere with the determination of the concentration of HTTA in the aqueous phase.

The HTTA concentrations were checked by means of a Beckman Carbonaceous Analyzer, which determines the total organic carbon in the aqueous phase. Reasonable agreement was found between the two analytical techniques when the proper corrections for kerosine and TBP solubilities in the aqueous phase were made.

Experiments were carried out by shaking 25 ml of organic phase (diluent/HTTA or diluent/HTTA/TBP) with 25 ml of aqueous phase (samarium nitrate/diluted HNO_3, pH 2.00 ± 0.02) in 125 ml glass-stoppered Erlenmeyer flasks, followed by centrifugation and analysis of the aqueous phase.

The distribution coefficients for samarium were determined by titrating the aqueous phase with EDTA using xylenol orange as an indicator (*24*). For details of the procedure see Davis et al. (*19*).

The distribution data were obtained at 25 ± 2°C, and the equilibrium values were obtained by 20 to 24 hr shaking. A wrist action shaker made by Burrell Corporation, Pittsburgh, Pennsylvania, was used at its maximum shaking capacity, averaging 330 oscillations per minute.

The pH measurements were made by means of a Beckman Expanded Scale pH Meter.

All the data shown in this paper were taken working with initial HTTA concentrations of 0.015 *M* unless otherwise noted. Several runs made at different HTTA concentrations showed that with this concentration we were working in the dilute region where ideal behavior of the HTTA solutions is observed. In the present work the distribution coefficient is defined as

$$q^{o/a} = \frac{\text{concentration of the species in the organic phase}}{\text{concentration of the species in the aqueous phase}}$$

RESULTS AND DISCUSSION

Distribution of HTTA

The distribution ratio of HTTA between kerosine and dilute nitric acid, pH 2, as a function of time from initial contact between the two phases is shown in Fig. 1, Curves A and B. At zero time, in Curve A, all HTTA was in the aqueous phase, and in Curve B all HTTA was in the organic phase. The shapes of the curves' approach to equilibrium are approximately the same, and the equilibrium value $q^{o/a} = 3.7$, is reached in about 1 hr. This means that under these conditions a substantial amount of the HTTA, 21%, is in the aqueous phase at equilibrium. Since the form of HTTA soluble in the aqueous phase is the ketohydrate and that in the organic phase the anhydrous or enol form (*2*), it appears that the rate of formation of the hydrate and the rate of dehydration are approximately the same when kerosine is the diluent, assuming that the chemical reaction is the controlling step.

The distribution ratio of HTTA between a number of diluents other than kerosine and dilute acid, pH 2, was measured and the equilibrium values are listed in Table 1.

TABLE 1

Distribution Coefficient of HTTA between Several Solvents and Dilute Nitric Acid, pH 2

Diluent	$q^{o/a}$
Chloroform	43
Benzene	40
Carbon tetrachloride	21
Cylohexane	5.5
Hexane	5.2
Kerosine	3.7

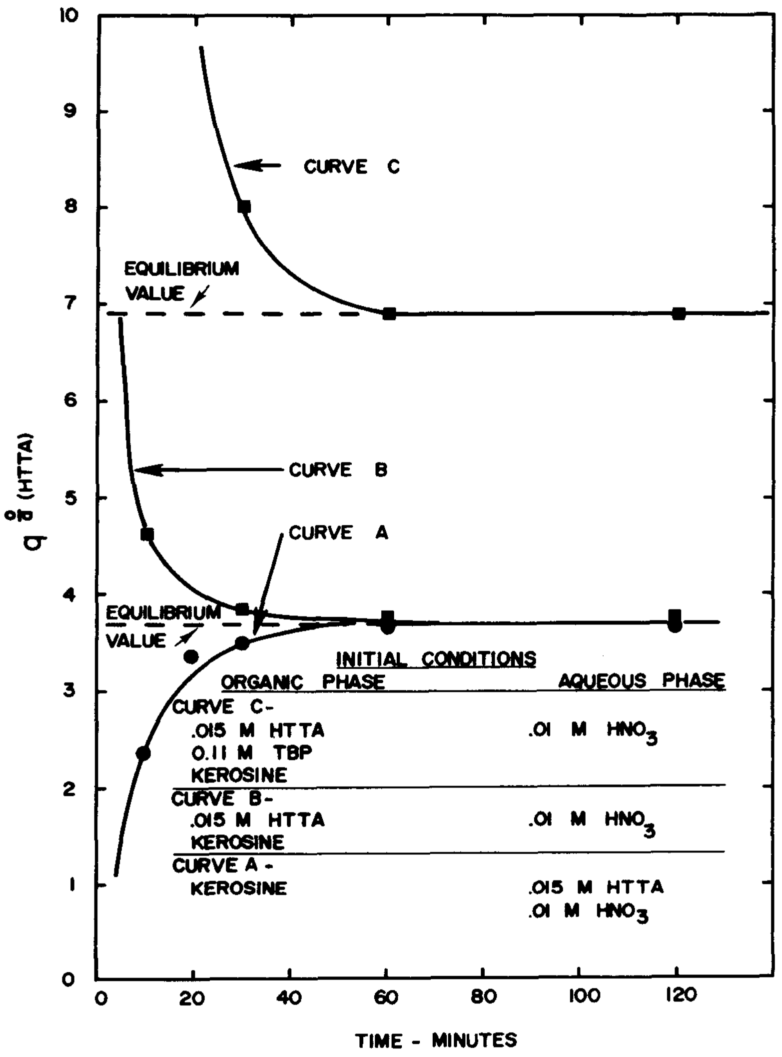


Fig. 1. Rate of approach to equilibrium distribution of HTTA.

The order of increasing HTTA distribution coefficient is kerosine < hexane < cyclohexane < carbon tetrachloride < benzene < chloroform. This order is almost the same as the one given by Healy (*11*) for decreasing extraction coefficients related to increasing water solubility in the organic diluent. Nevertheless, there are two differences. Healy did not report the values for kerosine as a diluent, and the positions of hexane and cyclohexane are switched, even though they are close together in our case.

The distribution coefficient of HTTA in benzene, $q^{o/a} = 40$, agrees with the value reported previously by King and Reas (*2*).

There is no change in the distribution equilibrium of HTTA when the pH is varied between 1 and 3. This is in agreement with the data for benzene reported by Poskanzer and Foreman (*22*).

Influence of TBP on the Distribution of HTTA and Samarium III

The effect of an addition of TBP in the system kerosine/HTTA/dilute nitric acid is to increase the distribution coefficient, as shown by Curve C in Fig. 1. The shape of this curve is different from the one when TBP is not present, but the equilibrium is still reached in about 1 hr.

A more complete picture of the influence of TBP on the equilibrium distribution coefficient of HTTA is presented in Fig. 2, Curve D. There, the distribution coefficients of HTTA are plotted against increasing concentrations of total TBP added initially in the organic phase. As the initial concentration of TBP in the organic phase increases, the equilibrium concentration of HTTA in the aqueous phase decreases, going from 21% of HTTA for no TBP to less than 2% at 0.73 *M* TBP in the organic phase.

Curve E in Fig. 2 also shows the variation of the distribution coefficient of HTTA as a function of the total TBP concentration in the organic phase, but this time 0.000715 *M* samarium nitrate was added to the aqueous phase. The distribution coefficients of Sm can be followed by Curve F in Fig. 2 as a function of the same initial concentrations of TBP in the organic phase. The region chosen exhibits both the synergistic and antagonistic effects of TBP.

The difference between Curves D and E is due to the fact that no correction was made for the amount of HTTA complexed by Sm in Curve E. The region of maximum difference between Curves D and E coincides with the region of maximum complexation of Sm with TBP in Curve F.

These HTTA distribution data can be considered as additional evidence of an interaction between the HTTA and the TBP to form an association product.

In the low TBP region (< 0.1 *M* TBP) the HTTA keeps the enolic form as shown by Healy (*3, 10*) to be due perhaps to the low solubility of water in the organic phase, and in this region the distribution coefficient of the metal increases with the TBP concentration. According to

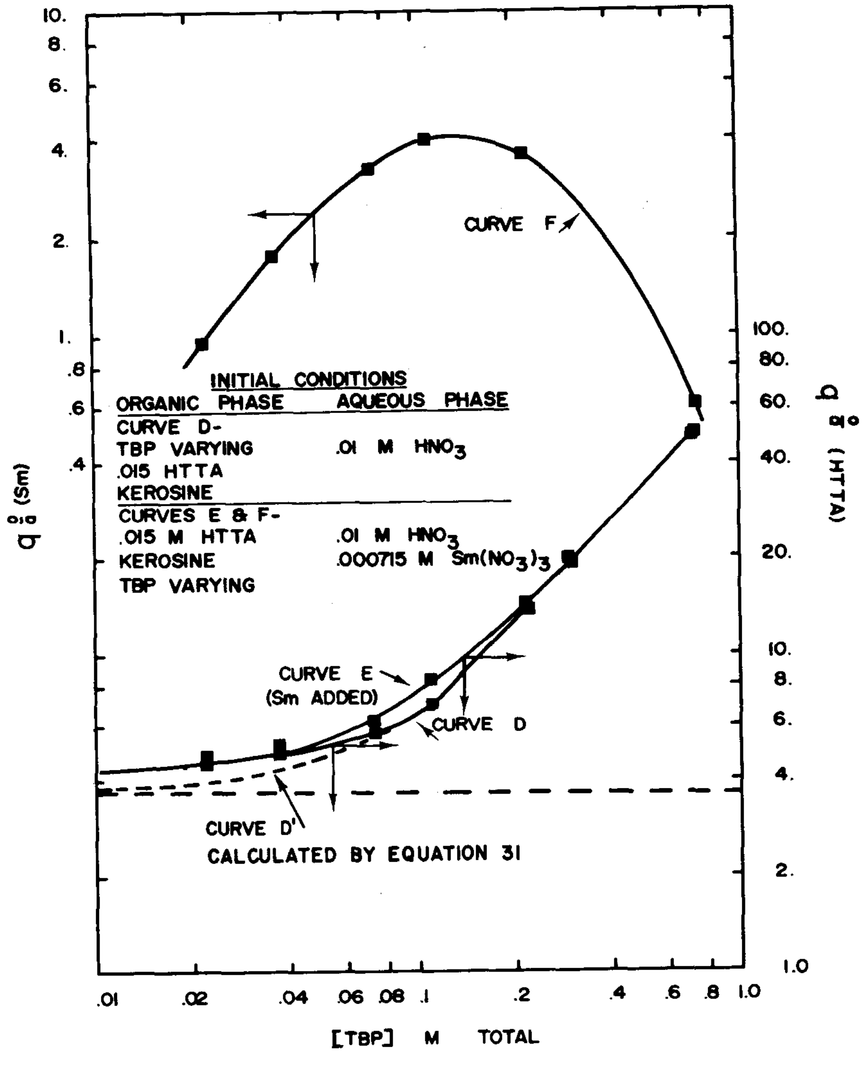


FIG. 2. Distribution coefficients at equilibrium of HTTA and Sm(III) as a function of total TBP concentrations.

Alcock et al. (*25*), as the TBP increases in the organic phase, so does the water solubility in the organic; in water equilibrated solutions, and between TBP concentrations of 0 and 0.73 *M* in kerosine, we can say that there is one molecule of water in the organic phase, approximately, for each three molecules of TBP.

Using the carbon analyzer, we have found that the solubility of the mixture kerosine/TBP is very low, in agreement with the data reported by Alcock et al. (*25*); at TBP concentrations of 0.73 *M* in the organic phase, only about 0.001 *M* TBP is present in the aqueous phase at low acidities.

Therefore, the presence of TBP brings water into the organic phase and this water causes a change of the HTTA from the enolic to the ketohydrate form (*3*). Since the ketohydrate cannot form a chelate, it is effectively removed from the extraction system. It seems that the increase in TBP, and with it the water in the organic phase, promotes antagonism by assisting in the formation of ketohydrate. The TBP increases the amount of water in the organic phase and also reduces the amount of the HTTA-hydrate distributing into the aqueous phase, according to the data presented here, probably by forming a HTTA-hydrate–TBP association product similar to that considered by Wang et al. (*16*). This mechanism explains some abnormalities reported in the literature when relating distribution coefficients of metal ions to HTTA and TBP concentrations (*26*).

Data has also been presented by Scruggs et al. (*15*), as previously discussed, which showed a small interaction between HTTA and TBP through NMR studies in anhydrous CCl_4 as diluent.

Finally, a third possible form of association product between HTTA and TBP would be the HTTA-enolate–TBP, as reported by Healy et al. (*3, 10*) in anhydrous systems with TBP in great excess. Under the same conditions, Ohwada (*27*), using IR measurements, concluded that the intermolecular hydrogen bond between HTTA and TBP is formed as a result of breakup of the conjugate chelation in the HTTA.

It does appear that the increased TBP causes a breakup of the anhydrous HTTA–TBP association product as reported by Healy (*3, 10*) with the subsequent formation of $HTTA \cdot H_2O \cdot n\text{-}TBP$. The formation of this complex evidently influences the extraction of the metal ion by decreasing the effective or free concentration of TBP and HTTA in the organic phase.

The following section will develop the theoretical interpretation of the equilibria involved in systems of this type.

Theoretical Analysis of the Equilibria in the System Kerosine/HTTA/TBP/Aqueous Phase

In the present section we will state the chemical equations which we believe control the extraction behavior in this system, and show that they explain all available experimental facts found by ourselves and other investigators.

This treatment may well be successful in explaining the experimental information if applied to other systems having the same general characteristics as the one discussed here.

Making a first assumption that only two forms of HTTA, the enol and the ketohydrate, play a significant role in the system, we can establish the following equilibria between phases for HTTA alone: (subscript "*o*" and "*a*" refer to the organic and aqueous phase, respectively)

$$(\mathrm{HTTA\cdot H_2O})^a \rightleftarrows (\mathrm{HTTA\cdot H_2O})^o \tag{5}$$

$$(\mathrm{HTTA\text{-}enol})^a \rightleftarrows (\mathrm{HTTA\text{-}enol})^o \tag{6}$$

The distribution for HTTA will be,

$$q^{o/a}(\mathrm{HTTA}) = \frac{(\mathrm{HTTA\cdot H_2O})_o + (\mathrm{HTTA\text{-}enol})_o}{(\mathrm{HTTA\cdot H_2O})_a + (\mathrm{HTTA\text{-}enol})_a} \tag{7}$$

As a second approximation we assume that the concentration of HTTA-enol in the aqueous phase is negligible in the kerosine system, using the data of King and Reas (*2*) for benzene. Thus

$$q^{o/a}(\mathrm{HTTA}) = \frac{(\mathrm{HTTA\cdot H_2O})_o + (\mathrm{HTTA\text{-}enol})_o}{(\mathrm{HTTA\cdot H_2O})_a} \tag{8}$$

When TBP is present in the system, from the data of Alcock et al. (*25*), essentially no TBP distributes to the aqueous phase and the water present in the kerosine is a function of the total concentration of TBP in it.

$$(\mathrm{H_2O})_o = a(\mathrm{TBP})\quad \text{total} \tag{9}$$

where $a = 0.33$ up to a TBP concentration of 0.73 *M*.

We can write the following chemical equilibria for the organic phase:

$$\mathrm{HTTA\text{-}enol}_{(o)} + \mathrm{H_2O}_{(o)} \overset{K_1}{\rightleftarrows} \mathrm{HTTA\cdot H_2O}_{(o)} \tag{10}$$

$$\mathrm{HTTA\cdot H_2O}_{(o)} + n\mathrm{TBP}_{(o)} \overset{K_2}{\rightleftarrows} \mathrm{HTTA\cdot H_2O}\cdot n\mathrm{TBP}_{(o)} \tag{11}$$

$$\mathrm{HTTA\text{-}enol}_{(o)} + n\mathrm{TBP}_{(o)} \overset{K_3}{\rightleftarrows} \mathrm{HTTA}\cdot n\mathrm{TBP}_{(o)} \tag{12}$$

Scruggs et al. (*15*) estimated the value for K_3, Eq. (12), to be of the order of 0.2 in CCl_4, and we will assume it is also small for kerosine and, therefore, neglect it.

From Eq. (10):

$$K_1 = \frac{(\mathrm{HTTA\cdot H_2O})_o}{(\mathrm{HTTA\text{-}enol})_o(\mathrm{H_2O})_o} \tag{13}$$

$$K_2 = \frac{(\mathrm{HTTA\cdot H_2O\cdot}n\mathrm{TBP})_o}{(\mathrm{HTTA\cdot H_2O})_o(\mathrm{TBP})_o{}^n} \tag{14}$$

We can also establish the following material balances for TBP and HTTA,

$$(\mathrm{TBP})_{\mathrm{total}} = (\mathrm{TBP})_o + n(\mathrm{HTTA\cdot H_2O\cdot}n\mathrm{TBP})_o \tag{15}$$

$$(\mathrm{HTTA})_{\mathrm{total}} = (\mathrm{HTTA\cdot H_2O})_o + (\mathrm{HTTA\cdot H_2O})_a + (\mathrm{HTTA\text{-}enol})_o + (\mathrm{HTTA\cdot H_2O\cdot}n\mathrm{TBP})_o \tag{16}$$

In order to simplify the writing, we will assign the following letters for the various terms:

A = $(\mathrm{HTTA\cdot H_2O\cdot}n\mathrm{TBP})_o$

B = $(\mathrm{HTTA\text{-}enol})_o$ or free HTTA

C = $(\mathrm{TBP})_{\mathrm{total}}$

D = $(\mathrm{TBP})_o$ or free TBP

E = $(\mathrm{HTTA\cdot H_2O})_a$

F = $(\mathrm{HTTA\cdot H_2O})_o$

G = $(\mathrm{HTTA})_{\mathrm{total}}$

$q^{o/a}(\mathrm{HTTA}) = q_1$

Thus Eqs. (8), (9), (13), (14), (15), and (16) become, respectively,

$$q_1 = \frac{\mathrm{F} + \mathrm{B}}{\mathrm{E}} \tag{17}$$

$$[\mathrm{H_2O}]_o = a\mathrm{C} \tag{18}$$

$$K_1 = \frac{\mathrm{F}}{a\mathrm{BC}} \tag{19}$$

$$K_2 = \frac{\mathrm{A}}{\mathrm{FD}^n} \tag{20}$$

$$\mathrm{C} = \mathrm{D} + n\mathrm{A} \tag{21}$$

$$\mathrm{G} = \mathrm{F} + \mathrm{B} + \mathrm{E} + \mathrm{A} \tag{22}$$

By eliminating F through combining Eqs. (19) and (20), (19) and (17), and (19) and (22), the new set of equations is:

$$B = \frac{A}{aK_1K_2CD^n} \tag{23}$$

$$B = \frac{q_1E}{aK_1C + 1} \tag{24}$$

$$B = \frac{G - E - A}{AK_1C + 1} \tag{25}$$

$$C = D + nA \tag{21}$$

By eliminating B through combining Eqs. (23) and (24), and (23) and (25), the new set is now:

$$A = \frac{aK_1K_2q_1ECD^n}{aK_1C + 1} \tag{26}$$

$$A = \frac{(G - E)K_2CD^n}{K_2CD^n + C + (1/aK_1)} \tag{27}$$

$$A = \frac{C - D}{n} \tag{28}$$

By eliminating A through combining Eqs. (26) and (28), and (27) and (28).

$$naK_1K_2q_1ECD^n + D(aK_1C + 1) = (aK_1C + 1)C \tag{29}$$

$$(C - D) = \frac{n(G - E)K_2CD^n}{K_2CD^n + C + (1/aK_1)} \tag{30}$$

Taking three values of E with the corresponding values of C from Fig. 2 in a high TBP concentration region where C $\cong$ D, we can determine n, K_1, and K_2:

$$n = 1$$
$$K_1 = 17$$
$$K_2 = 22$$

Combining Eqs. (29) and (30), and taking $n = 1$:

$$\frac{G - E}{E} = q_1\left(1 + \frac{1}{q_1(E/C) + (1/K_2C) + (1/aK_1K_2C^2)}\right) \tag{31}$$

This Eq. (31) shows more clearly the effect of the different constants and variables on the HTTA distribution coefficient.

The quotient (G − E)/E is the distribution coefficient of HTTA in a system with TBP present (q_2):

$$q_2 = \frac{(\mathrm{HTTA})_{\mathrm{total}} - (\mathrm{HTTA \cdot H_2O})_a}{(\mathrm{HTTA \cdot H_2O})_a} \tag{32}$$

By knowing K_1 and K_2, Eqs. (24) and (29) are useful for calculating free concentrations of HTTA and TBP in the organic phase, respectively. These two quantities are to be used when calculating metal equilibrium constants in this system.

With these constants and Eq. (29) we can fit the Curve D with Curve D′, Fig. 2.

This leads us to the conclusion that the form of the complex formed in the organic phase is $\mathrm{HTTA \cdot H_2O \cdot TBP}$, in agreement with Wang et al. (*16*), with an equilibrium constant $K_4 = K_1K_2 = 374$ for the reaction

$$\mathrm{HTTA\text{-}enol}_{(o)} + \mathrm{H_2O}_{(o)} + \mathrm{TBP}_{(o)} \overset{K_4}{\rightleftharpoons} \mathrm{HTTA \cdot H_2O \cdot TBP}_{(o)}$$

It should be pointed out that for diluents other than kerosine, the water present as a function of total TBP concentration and the new distribution coefficient of HTTA (q_1) must be known, as well as the new function $q^{o/a}(\mathrm{HTTA}) = q_2$ vs. TBP concentration.

Finally, the theoretical analysis developed above will be useful for finding an algebraic expression that fits the curve of the distribution coefficient of the metal ion vs. total concentration of HTTA and TBP.

It is implicit in the present development that the addition of TBP to the organic phase changes the character in such a way as to displace the equilibrium between the anhydrous and hydrated forms of HTTA in favor of the hydrate.

Diluent Effects on the System HTTA/TBP/Dilute HNO_3

A number of diluents other than kerosine were used to study their effect on the complexing agents HTTA/TBP. The distribution coefficients of HTTA as a function of TBP concentrations are shown in Fig. 3 for several diluents. In all the systems the distribution coefficients increase as the concentration of TBP increases. This effect is interpreted as indicating the formation of a HTTA-hydrate–TBP complex in all the organic phases.

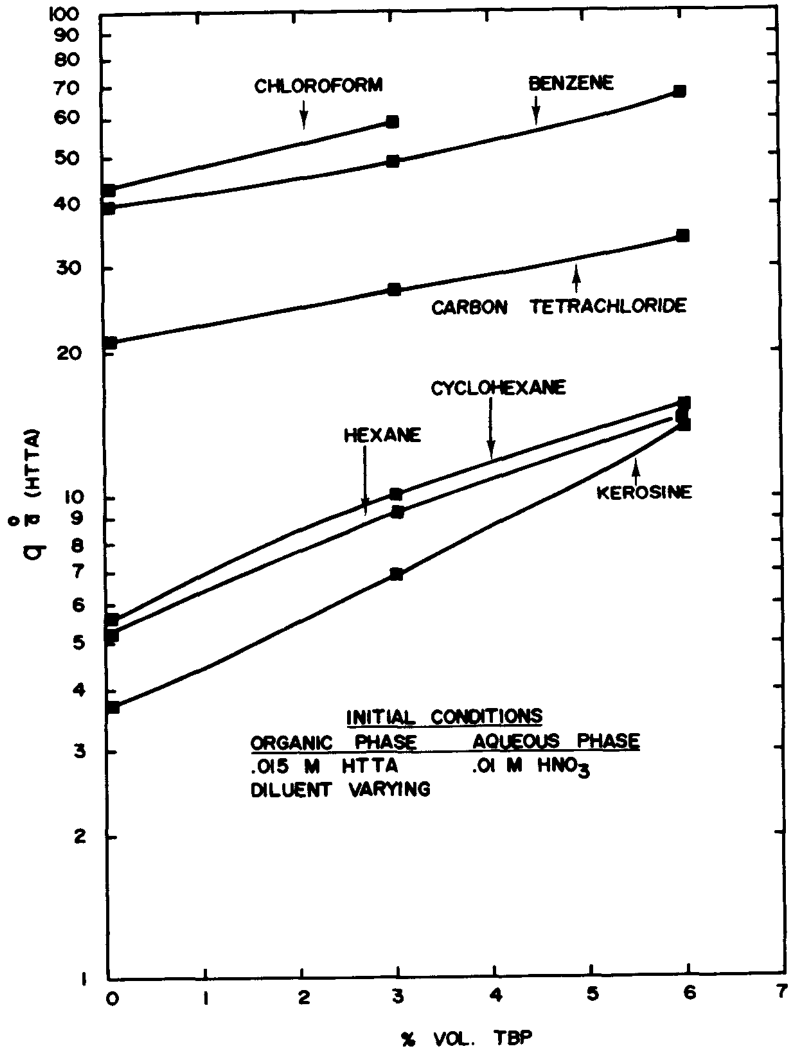


Fig. 3. Distribution coefficients of HTTA for several solvents as a function of total TBP concentrations.

When we used hexone in place of TBP the effect disappeared, Fig. 4, indicating no complex formation between HTTA and hexone.

It is also interesting to note that the distribution of HTTA remains constant upon increasing the ionic strength with sodium nitrate even though the distribution coefficient of Sm decreases in the region studied, Fig. 5.

Finally, the slope of the first part of the Curve F in Fig. 2 is supposed to give the number of molecules of TBP attached to the Sm(III) in the formation of the extractible complex. The value of the slope in our case is approximately 1, in open contradiction with previous results

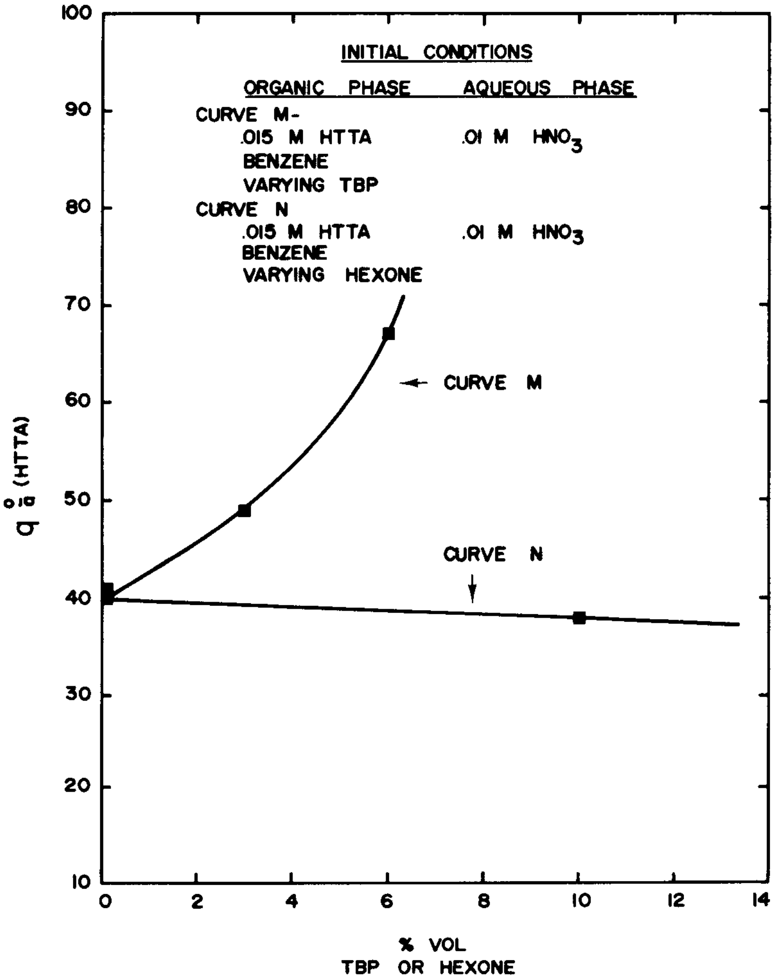


FIG. 4. Distribution coefficients of HTTA for benzene–TBP and benzene–hexone mixtures.

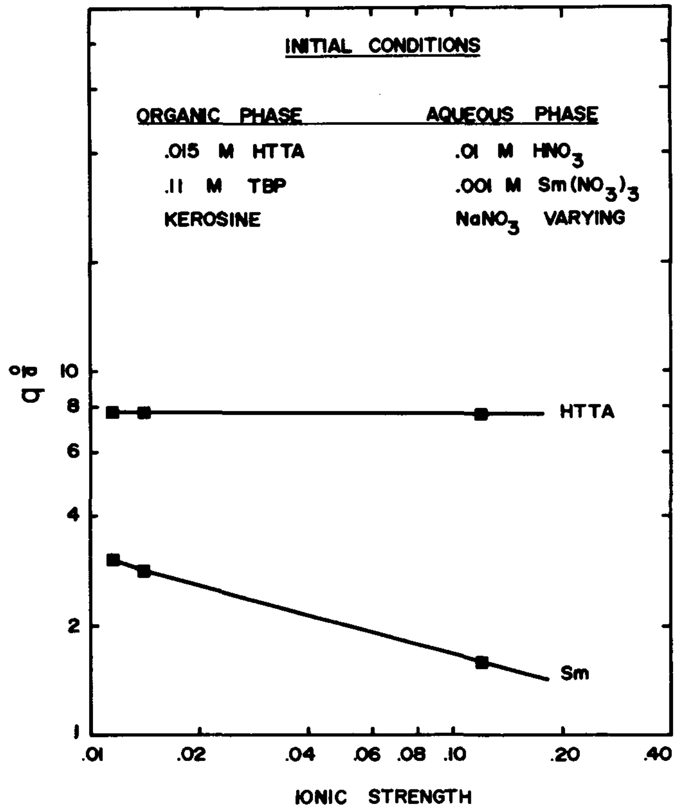


FIG. 5. Equilibrium distribution for HTTA and Sm(III) as a function of ionic strength.

(*19*). However, with the equilibria developed to explain the HTTA distribution curve, it is not clear that this line is one of constant HTTA-enol concentration and, therefore, the slope cannot be used to determine the form of the TBP complex.

Rate of Approach to Equilibrium

As we have seen in the introductory section, several authors (*19–21*) have reported the appearance of maxima when the distribution coefficients of some metals were plotted as functions of phase contact time in synergistic systems, using HTTA as one of the complexing agents.

A typical example of the extraction of Sm(III) for two different

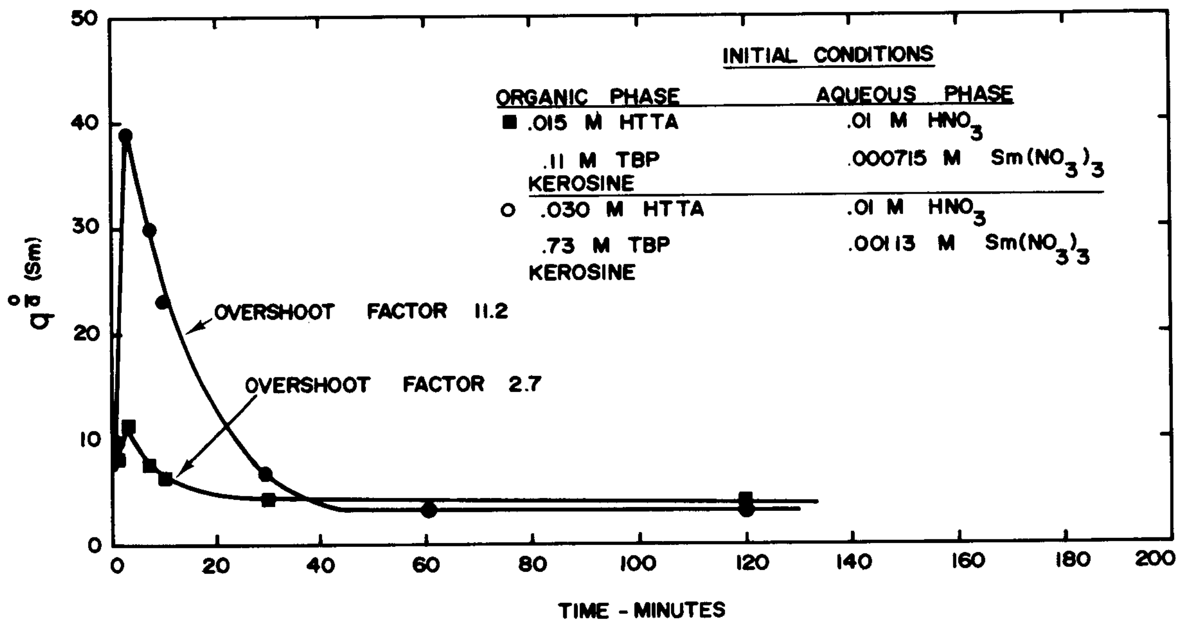


FIG. 6. Typical extraction overshoot for synergistic systems containing HTTA.

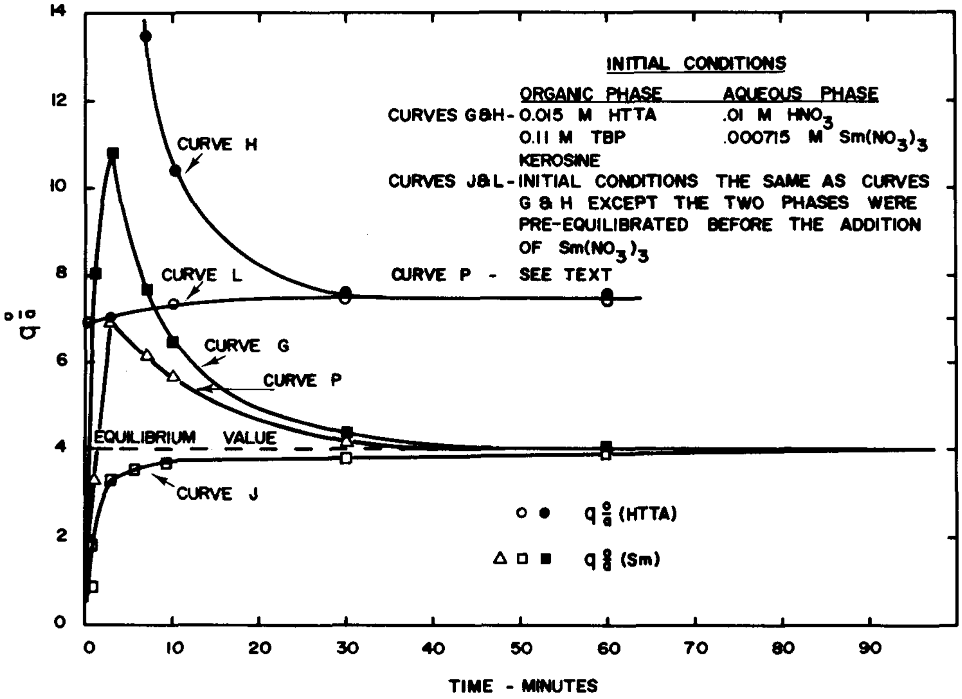


FIG. 7. Effect of preequilibration of phases on extraction overshoot.

organic phase compositions, using the HTTA/TBP mixture in kerosine, is shown in Fig. 6. The maximum extraction is reached after about 3 min shaking. The extraction coefficient then starts to decrease, reaching the equilibrium value in about 1 hr.

This behavior can be explained in the following way: The HTTA is in the enolic (anhydrous) form (*3*, *10*) when the preparation of the organic phase is made in the absence of water. As soon as this phase is contacted with the aqueous phase containing the metal ion, a relatively fast extraction of the metal ion by the enol form and a relatively slow transformation of the HTTA-enol form into the hydrate form occurs. When the rate of metal transfer into the organic phase decreases, the slow hydration reaction of the HTTA-enol starts to control the distribution coefficient. As we saw above, the distribution coefficient of the metal ion is proportional to the HTTA-enol concentration in the organic phase raised to a power, probably 2 or 3. In a previous paper (*19*) we interpreted our data to indicate a complex containing three HTTA molecules; however, present developments cast some doubt on the interpretation of all previous extraction data by ourselves and others.

The HTTA-hydrate going into the aqueous phase, as well as the hydrate remaining in the organic phase, cause a substantial reduction in the complex forming HTTA-enol. This leads to a slow decrease in the distribution coefficient of the metal ion, the rate depending upon the velocity of the hydration reaction. The time for the distribution of the metal to reach the equilibrium value will depend on the time for the HTTA-hydrate to reach an equilibrium distribution.

The following data are presented as proof of the above hypothesis.

First, the distribution coefficients of Sm(III) and HTTA were measured as a function of time for the system, with the following initial conditions: Organic phase, kerosine/HTTA 0.015 *M*/TBP 0.11 *M*; aqueous phase, samarium nitrate 0.000715 *M*/dilute nitric acid, pH 2.

The distribution coefficient of Sm vs. time are plotted in Fig. 7, Curve G. The overshoot shown by this curve was by a factor of approximately 2.7. The variation of the distribution coefficients of HTTA with time is also shown in Fig. 7, Curve H. The values of the distribution coefficients for the HTTA were calculated as the ratio between the HTTA, both hydrate and enol, in the organic phase and HTTA-hydrate concentration in the aqueous phase. The HTTA concentration in the organic phase was calculated by the difference between the initial amount of HTTA in the organic and the amount in the aqueous phase plus that complexed by the metal. For purposes of correction, the metal is assumed to be associated with three molecules of HTTA.

Second, the distribution coefficients of Sm(III) and HTTA were followed as a function of time for a system in which the aqueous and organic phases were preequilibrated before the addition of the metal to be extracted. This preequilibration permits the distribution of HTTA between the two phases, as well as the formation of an equilibrium amount of HTTA-hydrate in the organic phase, before the extraction of the metal ion and should prevent the overshoot, if our interpretation of the data is true.

The procedure used was the following: 250 ml of organic phase, kerosine/HTTA 0.015 *M*/TBP 0.11 *M* and 250 ml of aqueous phase, dilute nitric acid, pH 2, were equilibrated by shaking for 3 hr. The phases were separated after equilibration and the concentration of HTTA-hydrate in the aqueous phase was measured as usual. Samarium nitrate was dissolved in the aqueous phase to reach a concentration of

0.000715 *M*. Aliquots of 25 ml of this new solution and 25 ml of the preequilibrated organic phase were contacted for different periods of time.

The distribution coefficient of Sm vs. time is plotted in Curve J, Fig. 7, showing the disappearance of the maxima. The variation of the distribution coefficient of HTTA vs. time is shown as Curve L in Fig. 7. As we can see from Curves G and J, both distribution coefficients for Sm and HTTA approach the equilibrium value from both sides. In the first case, Curve G, all HTTA is initially in the organic phase while in the second case, Curve J, the HTTA is previously distributed in an equilibrium manner between the two phases. Because of the preequilibration of the phases, Curve J has lost the maxima and the equilibrium distribution of Sm is reached much more rapidly. On the other hand, the rate of approach to equilibrium distribution of the HTTA has changed from Curve H to Curve L. The shape of Curve L moving slightly upward means that as some HTTA is complexed by the Sm after preequilibration, the concentration of both HTTA-enol and HTTA-hydrate in the organic phase decreases a little, then some HTTA in the aqueous phase migrates back to the organic to maintain the equilibrium distribution. The over-all result is a slight increase in the distribution coefficient of HTTA.

Third, and as a final proof of the effect that the hydration of the HTTA-enol in the organic phase has on the distribution coefficient of the metal ions, the following experiment was performed. A preequilibration of the aqueous phase was carried out as before and samarium nitrate was added in the same amount as before also. Aliquots of this solution were contacted with a new organic phase containing the equilibrium amount of HTTA and TBP that correspond to the preequilibrated aqueous phase. In this experiment we are sure that no HTTA is going to the aqueous phase and that the HTTA in the organic phase is going to be in the enol form (no HTTA-hydrate).

The overshoot shown by Curve P, Fig. 7, indicates that the hydration reaction of the HTTA-enol in the organic phase is responsible for most of the overshoot and that the rate of hydration of HTTA is relatively slow.

The fast extraction of the metal ions followed by the slow hydration of the HTTA-enol and the consequent reduction in the complex forming HTTA-enol concentration in the organic phase explains the maxima noticed by other investigators as indicated below.

Healy (*20*) reports a time to reach equilibrium of a few minutes for TBP alone (no HTTA) and 1 to 3 hr with HTTA alone (no TBP).

When working with both in the synergistic system "the partition coefficient gradually increases with time reaching a maximum within a few hours, but in many instances this figure decreased again sometimes by a factor of up to five, final equilibrium being reached within four hours." This maxima is due mainly to the formation of HTTA·H_2O and HTTA·H_2O·TBP in the organic phase since, as a result of the high $q^{o/a}$ for HTTA in benzene, the amount of HTTA·H_2O distributing to the aqueous phase is very low.

Finston and Inoue (*21*) report the appearance of maxima in the synergistic extraction of Fe(III) in the benzene–hexone/HTTA/SCN system. They also noticed a lack of convergence in the extraction and stripping curves. It is our opinion that the maxima can be explained as before; the addition of hexone to the organic phase increases the solubility of water in it and, therefore, shifts appreciable amounts of HTTA-enol to HTTA-hydrate, as shown by Eq. (10). However, hexone differs from TBP in its behavior in that it does not extract HTTA·H_2O from the aqueous phase as shown in Fig. 4. This may be due to the lack of formation of a complex in the organic phase with HTTA·H_2O. The lack of convergence in the extraction and stripping curves could be due to the loss of HTTA into the aqueous phase in the preparation of the benzene–hexone/HTTA/Fe solution to be stripped. This means that the concentration of HTTA in the organic phase at the beginning of the stripping procedure is not the initial one but has been reduced by the amount of HTTA lost to the aqueous phase in preparation of the organic phase to be stripped. We have determined, as pointed out previously, that the distribution coefficient of HTTA in a benzene–hexone/HTTA/dilute nitric acid system decreases slightly as the hexone increases. For 30% hexone in benzene, the $q^{o/a}$ for HTTA = 34 compared with 40 for benzene with no hexone. The effect may become more complex as other substances are introduced into the system.

Poskanzer and Foreman (*22*) have proposed a preequilibration of the phases in HTTA extractions to reduce the equilibration time in some cases.

CONCLUSIONS

From the previous considerations it seems that the antagonistic effect reported everywhere in synergistic systems involving HTTA and TBP is due to several factors independent of the diluent. The increasing amount of TBP in the organic phase leads to an increase in the solubility of the water in this phase with the resulting formation of HTTA·H_2O and HTTA·H_2O·TBP. The over-all result of this, for concentrations of total TBP > 0.1 *M*, is the decrease of the distribution coefficient of the extracted metal. The explanation of this antagonism lies principally in the large reduction of the free HTTA-enol in the organic phase and, to a much smaller extent, to the reduction of the free TBP concentration in the same phase through formation of the HTTA·H_2O·TBP complex. This mechanism is close to the one proposed by Wang et al. (*16*) for the system Zn/hexafluoroacetylacetone/tri-*n*-octyl phosphine oxide.

Through the study of the variation of the distribution coefficients of HTTA and Sm with time, we arrived at the following conclusions:

(a) In the systems diluent/HTTA/dilute HNO_3, diluent/HTTA/TBP/dilute HNO_3, and diluent/HTTA/TBP/M^{3+}/dilute HNO_3, the equilibrium distribution is reached in about 1 hr.

(b) The maxima reported by several authors (*19–21*) is due to the formation of substantial amounts of metal complex in the organic phase in the first few minutes, followed by a destruction of this complex as the HTTA starts to hydrate, part going to form HTTA·H_2O·TBP, part remaining as HTTA·H_2O in the organic phase, and part being distributed in the aqueous phase. The result is a decrease of the free HTTA, enol form, in the organic phase and consequently of the $q^{o/a}$ of the metal.

(c) The controlling step is the hydration of HTTA.

(d) To avoid the overshoot and to speed up the reaching of equilibrium, a preequilibration of the phases in order to introduce an equilibrium amount of HTTA-hydrate in both phases is shown to be effective.

It now appears that, with the use of a method for preequilibration of the organic phase with water, the rate of extraction of the metal will not prevent use of a short residence time contactor for a Cm-Am purification process, using HTTA and TBP as the complexing agents. This technique eliminates the need for using TBP concentrations below 0.1 *M* as discussed in the previous paper (*19*).

The value of the equilibrium constant for the formation of HTTA·H_2O is $K_1 = 17$. The value of the equilibrium constant for the formation of HTTA·H_2O·TBP from the HTTA·H_2O is $K_2 = 22$. Both values are for a system using kerosine as the diluent and dilute nitric acid as the aqueous phase.

With some experimental data similar to that used in this work, it would be possible to calculate K_1 and K_2 for other diluents as well as the free concentrations of HTTA and TBP in the organic phase by using Eqs. (24) and (29).

FUTURE WORK

(a) Investigate the discrepancies in the composition of the metal complex.

(b) Develop a method to measure quantitatively the amount of HTTA-enol and/or HTTA-hydrate in the organic phase in order to be able to calculate directly the equilibrium constants for the formation of the $HTTA \cdot H_2O$, $HTTA \cdot H_2O \cdot TBP$, and $M(TTA)_n(TBP)_m$. The spectrophotometric method might be used in organic diluents other than kerosine.

(c) Find an algebraic expression to fit the whole curve of metal distribution as a function of total HTTA and TBP concentrations.

(d) Determine the distribution coefficients of all rare earths as a function of the concentration of the complexing agents.

(e) Compare the rate of extraction obtained in short residence time contactors with wrist-action shaking.

(f) Study separation of Am and Cm from rare earths in mixer settler solvent extraction equipment.

REFERENCES

1. J. C. Reid and M. Calvin, *J. Amer. Chem. Soc.*, *72*, 2948 (1950).
2. E. L. King and W. H. Reas, *J. Amer. Chem. Soc.*, *73*, 1806 (1951).
3. T. V. Healy, D. F. Peppard, and G. W. Mason, *J. Inorg. Nucl. Chem.*, *24*, 1429 (1962).
4. S. M. Wang, W. R. Walker, and N. C. Li, *J. Inorg. Nucl. Chem.*, *28*, 875 (1966).
5. J. G. Cuninghame, D. Scargill, and H. H. Willis, Brit. Rept., AERE, C/M215 (1954).
6. H. Irving and D. N. Edgington, *Proc. Chem. Soc.*, *1959*, 360.
7. H. Irving and D. N. Edgington, *J. Inorg. Nucl. Chem.*, *15*, 158 (1960).
8. H. Irving and D. N. Edgington, *Chem. Ind.* (London), *1961*, 77.
9. H. Irving and D. N. Edgington, *J. Inorg. Nucl. Chem.*, *21*, 169 (1961).
10. T. V. Healy, *Nucl. Sci. Eng.*, *16*, 413 (1963).
11. T. V. Healy, *J. Inorg. Nucl. Chem.*, *19*, 328 (1961).
12. J. R. Ferraro and D. F. Peppard, *J. Phys. Chem.*, *65*, 539 (1961).
13. L. Newman, *J. Inorg. Nucl. Chem.*, *25*, 304 (1963).
14. L. Newman and P. Klotz, *Inorg. Chem.*, *5*, 461 (1966).
15. R. L. Scruggs, T. Kim, and N. C. Li, *J. Phys. Chem.*, *67*, 2194 (1963).
16. S. M. Wang, D. Y. Park, and N. C. Li, "Solvent Extraction Chemistry," *International Conference on Solvent Extraction Chemistry* (*1966*), Wiley, New York, 1966.

17. R. W. Taft and E. H. Cook, *J. Amer. Chem. Soc.*, *81*, 46 (1959).

18. D. F. Peppard, W J Driscoll, R. J. Sironen, and S. McCarty, *J. Inorg. Nucl. Chem.*, *4*, 326 (1957).

19. M. W. Davis, Jr., J. W. Holt, and R. A. Tournier, Presented at International Solvent Extraction Conference, 1971, The Hague, Netherlands, Proceedings to be Published.

20. T. V. Healy, *J. Inorg. Nucl. Chem.*, *19*, 314 (1961).

21. H. L. Finston and Y. Inoue, *J. Inorg. Nucl. Chem.*, *29*, 2431 (1967).

22. A. M. Poskanzer and B. M. Foreman, Jr., *J. Inorg. Nucl. Chem.*, *16*, 323 (1961).

23. H. Irving and D. N. Edgington, *J. Inorg. Nucl. Chem.*, *10*, 306 (1959).

24. J. Korbl and R. Pribil, *Chemist-Analyst*, *45*(4), 102 (1956).

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

26. H. Irving and D. N. Edgington, *J. Inorg. Nucl. Chem.*, *20*, 321 (1961).

27. K. Ohwada, *J. Inorg. Nucl. Chem.*, *29*, 833 (1967).

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