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Extraction Theory and Form of the Extraction Complex for the Metals Dysprosium, Holmium, Thulium, and Curium in the Synergistic System Kerosene/HTTA/TBP/Dilute HNO_3*

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BRIEF SUMMARY OF WORK

Data were taken for the distribution of HTTA and the metals Dy, Ho, Tm, and Cm in the system kerosene/thenoyltrifluoroacetone (HTTA)/tributylphosphate (TBP)/dilute HNO_3. The theory first proposed by Tournier (*1*) and Tournier and Davis (*2*) for the HTTA distribution was modified and new values of the equilibrium constants resulting from the theory were determined by a least squares fit of the HTTA distribution data. The new values are $K_1 = 14$ and $K_2 = 3.45$.

An analysis of the HTTA distribution data indicates that one molecule of TBP associates with one molecule of $(HTTA \cdot H_2O)$ to form a complex. Analysis of distribution data for the metals Dy, Ho, Tm, and Cm using the modified theory indicates that the form of the metal complex is $M^{+3}(TTA)_2(NO_3)(TBP)_2$. This is different than the $M^{+3}(TTA)_3(TBP)_2$ reported by most investigators.

A log-log plot of qo/a as a function of $[H^+]$ under conditions of constant free TBP and HTTA and constant ionic strength indicates an inverse

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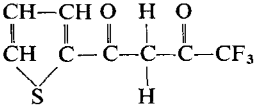
squared effect of $[H^+]$ on the metal distribution ratio, q o/a. This in turn supports the indication that two (TTA) molecules are associated with the metal complex. No experimental data to verify the presence of (NO_3^-) in the complex have as yet been obtained.

INTRODUCTION

Since thenoyltrifluoroacetone was synthesized by Reid and Calvin (*3*), there has been a considerable investigation of its use as an extracting agent, either by itself or in conjunction with another extracting agent.

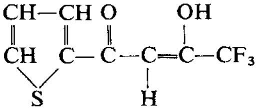
The HTTA can exist in three forms other than the extractable metal enolate form,

a)

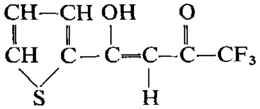


keto

b)

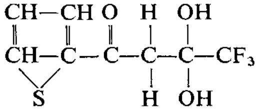


enol

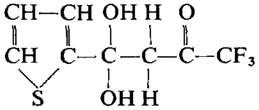


enol

c)

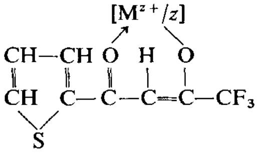


ketohydrate

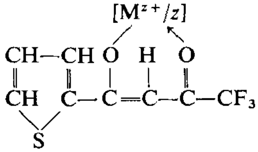


ketohydrate

d)



metal enolate



metal enolate

There has been little data reported concerning the form of HTTA or other chelating agents when in the presence of neutral ligands, such as TBP (*4–7*).

In studies involving HTTA and TBP the interaction of the metal with the HTTA and TBP has generally been described as

$$\mathrm{M_{aq}}^{n+} + m\mathrm{TBP_o} + n\mathrm{HTTA_o} \overset{K_e}{\rightleftharpoons} \mathrm{M(TTA)}_n\mathrm{(TBP)}_m + n\mathrm{H_{aq}}^{+}$$

where

$$K_e = \frac{[\mathrm{M(TTA)}_n\mathrm{(TBP)}_m]_\mathrm{o}[\mathrm{H}^+]_\mathrm{aq}}{[\mathrm{HTTA}]_\mathrm{o}^{\,n}[\mathrm{TBP}]_\mathrm{o}^{\,m}[\mathrm{M}^{n+}]_\mathrm{aq}} \tag{1}$$

Ideally, all the terms in brackets should be activities. In order to avoid complicated thermodynamic factors, the concentrations of the complexing agents are usually held low enough so that the concentrations may be used instead of the activities.

Then, the metal distribution ratio would be defined as

$$q\,\mathrm{o}/a = \frac{[\mathrm{M(TTA)}_n\mathrm{(TBP)}_m]_\mathrm{o}}{[\mathrm{M}^{n+}]_\mathrm{aq}} = \frac{K_e[\mathrm{TBP}]_\mathrm{o}^{\,m}[\mathrm{HTTA}]_\mathrm{o}^{\,n}}{[\mathrm{H}^+]_\mathrm{aq}} \tag{2}$$

Tournier and Davis (*2*) have, for the first time, proposed a theory to allow the calculation of the free concentrations of HTTA and TBP in the kerosene-dilute nitric acid system. This theory allows for formation of an HTTA·H_2O·TBP complex, as well as for the loss of an appreciable fraction of the HTTA to the aqueous phase. It also explains the phenomena called "antisynergism." The modified theory presented in this work more adequately allows for the increased solubility of water in the organic phase due to the presence of TBP. Most previous authors have used total concentrations of the complexing agents to determine the form of the extracted complex. This is felt to be totally inadequate.

THEORY

HTTA Distribution

Healy (*5*) has reported that HTTA retains the enol form in a variety of organics at low TBP concentrations [<0.1 *M*]. Reid and Calvin (*3*) and King and Reas (*8*) have reported that HTTA exists almost entirely as the ketohydrate in aqueous media with only about 1.6% existing in the enol form.

With these considerations and assuming kerosene also to favor the enol form at low TBP concentrations, the distribution ratio for HTTA in kerosene systems with no TBP is defined as

$$q_1 = \frac{[\mathrm{HTTA_{enol}}]_o}{[\mathrm{HTTA \cdot H_2O}]_{aq}} \tag{3}$$

The theory proposed by Tournier and Davis (*2*) included a term for the concentration of the ketohydrate in the expression for the distribution ratio.

When TBP is added to the organic phase, the solubility of water in the organic is increased. Alcock et al. (*7*) have indicated that, up to TBP concentrations of about 0.7 *M*, there is one molecule of water in the organic phase for every three molecules of TBP. In the presence of water, some of the HTTA in the organic will assume the ketohydrate form. The ketohydrate cannot form a chelate; so, it is effectively removed from the system as a complexing agent.

In addition to the presence of the ketohydrate in the organic phase, a complex formed by the hydrogen bonding of the TBP to the ketohydrate may occur (*4*). There is evidence that a similar complex of the enol and TBP does not occur to any significant extent (*5*, *6*).

The distribution ratio of HTTA when TBP is in the system is then defined as

$$q_2 = \frac{[\mathrm{HTTA_{enol}}]_o + [\mathrm{HTTA \cdot H_2O}]_o + [\mathrm{HTTA \cdot H_2O \cdot} n\mathrm{TBP}]_o}{[\mathrm{HTTA \cdot H_2O}]_{aq}} \tag{4}$$

The formation of the ketohydrate and its complex with TBP can be expressed by

$$(\mathrm{HTTA_{enol}})_o + (\mathrm{H_2O})_o \overset{K_1}{\rightleftharpoons} (\mathrm{HTTA \cdot H_2O})_o$$

and

$$(\mathrm{HTTA \cdot H_2O})_o + n(\mathrm{TBP})_o \overset{K_2}{\rightleftharpoons} (\mathrm{HTTA \cdot H_2O \cdot} n\mathrm{TBP})_o$$

where

$$K_1 = \frac{[\mathrm{HTTA \cdot H_2O}]_o}{[\mathrm{HTTA_{enol}}]_o[\mathrm{H_2O}]_o} \tag{5}$$

$$K_2 = \frac{[\mathrm{HTTA \cdot H_2O \cdot} n\mathrm{TBP}]_o}{[\mathrm{HTTA \cdot H_2O}]_o[\mathrm{TBP}]_o^n} \tag{6}$$

From Eq. (3), (4), (5), and (6), one can derive expressions for the theoretical HTTA distribution and the free concentrations of HTTA and TBP as functions of the total concentrations of each complexing agent in the system.

Ideally, all terms in brackets should be activities. The activity of the $HTTA_{enol}$ can be approximated in the TBP system by using the distribution data for HTTA in kerosene following the procedure described by King and Reas (*8*), For all other species the concentrations are assumed to be equal to the activities.

The activity coefficient of the $HTTA_{enol}$ can be approximated at a given concentration by dividing the distribution ratio at infinite dilution, q_0, by the distribution ratio at that concentration, q_1. Activity coefficients can be calculated from the data presented in Fig. 1. Based on this figure, a value of 3.5 has been assumed for q_0. By using a material balance of the HTTA, the concentration of the $HTTA_{enol}$ in the organic phase [with no TBP] can be calculated from

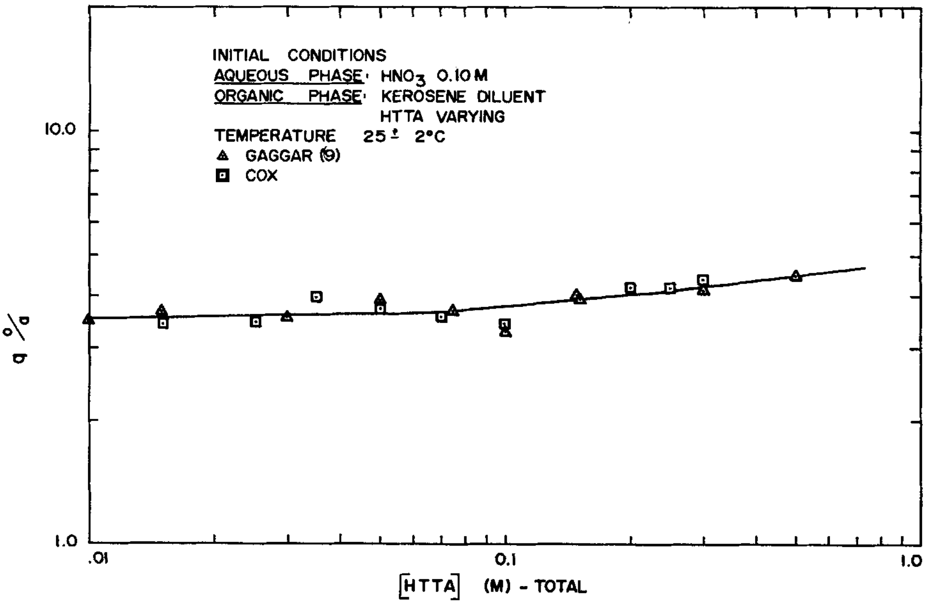


FIG. 1. Distribution ratios of HTTA as a function of the total HTTA concentration with no TBP in the system.

$$[\mathrm{HTTA_{enol}}]_o = \frac{q_1[\mathrm{HTTA}]_{\mathrm{total}}}{q_1 + 1} \tag{7}$$

A plot of the activity coefficient of the $\mathrm{HTTA_{enol}}$ as a function of the $\mathrm{HTTA_{enol}}$ concentration in the kerosene is shown in Fig. 2. Since the activity coefficient of the $\mathrm{HTTA_{enol}}$ is very close to unity, the terms for the concentrations of the enol are used in the following derivations.

The following substitutions are made to simplify the algebra involved

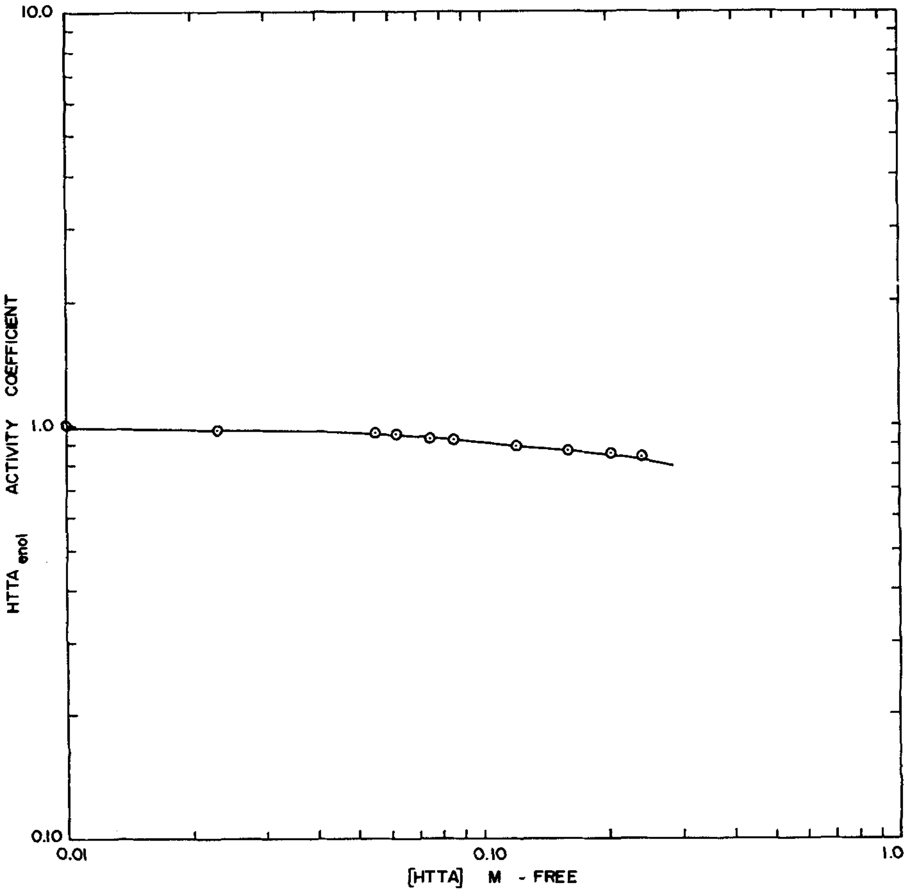


Fig. 2. Activity coefficients of $\mathrm{HTTA_{enol}}$ as a function of the free HTTA concentration.

in the derivations:

$A = [\mathrm{HTTA \cdot H_2O \cdot }n\mathrm{TBP}]_o$
$B = [\mathrm{HTTA_{enol}}]_o$ = uncomplexed or free HTTA
$C = [\mathrm{TBP}]_{\mathrm{total}}$
$D = [\mathrm{TBP}]_o$ = uncomplexed or free TBP
$E = [\mathrm{HTTA \cdot H_2O}]_{\mathrm{aq}}$
$F = [\mathrm{HTTA \cdot H_2O}]_o$
$G = [\mathrm{HTTA}]_{\mathrm{total}}$
$[\mathrm{H_2O}]_o = aC$ where $a = 0.33$

The previous equations for the system (with TBP) now can be written as

$$q_1 = B/E \tag{8}$$

$$q_2 = (B + A + F)/E \tag{9}$$

$$K_1 = F/aBC \tag{10}$$

$$K_2 = A/FD^n \tag{11}$$

Before these equations can be solved for the concentrations of the individual species in the system, some value for n in Eq. (11) must be known. If n is left as a variable, the equations are very nonlinear and very difficult to solve. However, an equation can be derived which can be used to find an approximation for n.

Equation (9) is the definition of the HTTA distribution when TBP is in the system:

$$q_2 = \frac{B + F + A}{E} \tag{9}$$

Substituting from Eq. (11) for A into Eq. (9)

$$q_2 = \frac{B + F + K_2FD^n}{E} \tag{12}$$

Substituting from Eq. (10) for F into Eq. (12)

$$q_2 = \frac{B + aK_1BC + aK_1K_2BCD^n}{E} \tag{13}$$

By substituting q_1 for the ratio B/E and rearranging, one can obtain

$$\frac{q_2 - q_1}{aq_1C} = K_1 + K_1K_2D^n \tag{14}$$

If the assumption is made that the free concentration of TBP is approximately equal to the total concentration, Eq. (14) can be written in the form

$$\frac{q_2 - q_1}{aq_1C} = X + YC^n \tag{15}$$

On a log-log plot of this equation, the slope approaches the value of n at the higher TBP concentrations. This procedure has been used previously for the determination of stability constants and stoichiometric coefficients

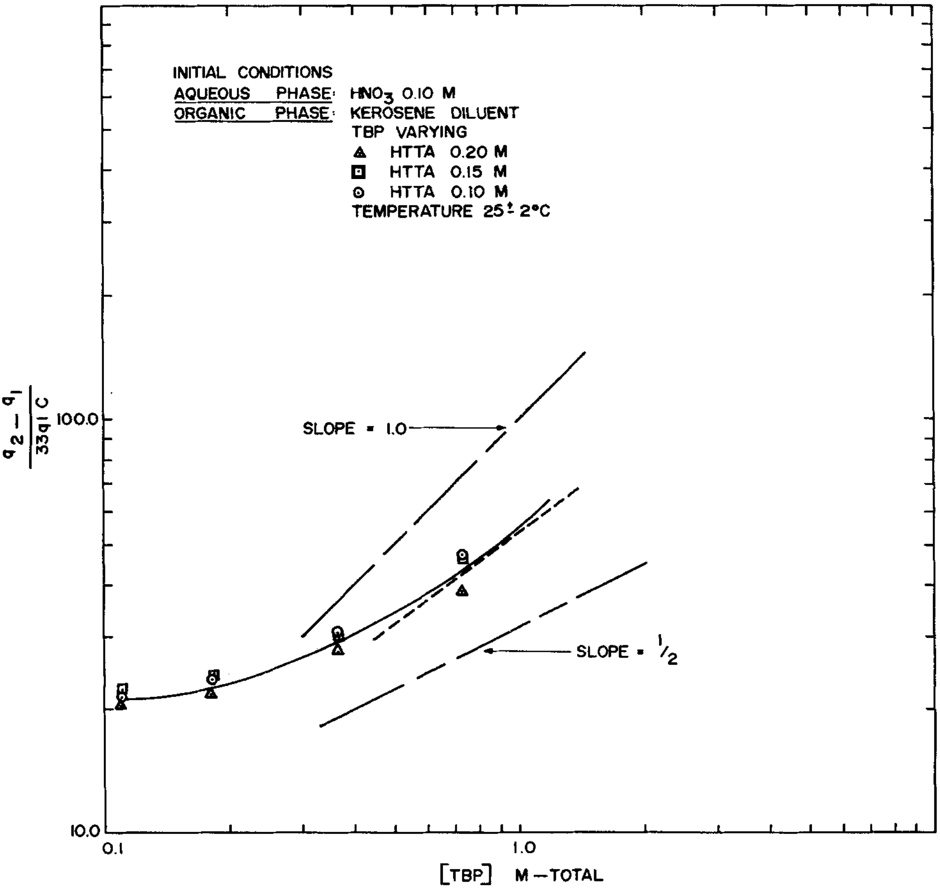


FIG. 3. Plot of Eq. (15) to approximate the number of TBP molecules complexed to each molecule of HTTA · H_2O.

for the formation of complexes (*10–13*). This plot is shown in Fig. 3. Based on this plot, a value of 1 was used for n.

Since equal volumes of the aqueous and organic phases were used, the material balances on HTTA and TBP are, respectively,

$$G = A + B + E + F \tag{16}$$

$$C = D + nA,\ n = 1 \tag{17}$$

The following equations can be derived for the concentrations of the individual chemical species.

$$A = K_2FD^n = \frac{K_2FC}{1 + K_2F} \tag{18}$$

$$A = \frac{aK_1K_2q_1C^2\left(\dfrac{G}{q_2 + 1}\right)}{1 + aK_1K_2q_1C\left(\dfrac{G}{q_2 + 1}\right)} \tag{19}$$

$$B = q_1E = \frac{q_1G}{q_2 + 1} \tag{20}$$

$$D = \frac{C}{1 + K_2F} = \frac{C}{1 + \left(\dfrac{aK_1K_2q_1CG}{q_2 + 1}\right)} \tag{21}$$

$$E = \frac{G}{q + 1} \tag{22}$$

$$F = aK_1BC = \frac{aK_1q_1CG}{q_2 + 1} \tag{23}$$

Equation (14) can be rearranged to a form which will allow a means of checking the approximation that $n = 1$ and the value of K_2 calculated by a fit of the theoretical HTTA distribution equation to the data:

$$\frac{q_2 - q_1}{aK_1q_1C} - 1 = K_2D^n \tag{24}$$

A log-log plot of Eq. (24) will give a slope equal to the value of n and an intercept at $D = 1$ equal to the value of K_2.

By substituting the expression for A from Eq. (19) and the expression for F from Eq. (23) into Eq. (9), the following equation for the theoretical

HTTA distribution can be derived:

$$q_2 = q_1 \left[1 + aK_1C\left(1 + \frac{K_2C}{1 + \dfrac{aK_1K_2q_1CG}{q_2 + 1}}\right)\right] \tag{25}$$

Metal Distribution

In the extraction of metals in systems using both HTTA and TBP as extracting agents, the extracted species may be a complex containing only HTTA or TBP. It is more likely, however, that the extracted species will be a mixed complex of both HTTA and TBP. Since some authors (*14*, *15*) report very small distribution ratios for the rare earths in systems containing only HTTA or TBP, concentrations of the complexes containing only one of the complexing agents are small enough to be ignored in systems where both complexing agents are used.

The general reaction for the formation of the mixed complex may be written as

$$(M^{\pm z})_{aq} + n(HTTA)_o + m(TBP)_o + z - n(NO_3^-)_{aq} \overset{K_e}{\rightleftharpoons} [M(TTA)_n(NO_3)_{z-n}(TBP)_m]_o + n(H^+)_{aq}$$

where

$$K_e = \frac{[M(TTA)_n(NO_3^-)_{z-n}(TBP)_m]_o[H^+]_{aq}^n}{[M^{+z}]_{aq}[NO_3]_{aq}^{z-n}[HTTA]_o^n[TBP]_o^m} \tag{26}$$

The metal distribution is defined as

$$q\,o/a = \frac{[M(TTA)_n(NO_3)_{z-n}(TBP)_m]_o}{[M^{+z}]_{aq}} \tag{27}$$

Equations (26) and (27) can be combined to give

$$q\,o/a = \frac{K_e[NO_3^-]_{aq}^{z-n}}{[H^+]_{aq}^n}[HTTA]_o^n[TBP]_o^m \tag{28}$$

Log-log plots of Eq. (28), holding the concentrations of the proper chemical species constant, will allow the determination of the number of H^+, TTA^-, NO_3^-, and TBP molecules associated with the formation of each molecule of the metal complex.

EXPERIMENTAL

Apparatus and Materials

The rare earths used for these experiments were obtained from Research Chemicals Division of Nuclear Corporation of America, Phoenix, Arizona, as the following forms, based on individual lot assays: $Nd(NO_3)_3 \cdot 6H_2O$, $Dy(NO_3)_3 \cdot 5.9H_2O$, $Ho(NO_3)_3 \cdot 5.9H_2O$, and $Tm(NO_3)_3 \cdot 5.85H_2O$. Stock solutions of the metals were prepared by dissolution of weighed amounts of the salts in previously prepared nitric acid solutions.

All acids were obtained from Fisher Scientific Company, Atlanta, Georgia. All pH measurements were made on a Beckman expanded scale pH meter with a microglass indicator electrode and a fiber-type calomel reference electrode. Standard pH buffer solutions were also obtained from Fisher Scientific Company.

The tri-*n*-butyl phosphate (TBP) was obtained from Matheson Coleman and Bell, Norwood, Ohio. It was purified by the method outlined by Irving and Edgington (*16*).

The thenoyltriflouroacetone (HTTA) was purchased from Columbia Organic Company, Columbia, South Carolina. The HTTA was purified by recrystallization from spectral quality hexane. The melting point of the recrystallized HTTA was 42.5–43°C. The HTTA was stored in a dessicator in the dark. All solutions of HTTA were stored in the dark.

The kerosene was obtained as a normal paraffin mixture from Continental Oil Company, Baltimore, Maryland. Designated N-C_{12}-C_{14}, the kerosene had the following distribution: C_{12} 9.5%, C_{13} 55.1%, C_{14} 35.3%, and C_{15} 0.1%. This is the same kerosene used by the Savannah River Plant, Aiken, South Carolina, in its solvent extraction process. The kerosene was used with no further purification.

The ^{244}Cm solutions were previously prepared by J. W. Holt (*17*) and C. S. Smith (*18*). All solutions were metal nitrates in HNO_3. The pH was adjusted as necessary.

Distribution ratios for curium were determined by use of an automatic flow counter produced by Tracerlab, Incorporated.

The aqueous HTTA concentrations were measured spectrally with a Carl Zeiss PMQ-II Spectrophotometer. All measurements were made at a wavelength of 267 nm.

All samples were agitated by use of a wrist-action shaker produced by the Burrell Corporation, Pittsburgh, Pennsylvania. The shaker was operated at the maximum frequency of about 330 oscillations per minute.

All glassware used in the radioactive studies was treated with a 10% Siliclad solution. Siliclad is produced by Clay Adams, a division of Becton Dickson and Company, Parsippany, New York.

All reagents were reagent grade or better.

Procedures

All experiments, except those involving radioactive materials, were conducted by contacting 25 ml portions of the aqueous and organic phases in a 125-ml glass stoppered iodine flask. Shaking was followed by centrifugation, after which the aqueous phases were isolated and analyzed.

The distribution ratios of the HTTA and the metals were determined in a similar fashion. The organic concentrations were calculated by use of a material balance after the aqueous concentrations were determined, with the distribution ratio defined as the total organic concentration of metal or HTTA divided by the aqueous concentration of the appropriate species.

As stated previously, the aqueous concentration of the HTTA was determined by a spectrophotometer. The concentrations in the organic phase could not be determined in this manner since the kerosene is opaque to light of a wavelength of 267 nm, the absorption peak for HTTA ketohydrate.

The concentrations of the rare earths in aqueous phases were determined by titration with a solution of the di-sodium salt of EDTA, using xylenol orange as an indicator. The preparation of the samples and the analyses were done following the procedures outlined by Korbl and Pribil (*19*).

The experiments to determine the distribution ratios for 244 C were carried out in the following manner. The aqueous phase was prepared by adding 1 ml of a 0.02-*M* solution of neodymium to 19 ml of a solution containing the curium tracer. In this manner the ionic strength of the solution was held constant as well as the total bulk of extractable material. One milliliter of the aqueous phase was contacted with 1 ml of an organic phase containing HTTA and TBP. As stated previously, the radioactive metal concentrations of the phases were measured by counting the α-emissions with an automatic flow counter. The metal concentrations in both phases were determined in this way. To avoid errors due to loss of the radioactive material, the material balance was checked, with those points having a balance of less than 90% being repeated.

After shaking and centrifugation, samples from each phase were prepared for analysis following the general procedures outlined by Tuck (*20*).

ANALYSIS OF DATA

All data, unless stated otherwise, were taken at HNO_3 concentrations of 0.10 or 0.05 *M* with total HTTA concentrations of 0.10, 0.15, or 0.20 *M*. The total TBP concentrations were varied from 0.011 to 0.73 *M*.

HTTA Distribution

The distribution data for HTTA are shown in Figs. 1, 4, and 5. A log-log plot of Eq. (14) to find an approximation for the number of TBP molecules

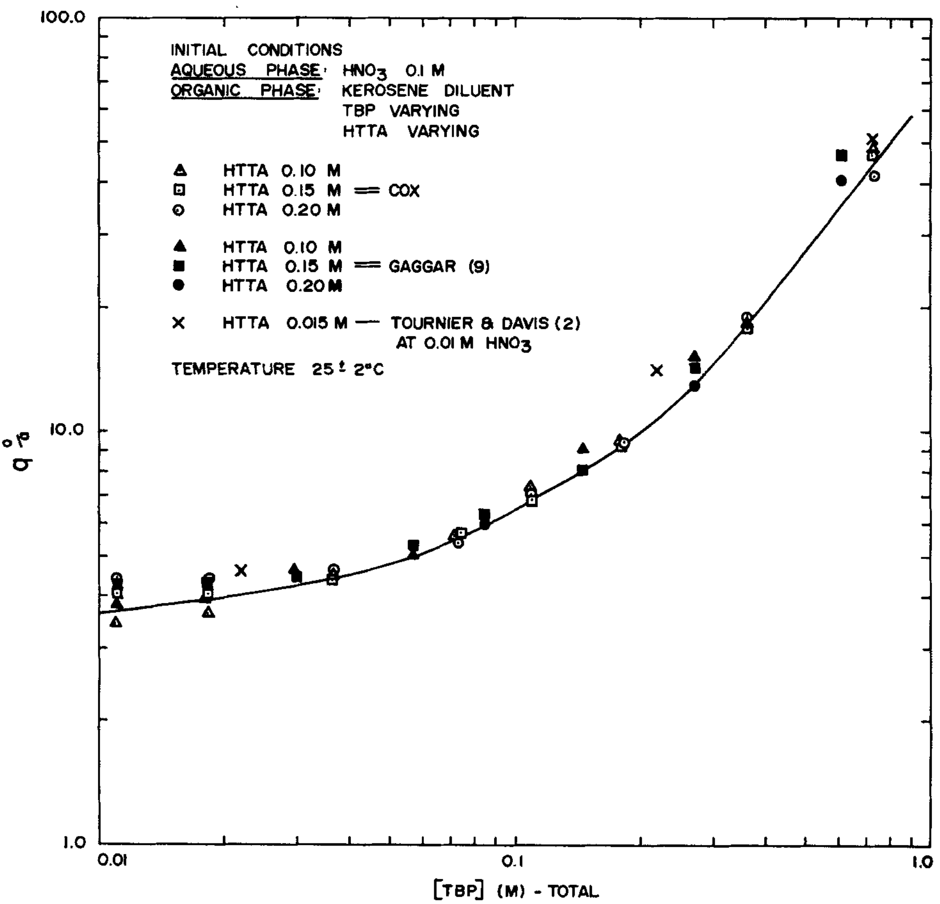


FIG. 4. Distribution ratios of HTTA as a function of the total HTTA and TBP concentrations.

associated with each molecule of HTTA·H_2O is shown in Fig. 3. At the higher concentrations of TBP, the slope of this curve should approximate this number. The actual slope is between 1.0 and 0.5, but since the slope is increasing, a value of 1 was used in all derivations.

The equilibrium constants K_1 and K_2 from Eqs. (5) and (6) were determined by a least squares fit of the theoretical distribution equation to the data using a computer (*21*). Values of 14.0 and 3.45 were determined for K_1 and K_2, respectively. The theoretical distribution curve is shown in

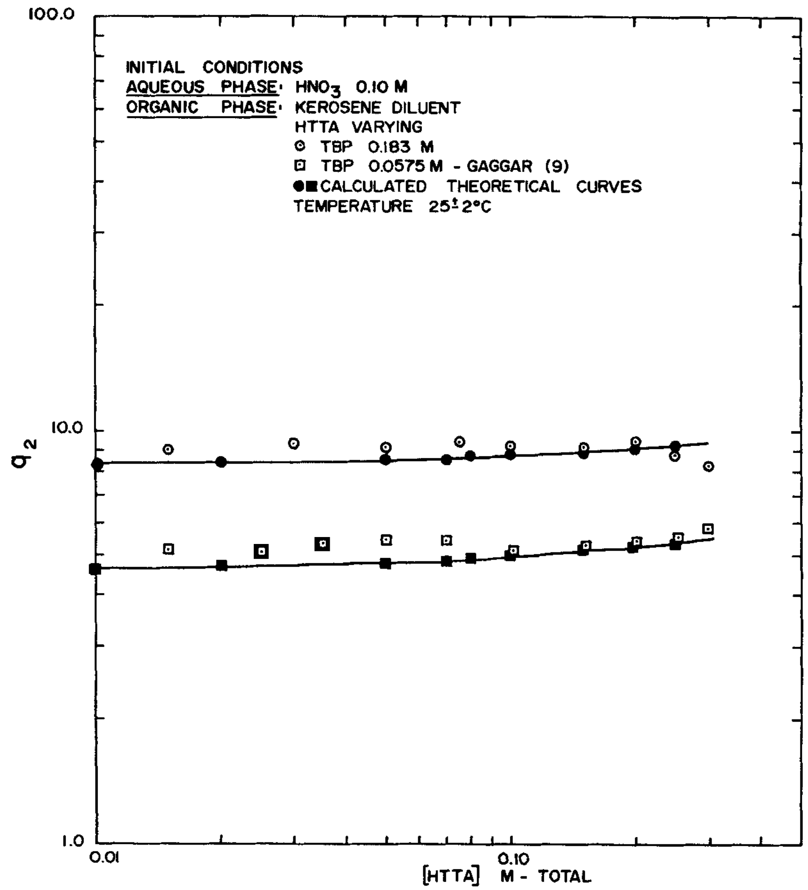


FIG. 5. Distribution ratios of HTTA as a function of the total HTTA concentration at constant total TBP concentrations.

Fig. 6. The free concentrations of the HTTA and TBP and the free HTTA activity were calculated from the data and are shown in Table 1. The relation of free HTTA activity and free TBP is shown graphically in Fig. 7.

The internal consistancy of the theoretical equations was checked by a log-log plot of Eq. (23), shown in Fig. 8. The theoretical slope of this plot is 1.0 while the theoretical intercept at $D = 1.0$ is 3.45. A least-squares fit of the points has a slope of 0.67 and an intercept of 2.5. The term

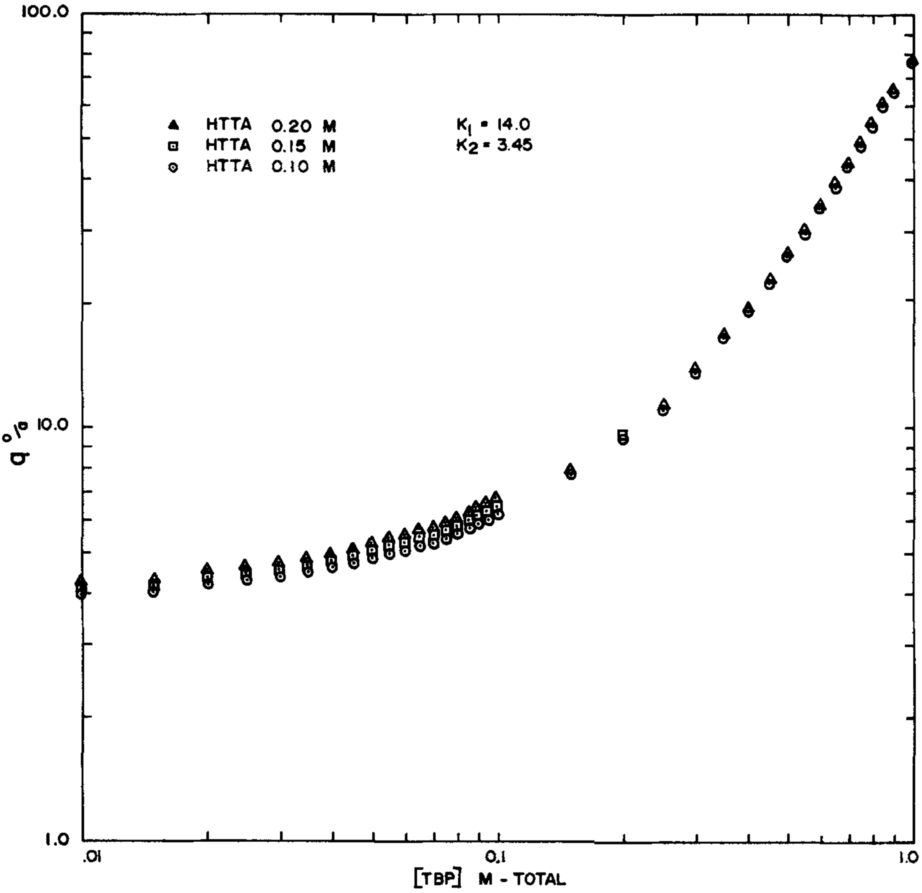


FIG. 6. Theoretical HTTA distribution curve as a function of the total HTTA and TBP concentrations.

TABLE 1

The Free $HTTA_{enol}$ Concentration, the Free HTTA Activity, and the Free TBP Concentration in the Kerosene Phase.

Total [HTTA] (*M*)	q_1	Total [TBP] (*M*)	q_2	Free [$HTTA_{enol}$] (*M*)	$HTTA_{enol}$ activity coefficient	Free [HTTA activity] (*M*)	Free [TBP] (*M*)
0.10	3.8	0.0110	3.44	0.0856	0.92	0.0788	0.0108
		0.0183	3.63	0.0821	0.93	0.0764	0.0179
		0.0365	4.53	0.0688	0.94	0.0647	0.0351
		0.0730	5.67	0.0570	0.95	0.0541	0.0685
		0.1100	7.06	0.0472	0.96	0.0453	0.1016
		0.1830	9.37	0.0367	0.96	0.0352	0.1653
		0.3650	18.26	0.0197	0.98	0.0193	0.3274
		0.7300	48.16	0.0077	0.99	0.0076	0.6701
0.15	3.9	0.0110	3.95	0.1182	0.89	0.1052	0.0108
		0.0183	4.08	0.1152	0.89	0.1025	0.0177
		0.0365	4.54	0.1056	0.90	0.0950	0.0344
		0.0730	5.64	0.0881	0.92	0.0811	0.0662
		0.1100	6.81	0.0749	0.93	0.0697	0.0972
		0.1830	9.20	0.0574	0.95	0.0545	0.1568
		0.3650	17.80	0.0311	0.96	0.0299	0.3091
		0.7300	46.80	0.0122	0.98	0.0120	0.6390
0.20	4.0	0.0110	4.26	0.1521	0.87	0.1323	0.0107
		0.0183	4.38	0.1487	0.87	0.1294	0.0175
		0.0365	4.59	0.1431	0.88	0.1259	0.0337
		0.0730	5.25	0.1280	0.88	0.1226	0.0635
		0.1100	6.94	0.1008	0.90	0.0907	0.0935
		0.1830	9.36	0.0772	0.92	0.0710	0.1494
		0.3650	17.70	0.0428	0.96	0.0411	0.2923
		0.7300	41.15	0.0190	0.98	0.0186	0.5980

$(q_2 - q_1)/q_1$ becomes somewhat uncertain where the values of q_1 and q_2 are close together; therefore, only data at TBP concentrations of 0.11 *M* or greater were used for the plot. Some variation from the theoretical was expected since the calculated theoretical value of the intercept, which should be equal to K_2, was from a fit of all the distribution data. Also, the concentrations of TBP and $HTTA \cdot H_2O$ may be great enough to cause a departure from ideality in the system.

Metal Distribution

It was desired to determine the form of the extracted metal complexes. In order to do this, a means must be available for calculating the free concentrations of the HTTA and TBP and the free HTTA activity when metal is in the system.

Tournier and Davis (*2*) have reported that the HTTA distribution at 0.015 *M* HTTA is not appreciably affected by a metal concentration of 0.001 *M*, the same metal concentration used in these experiments. Since the HTTA concentrations used for these investigations were considerably greater than 0.015 *M*, the effect of the metal on the HTTA distribution will be negligible. Tournier and Davis (*2*) have also reported that the HTTA

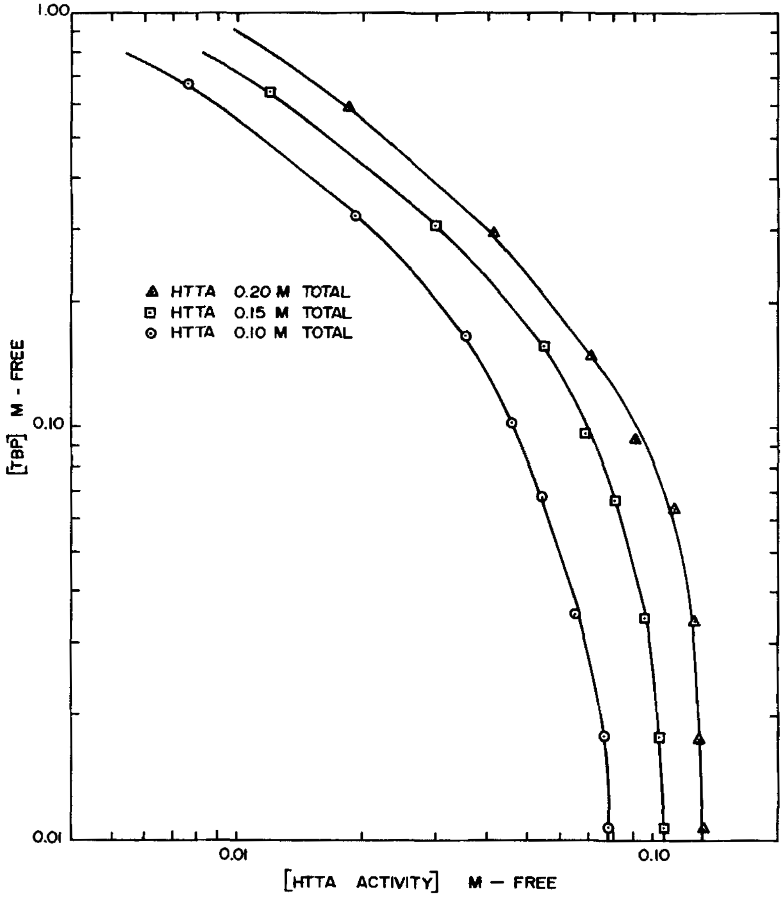


FIG. 7. Free TBP concentrations as a function of the free HTTA activity.

distribution is not affected by the ionic strength of the aqueous phase whereas the metal distribution can be strongly affected.

With no TBP in the system, Tournier and Davis (*2*) reported a value of 3.7 for the HTTA distribution ratio at 0.015 *M* HTTA and 0.01 *M* HNO_3 while a value of 3.55 was obtained by the author for the same HTTA concentration at 0.10 *M* HNO_3. The difference between these two values is within the ±10% experimental error reported by both Tournier and Davis (*2*) and this author. This indicates that the HTTA distribution is not affected by fairly large changes in the (H^+) concentration at low pH values.

Therefore, the relations shown in Table 1 and Fig. 7 for the free con-

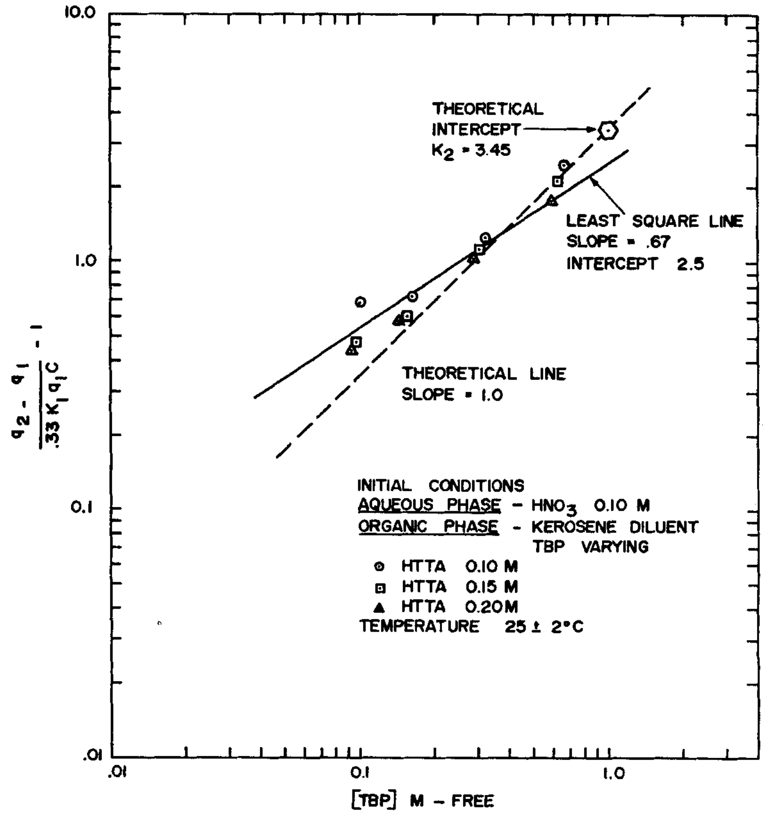


FIG. 8. Plot of Eq. (24) to show the number of TBP molecules complexed to each molecule of HTTA · H_2O and to check the value of K_2.

centrations of HTTA and TBP and the free HTTA activity will be used for the analysis of the metal distribution data.

The distribution data for the metals Dy, Ho, Tm, and Cm are shown in Figs. 9 through 14. The effect of ionic strength on the metal distribution is shown in Fig. 15. To aid in the analyses of these data, plots were made for the distribution of the metals as functions of free TBP. These are shown in Figs. 16, 17, and 18. From Fig. 7, the free HTTA activities for several free TBP concentrations were determined.

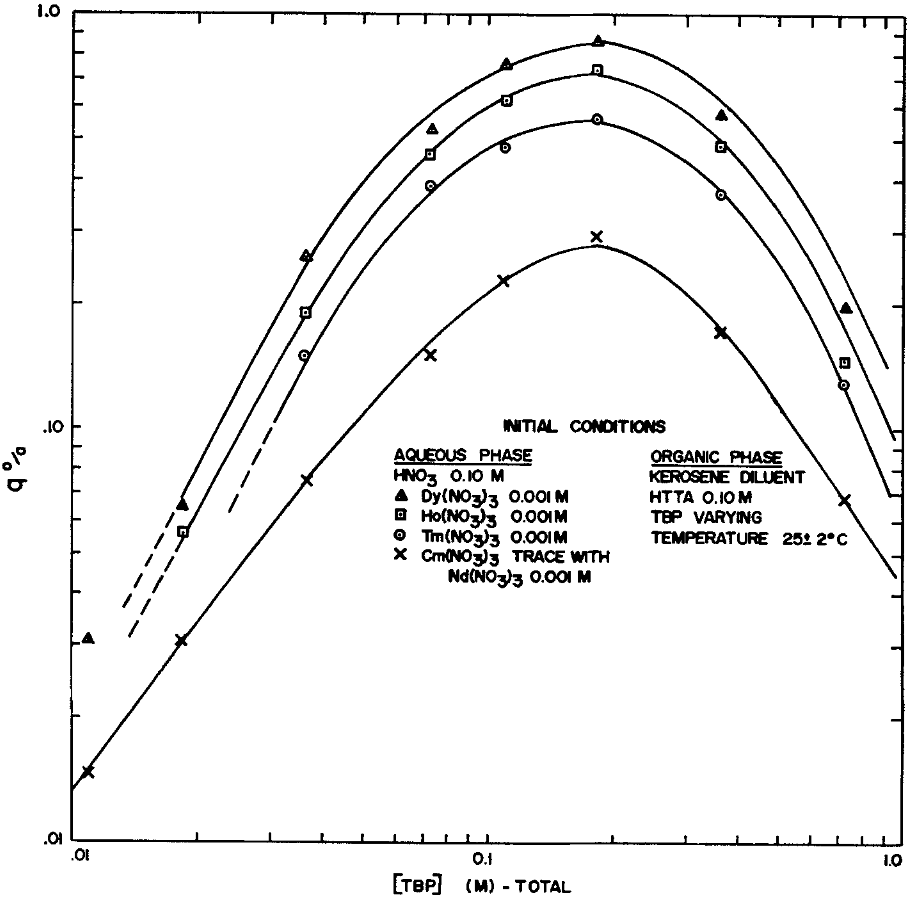


FIG. 9. Distribution ratios of Dy, Ho, Tm, and Cm at 0.10 *M* HNO_3 and 0.10 *M* total HTTA as a function of the total TBP concentration.

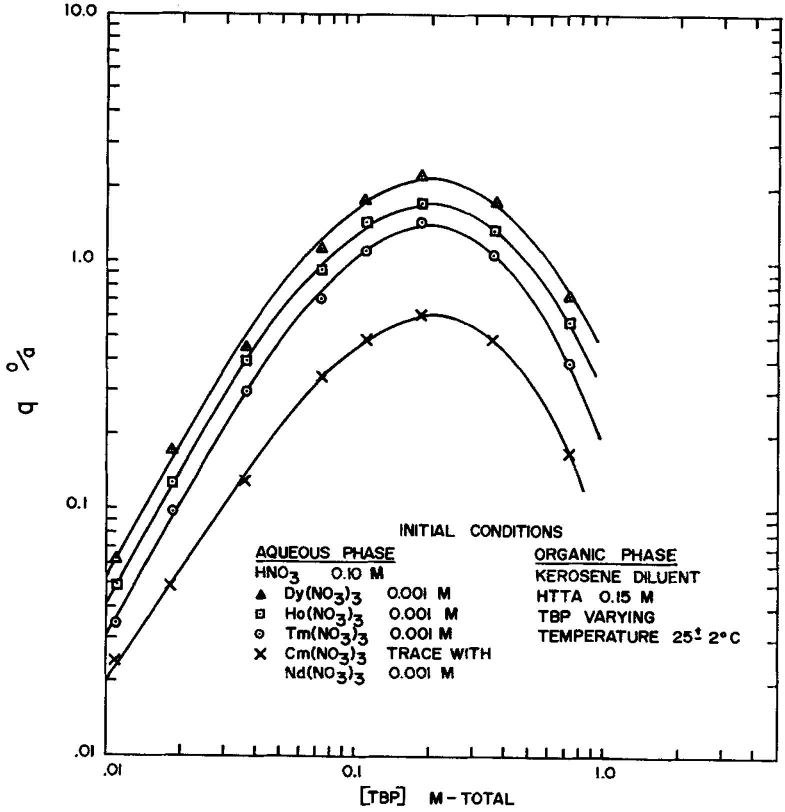


FIG. 10. Distribution ratios of Dy, Ho, Tm, and Cm at 0.10 M HNO_3 and 0.15 M total HTTA as functions of the total TBP concentration.

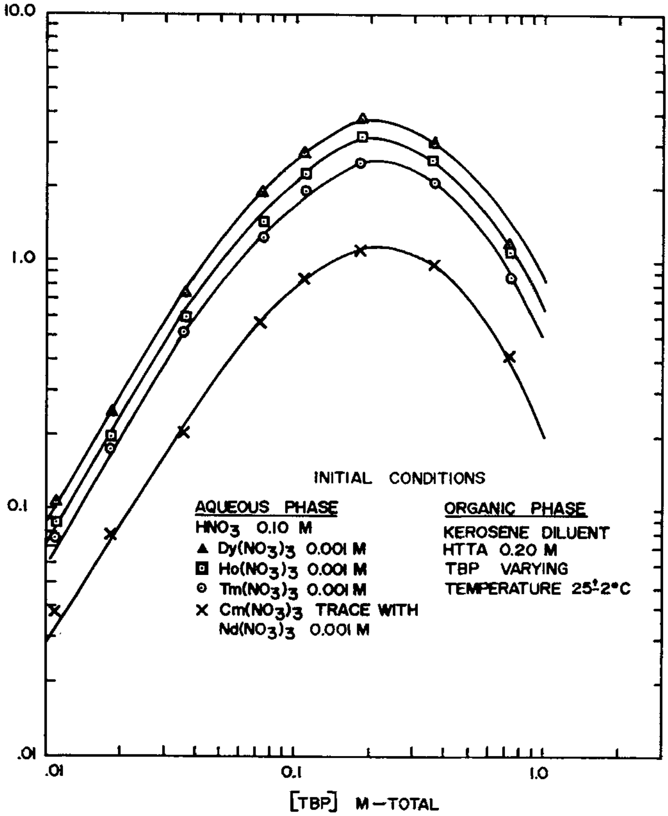


FIG. 11. Distribution ratios of Dy, Ho, Tm, and Cm at 0.10 *M* HNO_3 and 0.20 *M* total HTTA as functions of the total TBP concentration.

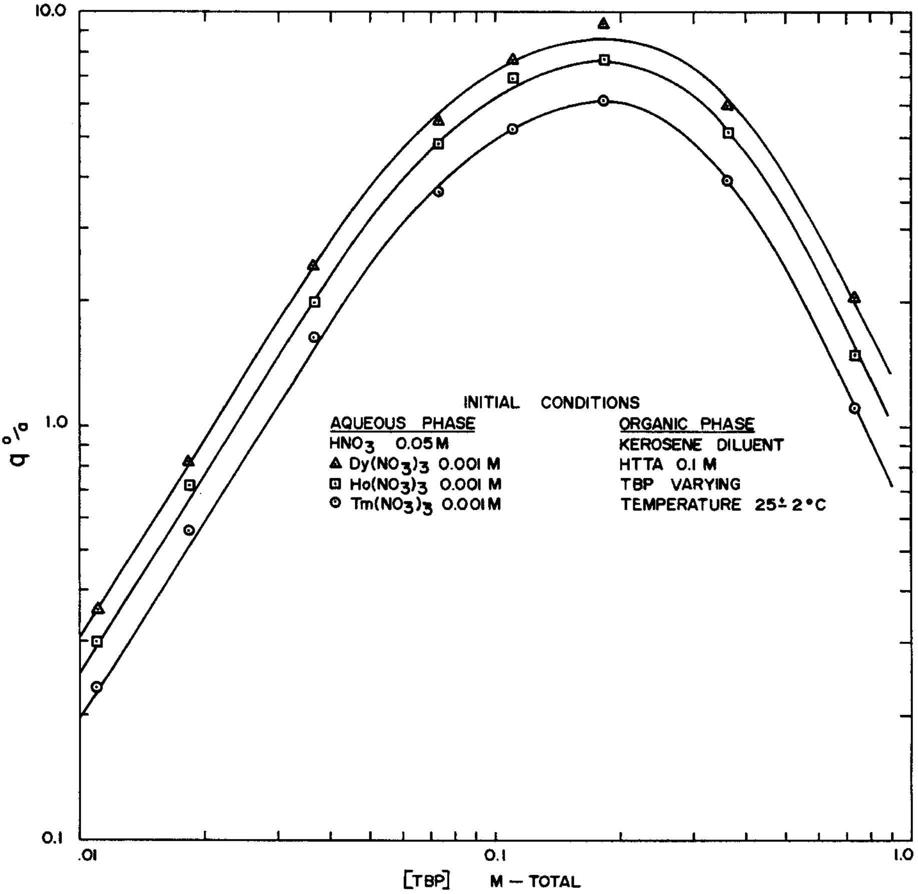


FIG. 12. Distribution ratios of Dy, Ho, and Tm at 0.05 M HNO_3 and 0.10 M total HTTA as functions of the total TBP concentration.

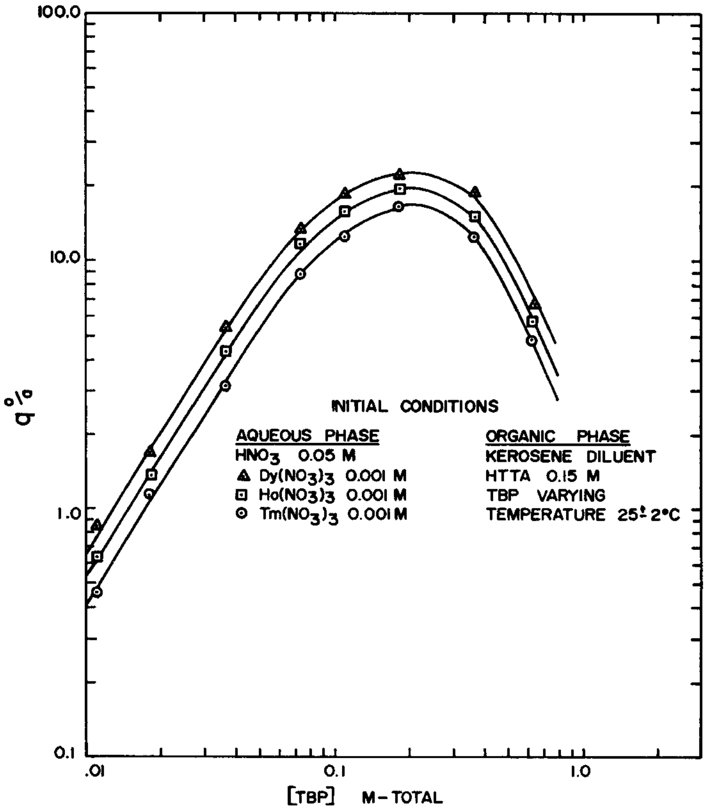


FIG. 13. Distribution ratios of Dy, Ho, and Tm at 0.05 *M* HNO_3 and 0.15 *M* total HTTA as functions of the total TBP concentration.

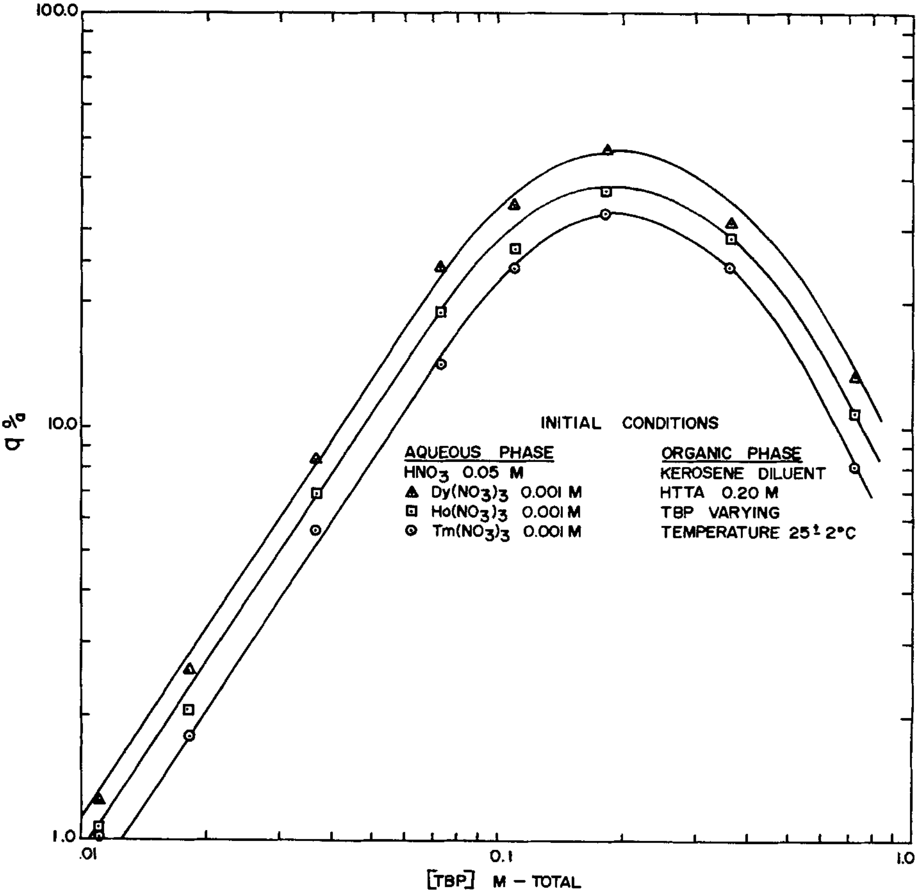


FIG. 14. Distribution ratios of Dy, Ho, and Tm at 0.05 *M* HNO_3 and 0.20 *M* total HTTA as functions of the total TBP concentration.

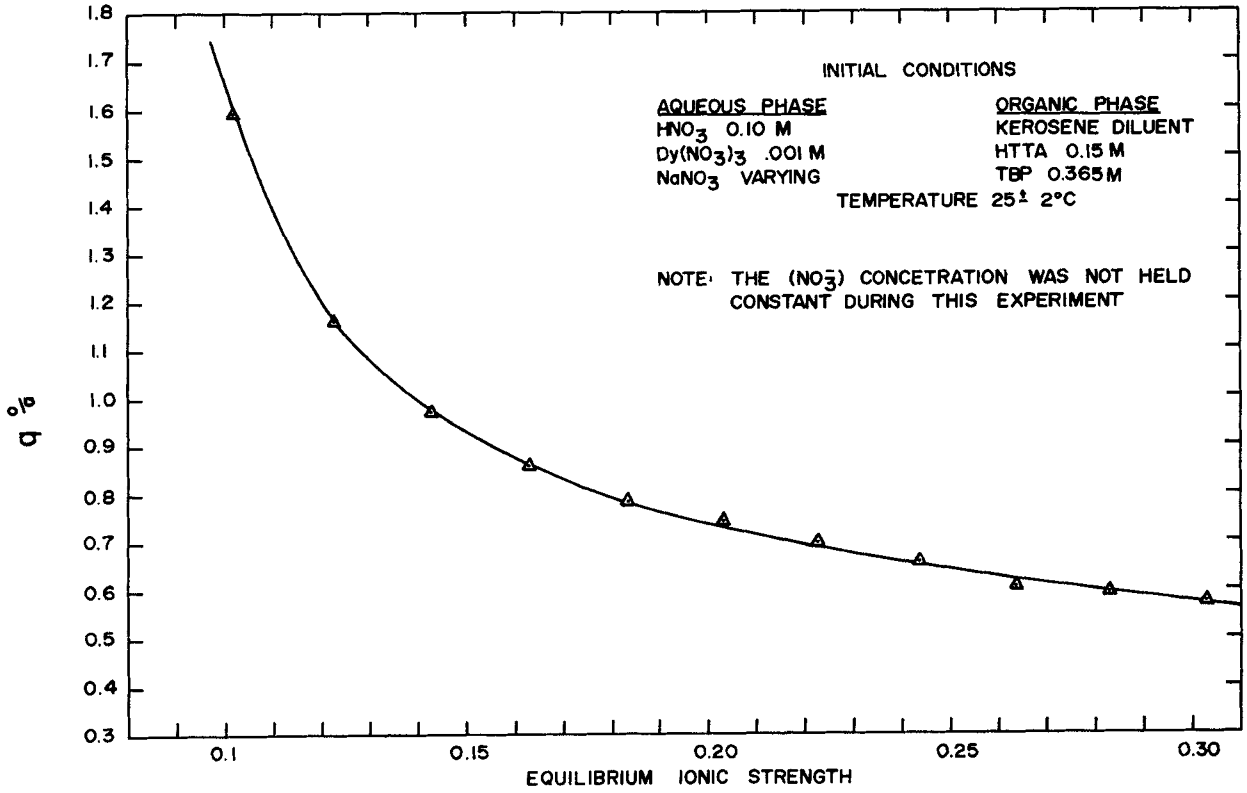


FIG. 15. Distribution ratios of Dy at 0.10 *M* HNO_3, 0.031 *M* free $HTTA_{enol}$, and 0.309 *M* free TBP as a function of ionic strength.

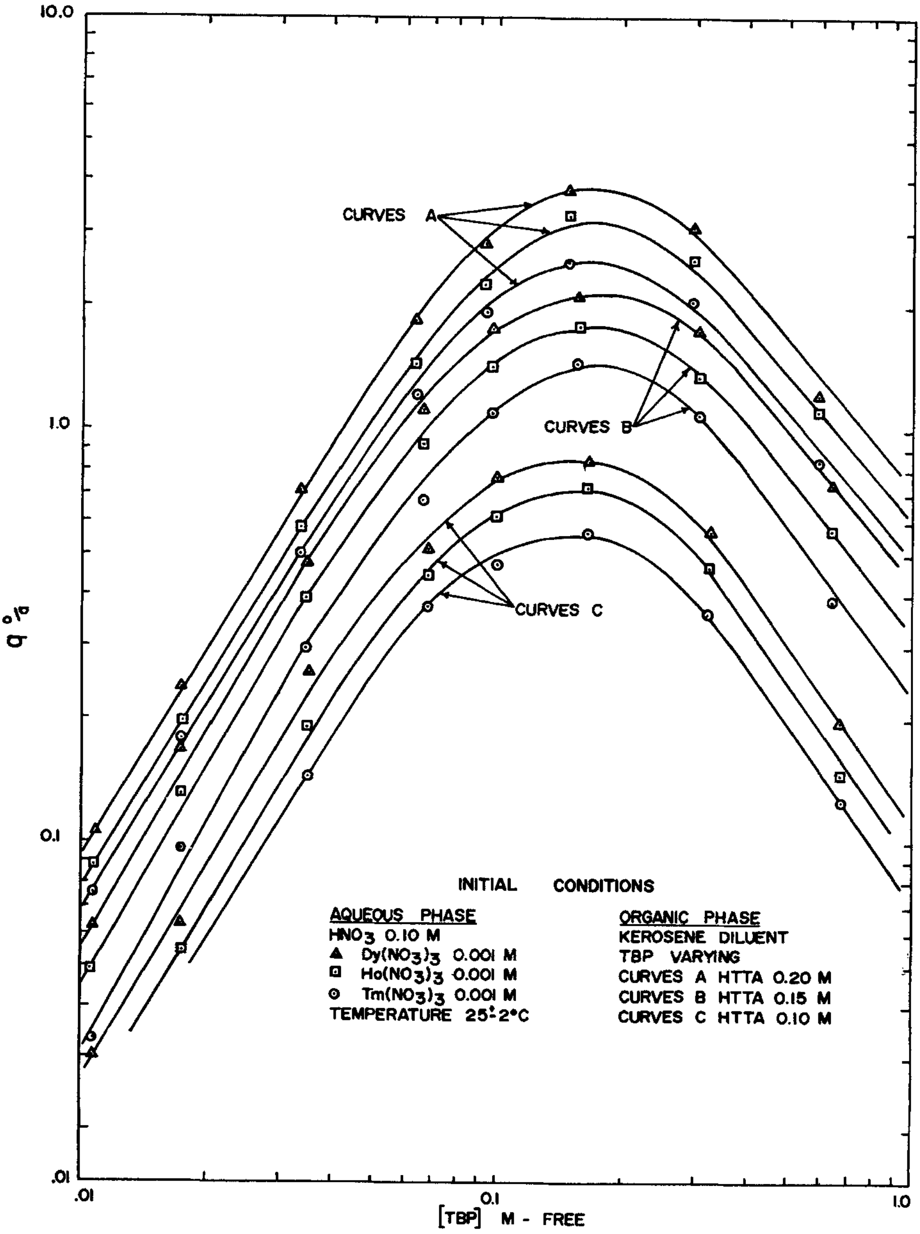


FIG. 16. Distribution ratios of Dy, Ho, and Tm at 0.10 *M* HNO_3 as functions of the free TBP and total HTTA concentrations.

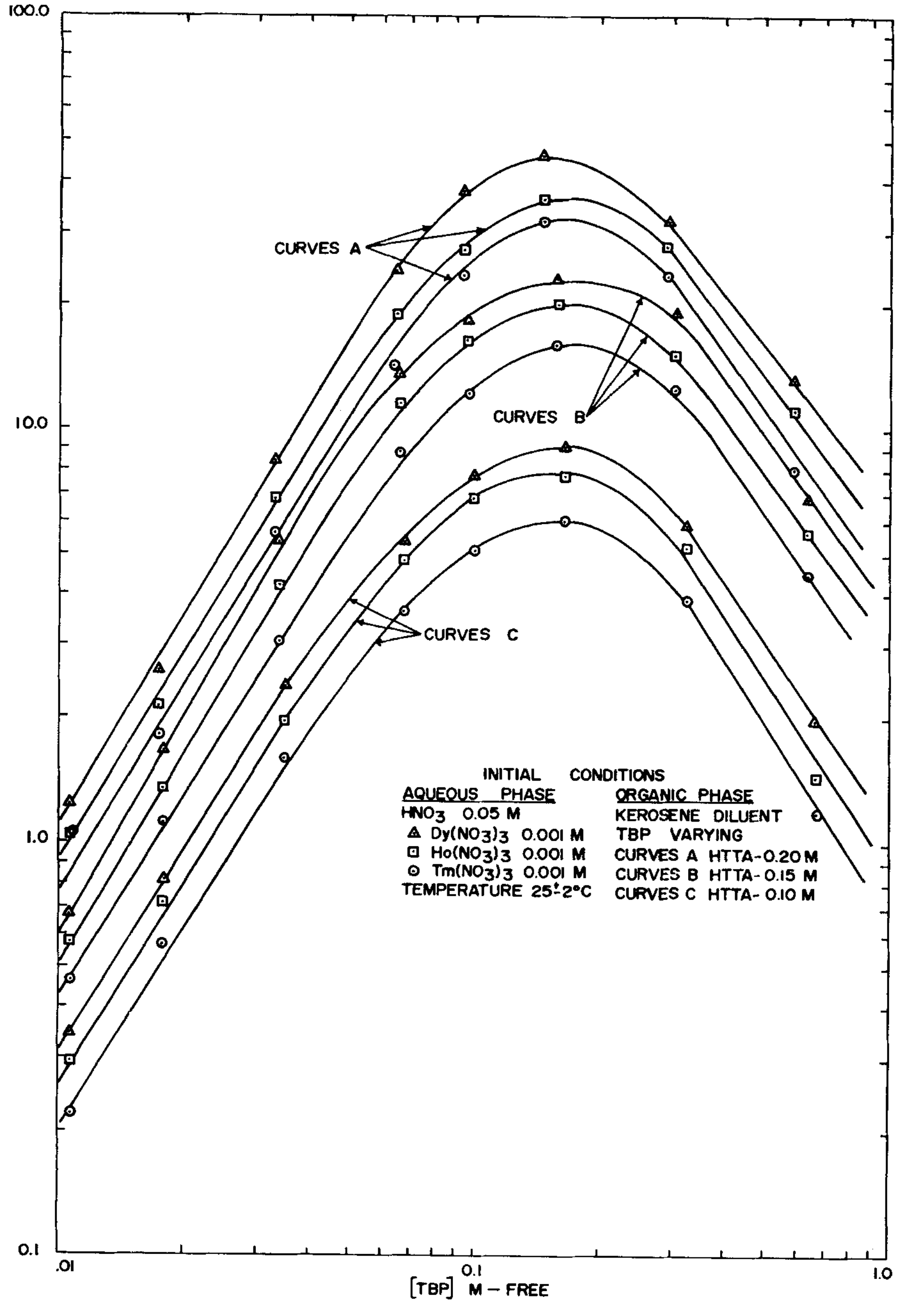


FIG. 17. Distribution ratios of Dy, Ho, and Tm at 0.05 M HNO_3 as functions of the free TBP and total HTTA concentrations.

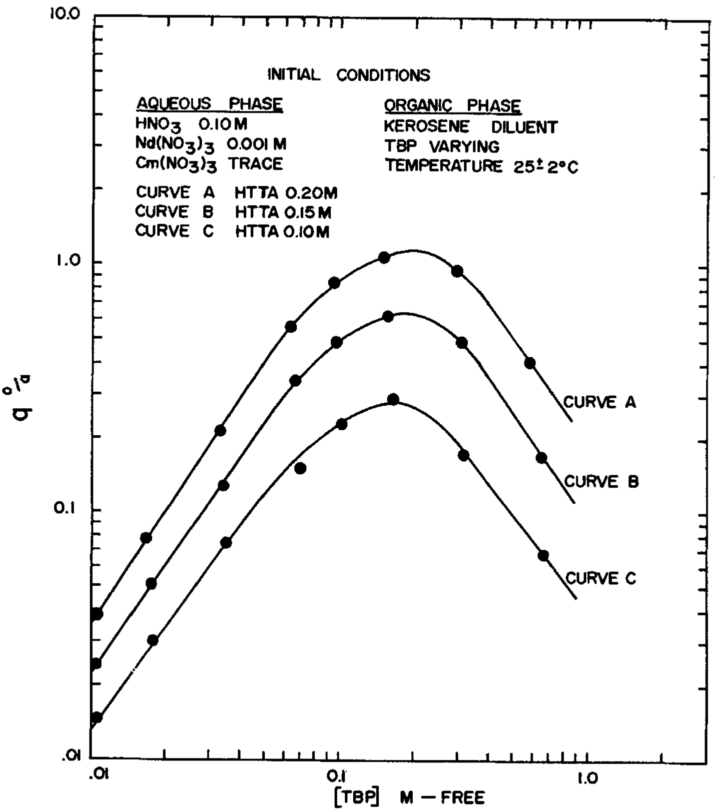


FIG. 18. Distribution ratios of Cm at 0.10 M HNO_3 as a function of the free TBP and total HTTA concentrations.

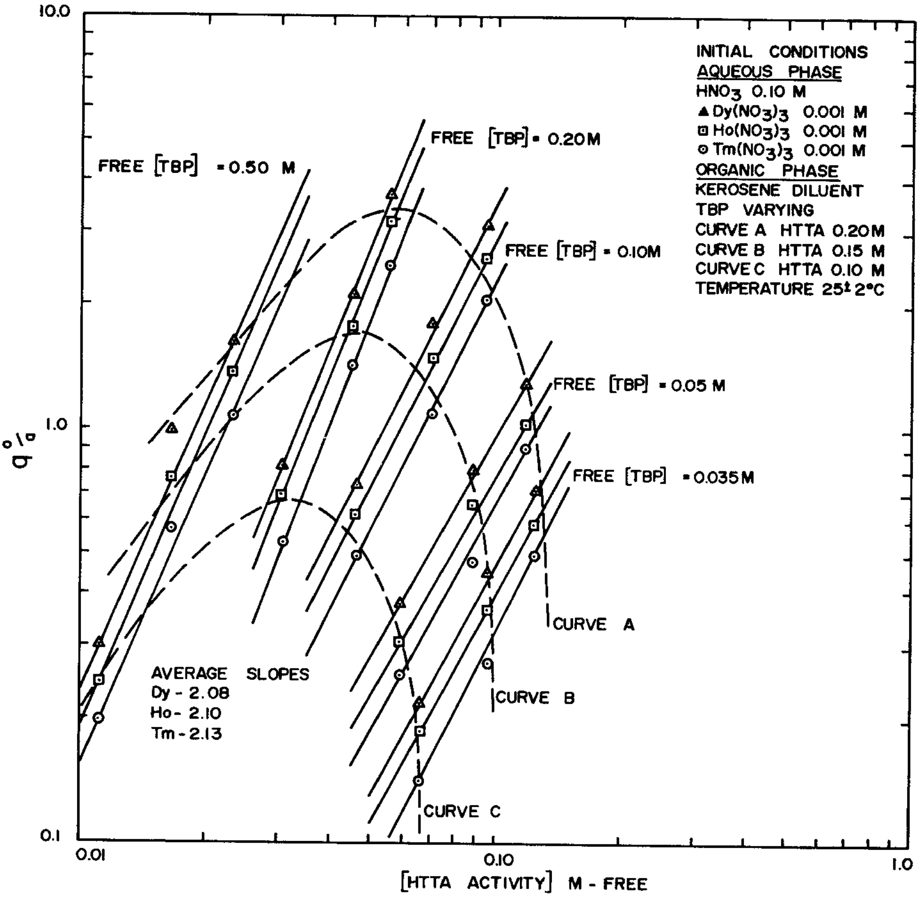


FIG. 19. Distribution ratios of Dy, Ho, and Tm at 0.10 *M* HNO_3 as functions of the free HTTA activity and the free TBP concentration.

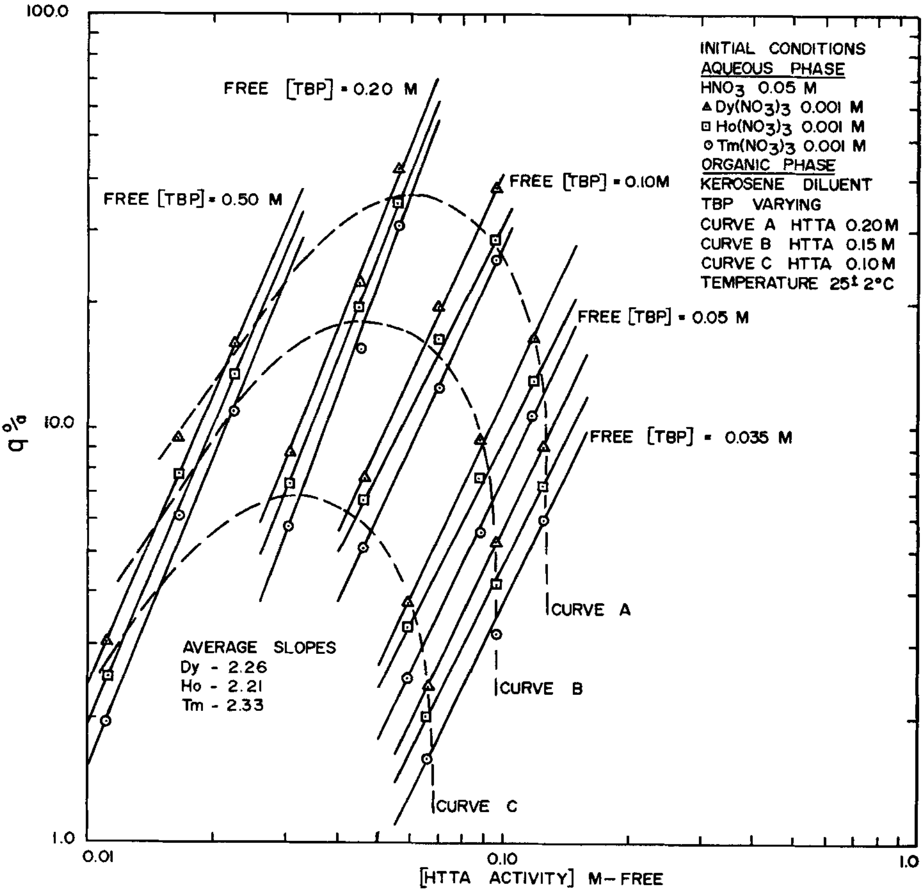


FIG. 20. Distribution ratios of Dy, Ho, and Tm at 0.05 M HNO_3 as functions of the free HTTA activity and the free TBP concentration.

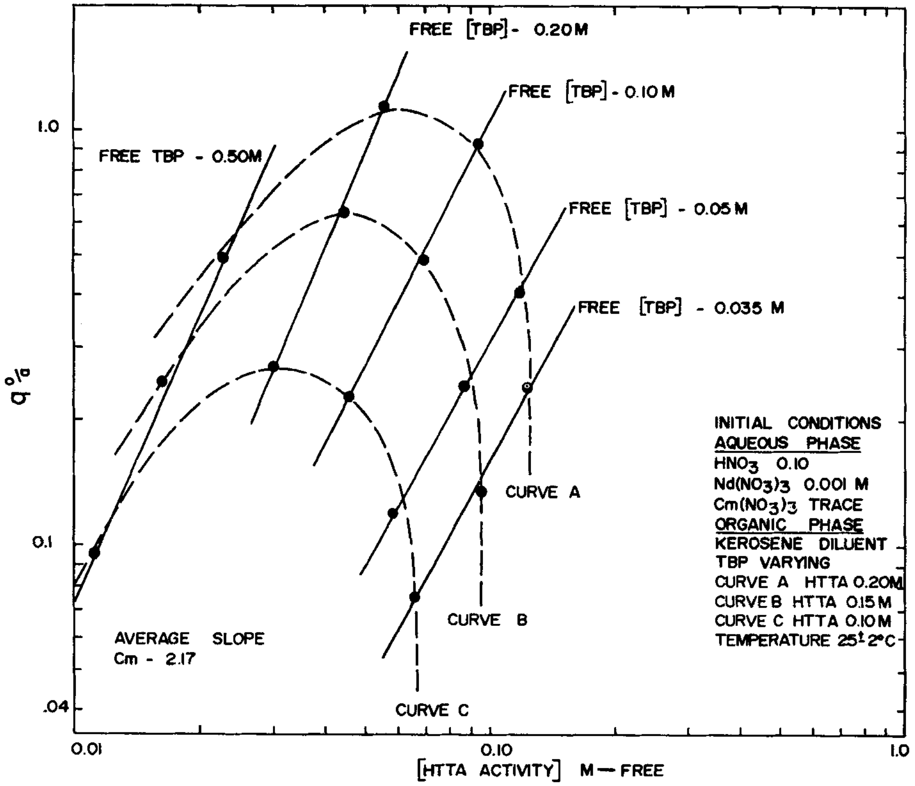


Fig. 21. Distribution ratios of Cm at 0.10 *M* HNO_3 as a function of the free HTTA activity and the free TBP concentration.

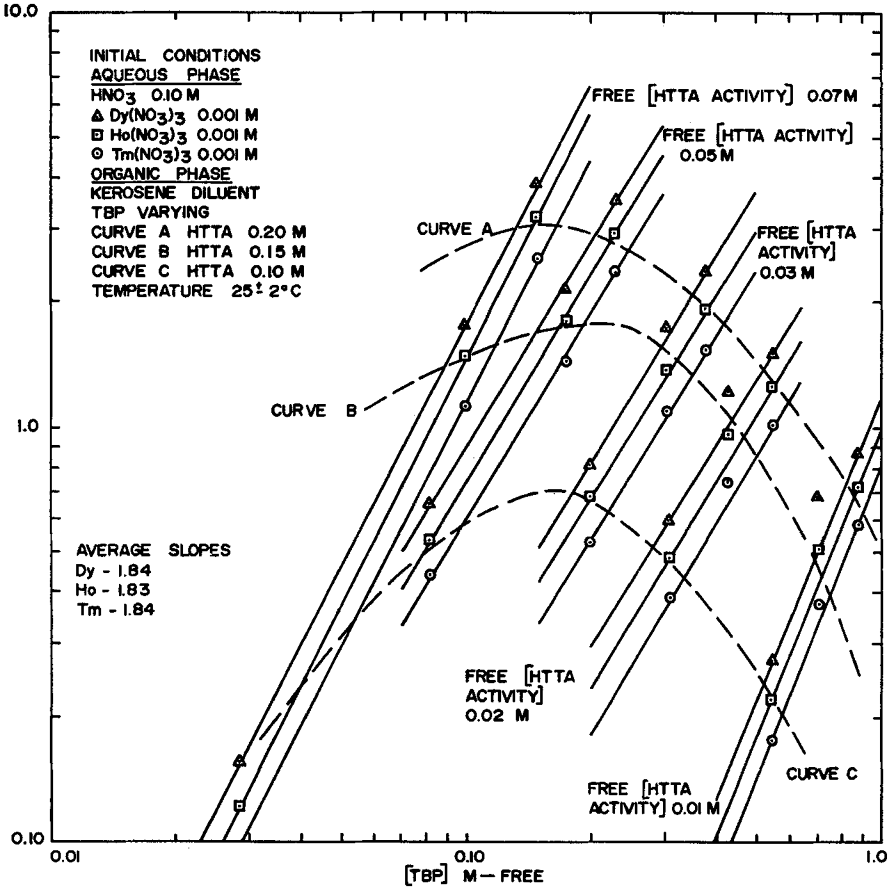


FIG. 22. Distribution ratios of Dy, Ho, and Tm at 0.10 *M* HNO_3 as functions of the free TBP concentration and the free HTTA activity.

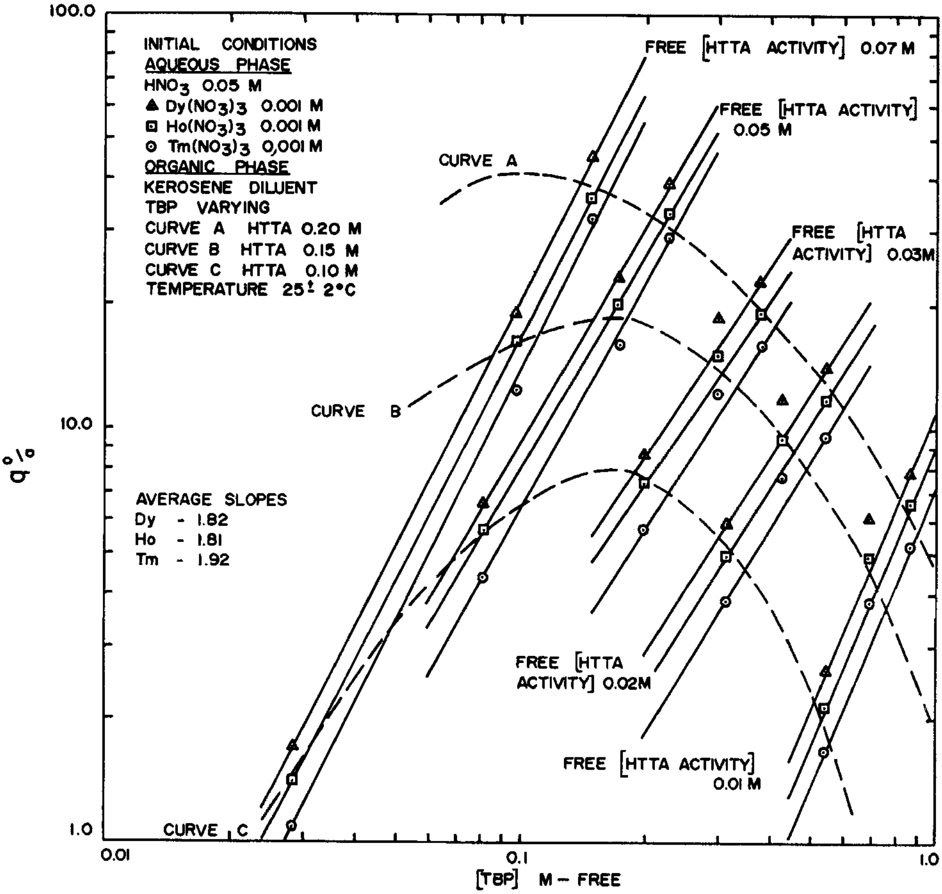


FIG. 24. Distribution ratios of Dy, Ho, and Tm at 0.05 M HNO_3 as functions of the free TBP concentration and the free HTTA activity.

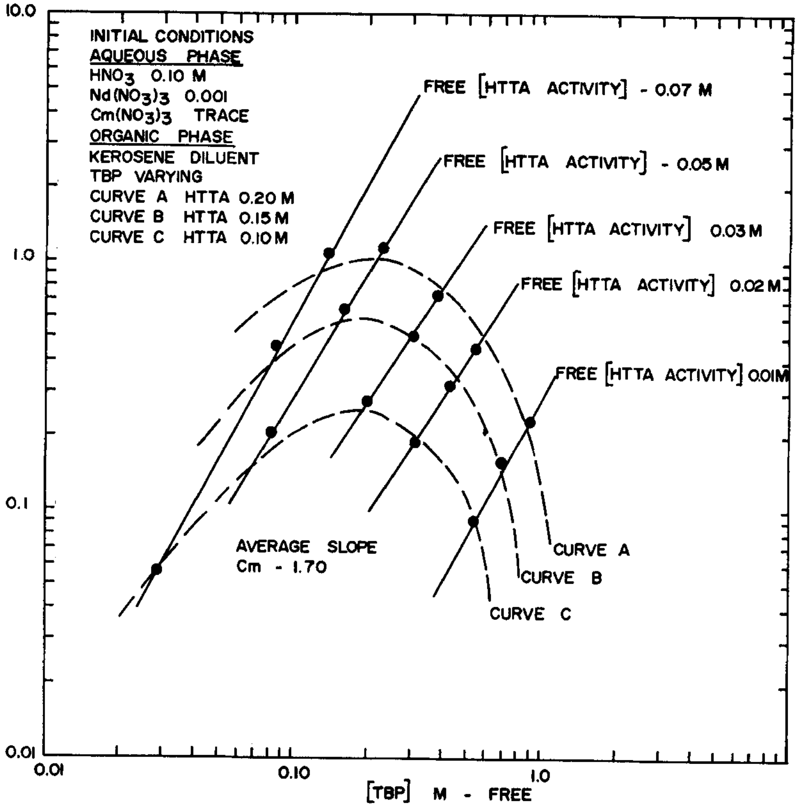


FIG. 24. Distribution ratios of Cm at 0.10 M HNO_3 as a function of the free TBP concentration and the free HTTA activity.

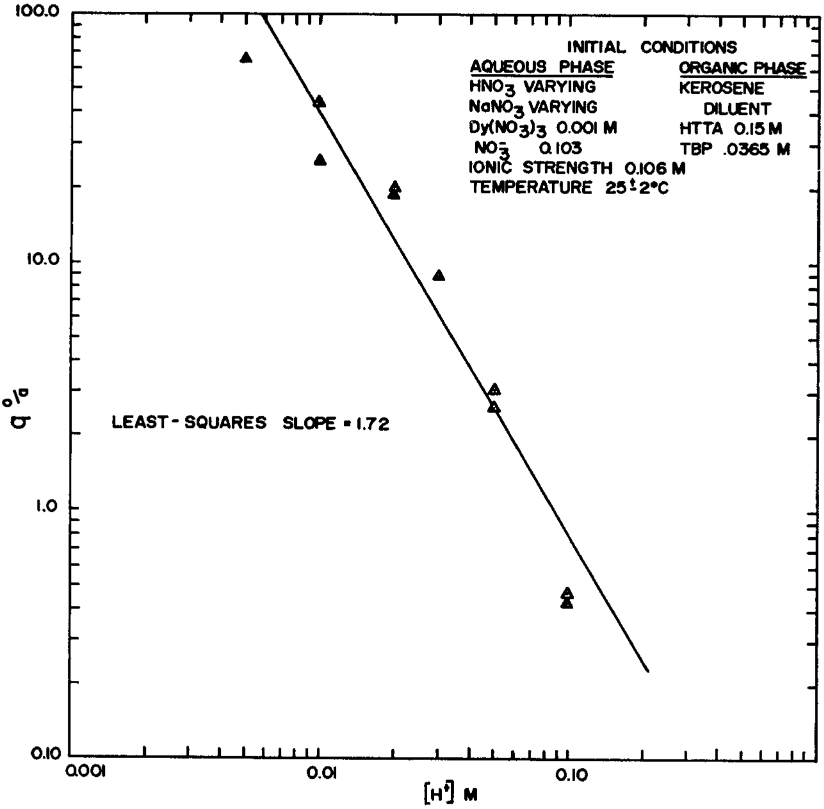


Fig. 25. Distribution ratios of Dy, 0.106 *M* free HTTA, 0.034 *M* free TBP, and 0.103 *M* (NO_3^-) at constant ionic strength as a function of the (H^+) concentration.

Log-log plots of Eq. (27) were made of q o/a as a function of free HTTA activity with the free TBP concentration as a parameter, the slopes of which should be the number of HTTA molecules involved in the formation of the metal complex. These plots are shown in Figs. 19, 20, and 21. The average slopes of the lines are 2.17 for Dy, 2.16 for Ho, 2.23 for Tm, and 2.17 for Cm, indicating that two molecules of HTTA are involved in the complex for each metal. Similar plots of qo/a as a function of the free TBP concentration with free HTTA activity as a parameter are shown in Figs. 22, 23, and 24. The average slopes of these lines are 1.83 for Dy, 1.82 for Ho, 1.88 for Tm, and 1.70 for Cm, indicating that there are probably two molecules of TBP involved in the formation of each metal complex.

The initial data were obtained at (H^+) concentrations of 0.10 and 0.05 *M*. Since the results presented here are in disagreement with those based on the theoretical equations presented by Tournier and Davis (*2*), additional data were obtained to determine the effect of the H^+ concentration on the distribution. In each sample the organic phase consisted of 0.15 *M* HTTA and 0.0365 *M* TBP in kerosene. The metal dysprosium was used at a concentration of 0.001 *M* for each sample. The ionic strength and the concentration of (NO_3^-) were maintained by replacing the HNO_3 with $NaNO_3$ as the pH was changed. A log-log plot of these data is shown in Fig. 25.

Healy (*22*) has reported the extraction of sodium with HTTA and TBP in benzene at a pH of 7.3. The distribution ratio at a TBP concentration of 0.2 *M* and a HTTA concentration of 0.15 *M* was about 1.5×10^{-2}. The ionic strength was approximately the same as that used in this work. However, the TBP concentration was considerably lower ([TBP] = 0.0365). It is not believed that the extraction of sodium would interfere with the slope analysis of Fig. 25 to an appreciable extent at these conditions.

The least squares slope of Fig. 25 is -1.72, indicating that two molecules of H^+ are formed with the complex. This can only be true if two molecules of $HTTA_{enol}$ are attached by a valence bond to the metal ion, as indicated by the slopes from Figs. 19, 20, and 21.

DISCUSSION OF RESULTS AND CONCLUSIONS

The theory for the HTTA distribution, as presented in this work, differs only slightly from the theory proposed by Tournier and Davis (*2*), although the describing equations are quite different. The difference lies in the definition of the HTTA distribution when there is no TBP in the system. Tournier and Davis (*2*) included a term for the HTTA ketohydrate in the expression for q_1:

$$q_1 = \frac{[\mathrm{HTTA_{enol}}]_o + [\mathrm{HTTA \cdot H_2O}]_o}{[\mathrm{HTTA \cdot H_2O}]_{aq}} \tag{29}$$

There is certainly some water in the kerosene phase due to natural solubility. There must, therefore, be a small amount of the ketohydrate in the kerosene phase. However, the addition of TBP to the system greatly increases the solubility of water in the kerosene, promoting the formation of appreciable amounts of the ketohydrate. In this light the amount of the ketohydrate present as a result of the natural solubility of water in kerosene is negligible. The expression for the HTTA distribution when there is no TBP in the system is then defined as

$$q_1 = \frac{[\mathrm{HTTA_{enol}}]_o}{[\mathrm{HTTA \cdot H_2O}]_{aq}} \tag{3}$$

The theoretical HTTA distribution equations based on these two definitions fit the HTTA distribution data equally well when a least-squares method is used to calculate the values of the equilibrium constants K_1 and K_2. Values of $K_1 = 18$ and $K_2 = 22$ were calculated from the equations proposed by Tournier and Davis (*2*), while values of $K_1 = 14.0$ and $K_2 = 3.45$ were calculated from a fit of the theoretical HTTA distribution equation presented in this work to the data.

Both theories show a good internal consistancy. From the equations presented by Tournier and Davis (*2*), an equation similar to Eq. (24) can be derived which allows a check of the calculated value of K_2 and the approximation that $n = 1$, which was made in both derivations. A log-log plot of this equation shows a slope of $n = 0.87$ and an intercept at $D = 1.0$ of $K_2 = 18$, compared to the calculated theoretical values of 1.0 and 22 obtained from the equations of Tournier and Davis (*2*). A log-log plot of Eq. (24) shows a slope of $n = 0.67$ and an intercept at $D = 1.0$ of $K_2 = 2.5$ compared with the theoretical values of 1.0 and 3.45 calculated from the equations presented in this work. The plot of Eq. (24) is shown in Fig. 25.

The scatter of the points in Fig. 25 is believed to be the result of a combination of experimental error, which is $\pm 10\%$, and a possible departure from ideality caused by the relatively high concentrations of the complexing agents used. Also, the value of 3.45 for the equilibrium constant K_2 was calculated by a least-squares fit of the theoretical HTTA distribution equation to all the experimental distribution data; so, some difference between this value and the value of the intercept at $D = 1$ in Fig. 25 was expected.

Analysis of the metal distribution data employing the equations developed by Tournier and Davis (*2*) to calculate the free concentrations of HTTA and TBP indicates that the probable form of the extracted complex is $M(TTA)_3(TBP)_{3 \text{ or } 4}$. A similar analysis of the metal distribution data based on the equations for the free concentration of HTTA and TBP and the free HTTA activity presented in this work indicates a complex of the form $M(TTA)_2(NO_3)(TBP)_2$. However, data were taken for the distribution of dysprosium as a function of the (H^+) concentration. The free concentrations of the HTTA and TBP were held constant as well as the ionic strength. A log-log plot of this data showed a negative squared dependence upon the (H^+) concentration. This indicates that only two HTTA molecules are valence bonded to the metal ion since one ion of (H^+) is released to the aqueous phase from each HTTA molecule thus bonded. This also indicates that one (NO_3^-) group is present in the complex to balance the charge on the trivalent metal ion. When these considerations are included in the analysis following the theory as presented by Tournier and Davis (*2*), the form of the metal complex must be $M(TTA)_2(NO_3)(TBP)_{3 \text{ or } 4}$ $(HTTA_{enol})$. Studies of molecular models indicate that steric forces would prohibit the formation of such a complex.

In this light the authors believe that the analyses of the data presented in this work support the modifications which were applied to the HTTA distribution theory as presented by Tournier and Davis (*2*). It is also felt that there is sufficient evidence to support the proposal of the complex $HTTA \cdot H_2O \cdot TBP$ and the complex $M(TTA)_2(NO_3)(TBP)_2$ for the trivalent lanthanides and curium.

FUTURE WORK

(1) Further investigation of the composition of the metal complexes.

(2) Development of methods to measure the concentrations of the individual chemical species in the system.

(3) Investigation of the extraction behavior of aluminum and iron and their separation from solutions containing the rare earths.

(4) Extension of the present theory and equations to a general theory for the extraction of metals in solvent extraction systems employing HTTA or TBP, or both, as extracting agents.

(5) Continuous extraction studies in short residence time contactors to investigate the use of this system on an industrial scale, with the

development of a means for recovering the organic solvent and the extracting agents.

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