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Synergistic Extraction of Neptunium (IV) by Mixtures of HTTA (Thenoyltrifluoroacetone) and TBP (Tri-*n*-butylphosphate)

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Abstract

The results obtained on the extraction of Np(IV) into mixtures of HTTA and TBP by solvent extraction and spectrophotometric methods are reported here. The predominant extractable species, when perchloric acid was employed for extraction, was found to be $Np(TTA)_4 \cdot TBP$ when benzene was used as the solvent and probably $Np(TTA)_3 \cdot 3TBP^+ClO_4^-$ when nitrobenzene was used as the solvent. On the other hand, when nitric acid was employed for the extraction into a benzene solution of the mixture, a number of extractable species, $Np(NO_3)_{4-x}(TTA)_x \cdot y TBP$ ($x = 0, 1, 2, 3$, and 4, and $y = 0, 1$, and 2), appear to be involved. Values of some equilibrium constants are reported.

INTRODUCTION

The synergistic extraction of metal ions by mixtures of a chelating agent and a neutral donor can be conveniently grouped into two types: (1) synergism as a consequence of addition of neutral donors to the metal chelates without any replacement of the chelated ligands, e.g., $UO_2(TTA)_2 \cdot TBP$. This type arises mainly when the aqueous medium employed for the extraction of the metal ion is poorly complexing such as perchlorate from which the neutral donor alone is practically not capable of extracting the metal. (2) Synergism by replacement of a chelate anion with other anion, e.g., $UO_2(NO_3)(TTA) \cdot TBP$. This type arises when the medium employed is such that the neutral donor alone is capable of extracting the metal [in the example given, as $UO_2(NO_3)_2 \cdot 2\,TBP$ from nitric acid]. This classification is only a matter of convenience since both the types of synergistic complexes may be encountered together in a given system. The former type involving the formation of adducts of neutral donors with metal chelates has been studied extensively for many metal ions. The latter type has, however, received much less attention, mainly because of the complexity of the equilibria involved. It is our endeavor to investigate this latter type to understand the synergistic behavior involved and to compare it with the synergistic behavior from noncomplexing media.

Cunninghame et al. (*1*) postulated the formation of the complexes $M(NO_3)_{3-x}(TTA)_x \cdot yTBP$ (with $x=0$, 1, 2, and 3, and $y = 1$, 2, and 3) for the extraction of Pr(III) and Nd(III) by mixtures of HTTA and TBP from nitrate medium. For the same extractants and medium, Irving and Edgington (*2–4*) have postulated the extraction of the species $UO_2(NO_3)(TTA) \cdot TBP$ for U(VI), $Th(NO_3)(TTA)_3 \cdot TBP$ and $Th(NO_3)_2(TTA)_2 \cdot 2TBP$ for Th(IV), and $M(NO_3)(TTA)_3 \cdot TBP$ for M = Np(IV), Pu(IV), etc. Finston and Gnizi (*5*), as well as Sekine and Dyrssen (*6*), while commenting on the work of Irving and Edgington, observed that the latter should have studied the effect of changing nitrate concentration to establish the participation of nitrate in the extracting species, thereby expressing some doubts regarding the nitrate participation in the synergistic species. Finston and Gnizi (*5*), in fact, studied the extraction of Fe(III) from thiocyanate medium into mixtures of MIBK (methyl isobutyl ketone) and HTTA, and concluded that there is no mixed complex involving thiocyanate in the extracted species. They have given a similar interpretation to their data on the extraction of Zr(IV) from thiocyanate medium into mixtures of MIBK and HTTA. Davis and co-workers (*7–9*) have studied the extraction of several trivalent lanthanides into mixtures of HTTA and TBP from nitric acid medium and interpreted their data as involving the extractable complexes $M(NO_3)(TTA)_2 \cdot 2TBP$. Recently we have studied the extraction of Am(III) (*10*) and Tm(III) (*11*) from a thiocyanate medium into mixtures of HTTA and DPSO (dipentyl sulfoxide) and established that a mixture of species having the composition $M(SCN)_{3-x}(TTA)_x \cdot yDPSO$ [M = Am(III) or Tm(III), $x = 0$, 1, 2, and 3, and $y = 0$, 1, 2, 3, and 4] is involved in their extraction. Thus it appeared worthwhile to study the synergistic extraction of metals from different aqueous media, and we have initiated a program on the extraction of actinides from different complexing media into mixtures of HTTA and several neutral donors. This paper reports the work on the synergistic extraction of Np(IV) from nitric acid medium into benzene solutions of HTTA and TBP as studied by solvent extraction methods, and the results obtained are further confirmed by spectrophotometric work. The synergism involving the adduct formation of tetravalent actinide complexes of HTTA and TBP was reported only in the case of Th(IV) (*6*, *12*). Hence such a study involving Np(IV) was conducted by the extraction of Np(IV) from perchloric acid medium, and the results obtained both by solvent extraction and spectrophotometric methods are also included here.

EXPERIMENTAL

Materials

^{237}Np was obtained from AERE, Harwell, United Kingdom, and its radiochemical purity was ascertained by alpha spectrometry. ^{238}Np was prepared by neutron irradiation of ^{237}Np, purified from fission products by the HTTA extraction method (*13*), and its purity was ascertained by gamma ray spectrometry and half-life determination. HTTA supplied by E. Merck, West Germany, was dried under vacuum over P_2O_5 for several hours (*14*). The benzene solution of HTTA was preequilibrated with dilute perchloric acid for a few hours to allow hydration of HTTA (*15*). TBP was steam distilled over dilute alkali as described by Alcock et al. (*16*) and dried under vacuum. Ferrous sulfamate was freshly prepared (*17*) whenever required. All other chemicals used were of A.R. grade.

Procedure

In the solvent extraction experiments, suitable aliquots of ^{237}Np and ^{238}Np were mixed to facilitate the estimation of Np by gamma counting. This is an improvement over the method used by Irving and Edgington (*3*) where alpha plancheting was done. The initial ^{237}Np concentration in the aqueous phase prior to equilibration was always adjusted around 1 to 2 μg/ml. Np(IV) in nitric acid was prepared by reducing Np with ferrous sulfamate, and about 10^{-3} *M* ferrous sulfamate was always used as holding reductant. Np(IV) in perchloric acid was prepared by extracting Np(IV) from nitric acid into ~0.03 *M* tetraheptylammonium nitrate in xylene and then stripping the same into perchloric acid. About

10^{-3} *M* ferrous sulfamate was kept as holding reductant in this medium also. Three milliliter aliquots of Np(IV) in the aqueous phase were equilibrated with an equal volume of the organic phase containing the mixtures of HTTA and TBP in the desired composition. The equilibration was done for 45 min in a thermostated water bath kept at 25 ± 0.1 °C, covering the vials with black paper to protect the solutions against light. The solutions were allowed to settle, and 2.0 ml aliquots from both phases were withdrawn for gamma counting using a 3 in. × 3 in. well-type scintillation detector. The remaining solution in the aqueous phase was used to confirm the oxidation state of Np by the HTTA extraction method. The oxidation state of Np(IV) was found to remain unchanged. The equilibrium value of the organic HTTA concentration was calculated by knowing its initial concentration and using the K_d (distribution coefficient) of 40 (*18*) for its distribution between benzene and dilute acid. The free TBP in the organic phase was calculated by subtracting the concentration of the acid extracted. The interaction between HTTA and TBP was not considered in these calculations. Wherever activities of HTTA were given, they were obtained by using the relation given by King and Reas (*18*).

For spectrophotometric studies, about 100 mg of ^{237}Np in nitric acid was adjusted to Np(IV) by heating the solution with hydrazine in a water bath (*19*). The oxidation state of Np(IV) was checked by HTTA extraction. The stock of Np(IV) in perchloric acid was obtained by precipitating Np(IV) as hydroxide followed by dissolution in perchloric acid. Suitable amounts of Np(IV), taken in perchloric acid or nitric acid as desired, were then extracted into mixtures of HTTA and TBP, and the spectra of the organic extracts were recorded using a Cary-14 recording spectrophotometer with blanks prepared identically but without Np. The neptunium content in the organic extracts was estimated by stripping Np into 1 *M* nitric acid containing 0.1 *M* HF and then measuring the alpha count rate by radiometry.

RESULTS AND DISCUSSION

Extraction of Np(IV) from Perchlorate Medium

Solvent Extraction Studies

The extraction of Np(IV) from perchloric acid into HTTA in benzene is given by the equilibrium represented by (*20*, *21*)

$$\mathrm{Np}^{4+}_{(\mathrm{aq})} + 4\mathrm{HTTA}_{(\mathrm{org})} \overset{K_{\mathrm{A}}}{\rightleftharpoons} \mathrm{Np(TTA)}_{4(\mathrm{org})} + 4\mathrm{H}^{+}_{(\mathrm{aq})} \qquad (1)$$

The equilibrium constant, K_A, for the equilibrium represented by Eq. (1) is

$$K_A = \frac{[\mathrm{Np(TTA)_4}]_{(\mathrm{org})}[\mathrm{H^+}]^4_{(\mathrm{aq})}}{[\mathrm{Np^{4+}}]_{(\mathrm{aq})}[\mathrm{HTTA}]^4_{(\mathrm{org})}} \tag{2}$$

$$= K_{d(A)}[\mathrm{H^+}]^4_{(\mathrm{aq})}[\mathrm{HTTA}]^{-4}_{(\mathrm{org})} \tag{3}$$

where

$$K_{d(A)} = \frac{[\mathrm{Np(TTA)_4}]_{\mathrm{org}}}{[\mathrm{Np^{4+}}]_{\mathrm{aq}}} \tag{4}$$

Here $\mathrm{Np(TTA)_4}$ is the only metallic species extracted by HTTA, and $\mathrm{Np^{4+}}$ is the only metallic species in the aqueous phase if we neglect the aqueous phase HTTA complexing of $\mathrm{Np^{4+}}$ (*22*). On the other hand Np(IV) is practically inextractable from perchloric acid into a benzene solution of TBP. The results obtained on the extraction of Np(IV) from 1.0 *M* perchloric acid into mixtures of HTTA and TBP of varying composition are shown in Fig. 1. The synergistic enhancement in the extraction of Np(IV) is clearly seen from these data, and it can be attributed to the formation of the species of the type represented by

$$\mathrm{Np(TTA)}_{m(\mathrm{org})} + n\text{-}\mathrm{TBP}_{(\mathrm{org})} \rightleftharpoons \mathrm{Np(TTA)}_m\cdot n\text{-}\mathrm{TBP}_{(\mathrm{org})} \tag{5}$$

The data in Fig. 1 have been obtained by keeping the total concentration of [HTTA] + [TBP] constant ($C = 0.05\ M$). Thus if

$$[\mathrm{HTTA}] + [\mathrm{TBP}] = C \tag{6}$$

and the fraction of HTTA is x, then

$$[\mathrm{HTTA}] = xC \tag{7}$$

and

$$[\mathrm{TBP}] = (1 - x)C \tag{8}$$

By applying the method of continuous variations to the extraction of metal ions with mixed solvents as suggested by Gal and Nikolic (*23*), the familiar Job relation

$$\frac{m}{n} = \frac{x_{\max}}{(1 - x_{\max})} \tag{9}$$

is obtained. From the data presented in Fig. 1 ($\mathrm{HClO_4}$), it is clearly seen that $x_{\max}/(1 - x_{\max}) = 0.8/0.2 = 4$. As we know that $m = 4$ from

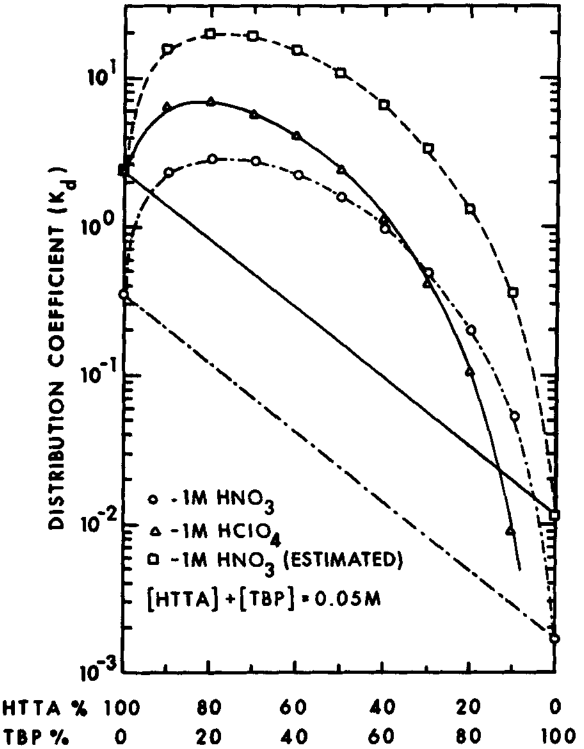

FIG. 1. Variation of distribution coefficient of Np(IV) with varying composition of HTTA and TBP.

Eq. (1), it is clear that $n = 1$. Thus the species extracted (Eq. 5) becomes $Np(TTA)_4 \cdot TBP$. It is clear that complexes with $n > 1$ are not formed. Otherwise, with great excess of ligands (extractants) used as compared to the metal, the maximum of extraction would have been different. The extraction of $Np(TTA)_4 \cdot TBP$ can be represented by the equilibrium

$$Np^{4+}_{(aq)} + 4HTTA_{(org)} + TBP_{(org)} \rightleftharpoons Np(TTA)_4 \cdot TBP_{(org)} + 4H^+_{(aq)} \tag{10}$$

$$K_{AB} = \frac{[Np(TTA)_4 \cdot TBP][H^+]^4}{[Np^{4+}][HTTA]^4[TBP]} \tag{11}$$

$$= K_{d(AB)} \cdot [H^+]^4[HTTA]^{-4}[TBP]^{-1} \tag{12}$$

where

$$K_{d(\mathrm{AB})} = \frac{[\mathrm{Np(TTA)_4 \cdot TBP}]}{[\mathrm{Np}^{4+}]}$$

is the distribution coefficient of the adduct. Now, if the total synergistic distribution coefficient observed at any fraction of x is $K_d{}^x$, it can be shown that

$$K_d^x = K_{d(\mathrm{A})}^x + K_{d(\mathrm{AB})}^x \tag{13}$$

where $K_{d(\mathrm{A})}^x$ is the distribution coefficient of Np(IV) into HTTA at a given value of x (it follows that $K_{d(\mathrm{A})}^x = K_{d(\mathrm{A})} \cdot x^4$ when $K_{d(\mathrm{A})}$ is the distribution coefficient at $x = 1$). Also from Eq. (12) it can be shown that

$$K_{d(\mathrm{AB})} = \frac{K_{d(\mathrm{AB})}^x}{x^4(1 - x)} = K_{\mathrm{AB}} \cdot [\mathrm{H}^+]^{-4} \cdot C^5 \tag{14}$$

The values of K_d^x, $K_{d(\mathrm{A})}^x$, and $K_{d(\mathrm{AB})}^x$ obtained as a function of x using the data from Fig. 1 are given in Table 1. The remarkable constancy of $K_{d(\mathrm{AB})}$ obtained with almost all the values of x is further proof that only one synergistic complex is involved in the extraction. Using Eq. (14) and the average value of $K_{d(\mathrm{AB})} = 72$ (for $1 > x > 0.1$), the value of K_{AB} was calculated and was found to be $\log K_{\mathrm{AB}} = 8.36$.

It was decided to further confirm the extraction of the species $\mathrm{Np(TTA)_4 \cdot TBP}$ and determine K_{AB} by an alternate approach by solvent extraction studies. The variation of K_d as a function of concentration of HTTA was studied from 1.0 *M* perchloric acid medium, keeping a fixed

TABLE 1

Distribution Coefficient Data as a Function of x ($\mathrm{HClO_4}$ medium)

x	K_d^x	$K_{d(\mathrm{A})}^x$	$K_{d(\mathrm{AB})}^x$	$K_{d(\mathrm{AB})}$
1	2.32	2.32	0	0
0.9	6.34	1.52	4.82	73.5
0.8	6.80	0.950	5.85	71.4
0.7	5.72	0.557	5.16	71.7
0.6	4.04	0.301	3.74	72.2
0.5	2.43	0.145	2.29	73.0
0.4	1.12	0.0594	1.06	68.9
0.3	0.396	0.0188	0.377	66.5
0.2	0.104	0.00371	0.100	78.4
0.10	0.00901	0.000232	0.00878	97.6

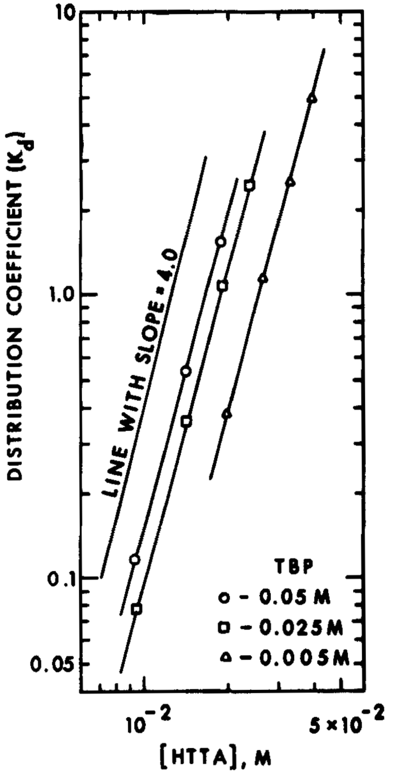

FIG. 2. Variation of distribution coefficient of Np(IV) with HTTA concentration at fixed TBP concentration (extracted from 1.0 *M* perchloric acid).

TBP concentration, and these data are presented in Fig. 2. The values of slopes close to 4 obtained at different concentrations of TBP confirm that the extracted species always contained four molecules of TTA. The variation of K_d as a function of the concentration of TBP was studied from 1.0 *M* perchloric acid medium at a fixed concentration of HTTA, and these data are presented in Fig. 3. The values of slopes considerably less than 1 suggest that $Np(TTA)_4$ and $Np(TTA)_4 \cdot TBP$ are the two species involved in the extraction of Np(IV) from perchloric acid medium into mixtures of HTTA and TBP in benzene. From Eqs. (3) and (12) it can be obtained that

$$\frac{K_{d(\mathrm{AB})}}{K_{d(\mathrm{A})}} = \frac{K_{\mathrm{AB}}}{K_{\mathrm{A}}} \cdot [\mathrm{TBP}] = \beta_{\mathrm{AB}}[\mathrm{TBP}] \qquad (15)$$

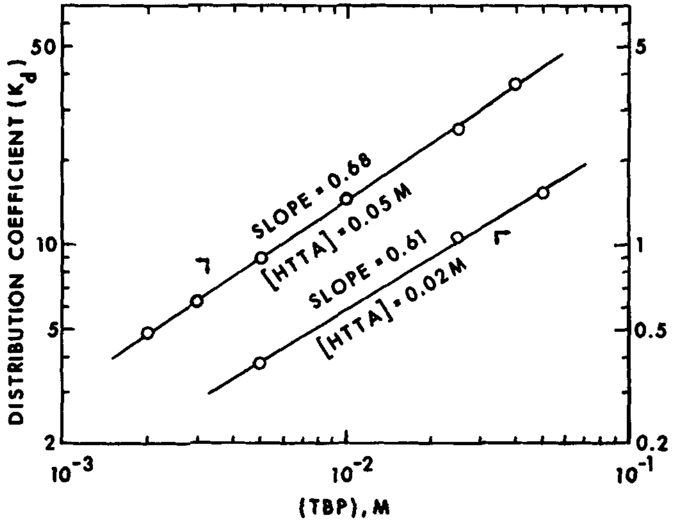

FIG. 3. Variation of distribution coefficient of Np(IV) with TBP concentration at fixed HTTA concentration (extracted from 1.0 *M* perchloric acid).

where β_{AB} is the equilibrium constant for the equilibrium represented by

$$\mathrm{Np(TTA)_{4(org)}} + \mathrm{TBP_{(org)}} \overset{\beta_{AB}}{\rightleftharpoons} \mathrm{Np(TTA)_4 \cdot TBP_{(org)}} \tag{16}$$

When K_d^s, the distribution coefficient observed with mixtures of HTTA and TBP, is obtained at a fixed HTTA concentration and varying [TBP] (as in Fig. 3), it can be seen that

$$K_{d(AB)} = K_d^s - K_{d(A)} \tag{17}$$

Thus

$$\frac{K_d^s - K_{d(A)}}{K_{d(A)}} \Big/ [\mathrm{TBP}] = \beta_{AB} \tag{18}$$

Thus K_d^s was obtained as a function of [TBP] at a fixed [HTTA], and from the relation given by Eq. (18) the β_{AB} values were calculated. As seen from the data in Table 2, they remained constant with changes in [TBP] as expected, with an average value of $\beta_{AB} = 565 \pm 24$. Using the value of $K_A = 3.7 \times 10^5$ obtained from the present data, the value $K_{AB} = \beta_{AB} \cdot K_A = 2.1 \times 10^8$ is obtained. This value, $\log K_{AB} = 8.32$, is in excellent agreement with that (8.36) obtained earlier by Job's method.

TABLE 2

Distribution Coefficient Data for the Calculation of β_{AB} ([HTTA] = 0.05 *M*, $K_{d(A)} = 2.31$)

[TBP], *M*	K_d^s	$\beta_{AB} = \frac{(K_d^s - K_{d(A)})/K_{d(A)}}{[TBP]}$
0.002	4.92	565
0.003	6.29	575
0.005	9.02	581
0.010	14.8	541

Spectrophotometric Studies

The absorption spectra of Np(IV) extracted from 1 *M* perchloric acid into 0.2 *M* HTTA in benzene and 0.1 *M* HTTA + 0.1 *M* TBP in benzene are shown in Fig. 4. As seen from this figure, the spectra in HTTA and HTTA + TBP differ completely, viz., changes in the position of absorption maxima, intensities as well as in the sharpness of the absorption bands. The spectrum in the mixture of extractants is obviously due to the presence of $Np(TTA)_4 \cdot TBP$. An identical absorption spectrum was obtained when dry TBP was added to a HTTA extract of Np(IV) and this spectrum remained unchanged with different amounts of TBP, thus confirming that the species extracted from perchloric acid into mixtures of HTTA and TBP is $Np(TTA)_4 \cdot TBP$ and does not involve any perchlorate ion in the extracted complex. The increase in the molar extinction coefficients of the mixed complex as compared to those of the metal chelate alone is a very general phenomenon observed in several synergistic studies (*24*, *25*).

It was reported (*26–28*) that when nitrobenzene was used as the solvent for mixtures of HTTA and TOPO (tri-*n*-octyl phosphine oxide), several lanthanide(III) ions were found to be extracted from perchlorate media as the ion-pairs $Ln(TTA)_2(TOPO)_5^+ClO_4^-$. Out of curiosity we wanted to see if such an ion pair is formed in the present system. Figure 5 presents the absorption spectrum of Np(IV) extracted from perchloric acid into 0.1 *M* HTTA + 0.1 *M* TBP in nitrobenzene. As is clearly evident, this spectrum in all its aspects is different from that of $Np(TTA)_4 \cdot TBP$ and must be due to the formation of an ion pair. We have not investigated the composition of this ion pair but in analogy with the trivalent lanthanide species it may possibly be $Np(TTA)_3(TBP)_3^+ClO_4^-$. More work is required to establish this.

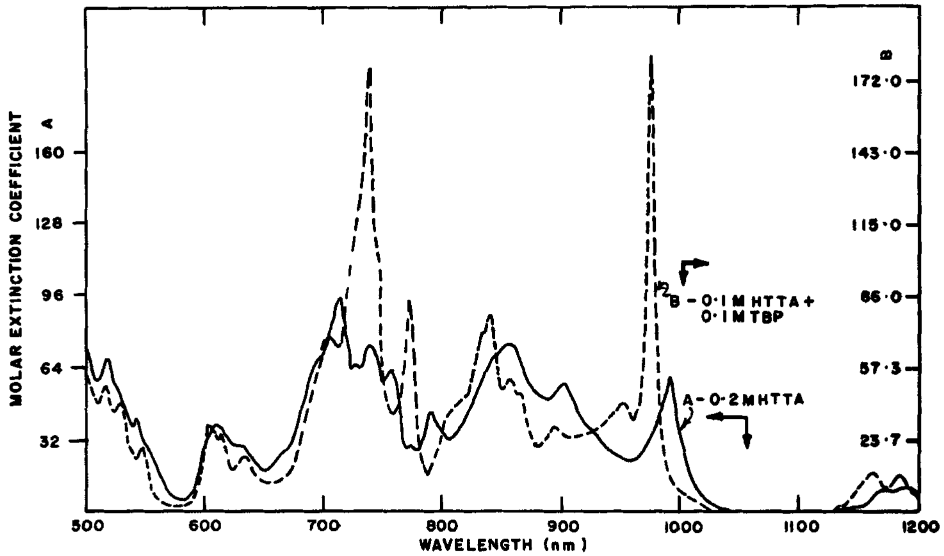

FIG. 4. Absorption spectra of Np(IV) extracted into benzene solutions of 0.2 *M* HTTA and a mixture of 0.1 *M* HTTA and 0.1 *M* TBP from 1.0 *M* perchloric acid.

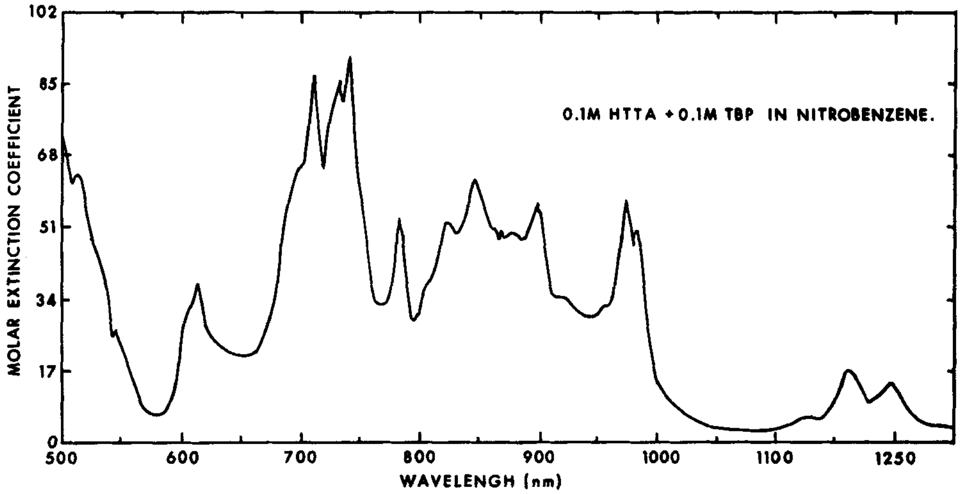

FIG. 5. Absorption spectrum of Np(IV) extracted into a mixture of 0.1 *M* HTTA and 0.1 *M* TBP in nitrobenzene from 1.0 *M* perchloric acid.

Extraction of Np(IV) from Nitrate Medium

Solvent Extraction Studies

The extraction of Np(IV) from nitric acid medium into HTTA in benzene is given by the equilibrium represented by Eq. (1), and the equilibrium constant K_A is given by (*29*)

$$K_A = K_{d(A)}\left(1 + \sum_1^n \beta_n[NO_3^-]^n\right)[H^+]^4[HTTA]^{-4} \tag{19}$$

where

$$K_{d(A)} = \frac{[Np(TTA)_4]_{(org)}}{[Np(IV)]_{(aq)}} \tag{20}$$

and

$$[Np(IV)]_{(aq)} = [Np^{4+}] + [Np(NO_3)^{3+}] + [Np(NO_3)_2^{2+}] + \cdots \tag{21}$$

$$= Np^{4+}\left(1 + \sum_1^n \beta_n[NO_3^-]^n\right) \tag{22}$$

and β_n is the concentration equilibrium constant represented by the equilibrium

$$Np^{4+} + nNO_3^- \overset{\beta_n}{\rightleftharpoons} Np(NO_3)_n^{4-n} \tag{23}$$

The extraction of Np(IV) from nitric acid medium into TBP in benzene is given by the equilibrium (*30*)

$$Np^{4+} + 4NO_3^- + 2TBP \overset{K_B}{\rightleftharpoons} Np(NO_3)_4 \cdot 2TBP \tag{24}$$

The equilibrium constant K_B is given by

$$K_B = \frac{[Np(NO_3)_4 \cdot 2TBP]}{[Np^{4+}][NO_3^-]^4[TBP]^2} \tag{25}$$

$$= K_{d(B)}\left(1 + \sum_1^n \beta_n[NO_3^-]^n\right)[NO_3^-]^{-4}[TBP]^{-2} \tag{26}$$

where

$$K_{d(B)} = \frac{[Np(NO_3)_4 \cdot 2TBP]_{(org)}}{[Np(IV)]_{(aq)}} \tag{27}$$

The results obtained on the extraction of Np(IV) from 1.0 *M* nitric acid medium into mixtures of HTTA and TBP of varying composition are included in Fig. 1. The enhancement in the extraction of Np(IV) when a mixture of extractants were used is clearly seen from these data. The K_d^x values are corrected for the nitrate complexing of Np(IV) in the aqueous phase by multiplying them by the factor $(1 + \sum_1^n \beta_n[\mathrm{NO}_3^-]^n)$ designated as F), and the $K_d^x F$ values are included in Fig. 1 to enable a direct comparison of these data with the perchlorate data. If the species extracted from nitric acid medium were the same as those extracted from perchloric acid, the perchloric acid curve and the corrected nitric acid data curve should have merged with each other. As one cannot rule out the formation of $\mathrm{Np(TTA)_4 \cdot TBP}$ even in the extraction from nitric acid, and as the $K_d^x F$ values are much higher than from perchlorate data, it is inferred that additional species are involved in the synergistic extraction from nitric acid. The additional species can be those involving the participation of nitrate ions in the complex. On the other hand, as $x_{\max}/(1 - x_{\max})$ still shows the value of $0.8/0.2 = 4$, one may argue that higher extraction in the nitrate medium may be due to the extraction of three species, viz., $\mathrm{Np(TTA)_4}$, $\mathrm{Np(TTA)_4 \cdot TBP}$, and $\mathrm{Np(NO_3)_4 \cdot 2TBP}$ as compared to only two, viz., $\mathrm{Np(TTA)_4}$ and $\mathrm{Np(TTA)_4 \cdot TBP}$, in the extraction from perchlorate medium. Assuming the said three species for Np(IV) extraction from nitric acid medium, we have attempted to calculate $K_{d(\mathrm{AB})}$ as a function of x by using the relation

$$K_d^x F = K_{d(\mathrm{A})}^x F + K_{d(\mathrm{B})}^x F + K_{d(\mathrm{AB})}^x F \qquad (28)$$

where $K_{d(\mathrm{B})}$ is the distribution coefficient when $x = 0$. It follows that $K_{d(\mathrm{B})}^x = K_{d(\mathrm{B})}(1 - x)^2$. As can be seen from the data given in Table 3,

TABLE 3

Variation of $K_{d(\mathrm{AB})}F$ as a Function of x ($\mathrm{HNO_3}$ medium)

x	$K_d^x F$	$K_{d(\mathrm{A})}^x F$	$K_{d(\mathrm{B})}^x F$	$K_{d(\mathrm{AB})}^x F$	$K_{d(\mathrm{AB})}F$
1	2.32	2.32	0	0	0
0.9	15.6	1.52	0.000113	14.1	215
0.8	19.1	0.950	0.000452	18.2	222
0.7	18.7	0.557	0.00102	18.1	251
0.6	15.1	0.301	0.00181	14.8	286
0.5	10.8	0.145	0.00283	10.7	342
0.4	6.52	0.0594	0.00407	6.46	419
0.3	3.32	0.0188	0.00554	3.30	582
0.2	1.31	0.00371	0.00723	1.31	1023
0.1	0.354	0.000232	0.00915	0.345	3933
0	0.0113	0	0.0113	0	0

$K_{d(\mathrm{AB})}F$ is not constant with changing x, and it is continuously increasing with decreasing x. All the $K^x_{d(\mathrm{AB})}F$ values are higher than those obtained from perchlorate medium extraction (Table 1). Thus it appears that additional species involving nitrate participation are extracted from nitric acid medium. Assuming the value of $K_{d(\mathrm{AB})}F(= 72.0)$ from the perchlorate data (Table 1), an attempt is made to explain the data given in Table 3 by assuming one more extractable species. At relatively high [HTTA] as compared to [TBP], it is reasonable to assume that one TTA molecule from $\mathrm{Np(TTA)_4}$ is replaced by a molecule of nitrate and TBP, resulting in the formation of the species $\mathrm{Np(NO_3)(TTA)_3 \cdot TBP}$. In fact, this was the species suggested by Irving and Edgington (*3*) as the predominant species extracted into HTTA + TBP. Thus, assuming the equilibrium given by

$$\mathrm{Np^{4+} + 3HTTA + HNO_3 + TBP} \overset{K_{\mathrm{AC}}}{\rightleftharpoons} \mathrm{Np(NO_3)(TTA)_3 \cdot TBP + 4H^+} \tag{29}$$

where

$$K_{\mathrm{AC}} = \frac{[\mathrm{Np(NO_3)(TTA)_3 \cdot TBP}][\mathrm{H^+}]^4}{[\mathrm{Np^{4+}}][\mathrm{HTTA}]^3[\mathrm{HNO_3}][\mathrm{TBP}]} \tag{30}$$

and

$$K_{d(\mathrm{AC})} = \frac{[\mathrm{Np(NO_3)(TTA)_3 \cdot TBP}]_{(\mathrm{org})}}{[\mathrm{Np(IV)}]_{(\mathrm{aq})}} \tag{31}$$

then it follows that

$$K^x_d F = K^x_{d(\mathrm{A})}F + K^x_{d(\mathrm{B})}F + K^x_{d(\mathrm{AB})}F + K^x_{d(\mathrm{AC})}F \tag{32}$$

The values of $K_{d(\mathrm{AC})}F = K^x_{d(\mathrm{AC})} \cdot F/x^3(1 - x)$ were calculated and are given in Table 4. It appears from this table that $K_{d(\mathrm{AC})}F$ remains constant in the region where $x = 0.9$ to 0.6, indicating that the species assumed is predominant in this region. But the increase in the values of $K_{d(\mathrm{AC})}F$ below $x = 0.6$ suggests that more species are involved in the extraction. Taking the average value of $K_{d(\mathrm{AC})}F = 125$, the value of K_{AC} was calculated using the relation

$$\log K_{\mathrm{AC}} = \log K_{d(\mathrm{AC})}F + 4 \log [\mathrm{H^+}] - 4 \log \mathrm{C} \tag{33}$$

and it was found to be $\log K_{\mathrm{AC}} = 7.30$. Thus the equilibrium constant β_{AC} for the equilibrium represented by

$$\begin{aligned} &\mathrm{Np(TTA)_{4(org)} + TBP \cdot HNO_{3(org)}} \\ &\quad \overset{\beta_{\mathrm{AC}}}{\rightleftharpoons} \mathrm{Np(NO_3)(TTA)_3 \cdot TBP_{(org)} + HTTA_{(org)}} \end{aligned} \tag{34}$$

TABLE 4

Variation of $K_{d(\mathrm{AC})}F$ as a Function of x (HNO_3 medium)

x	$K^x_{d(\mathrm{AB})}F^a$	$K^x_{d(\mathrm{AC})}F$	$K_{d(\mathrm{AC})}F$
0.9	4.82	9.28	127
0.8	5.85	12.4	121
0.7	5.16	12.9	125
0.6	3.74	11.1	128
0.5	2.29	8.41	135
0.4	1.06	5.40	141
0.3	0.377	2.92	154
0.2	0.100	1.21	189
0.1	0.00878	0.336	373

[a] Values taken from Table 1. K^x_dF, $K^x_{d(\mathrm{A})}F$, and $K^x_{d(\mathrm{B})}F$ values are the same as those given in Table 3.

is given by

$$\beta_{\mathrm{AC}} = \frac{K_{\mathrm{AC}}}{K_{\mathrm{A}}} = \frac{2.0 \times 10^7}{3.7 \times 10^5} = 54 \qquad (35)$$

The present value of log $K_{\mathrm{AC}} = 7.30$ is in reasonable agreement with the value of 7.75 reported by Irving and Edgington (*3*). However, as the diluents used in the two studies are different, such an agreement is fortuitous as the diluents influence the synergistic extraction enormously (*31*). With cyclohexane as the diluent, the solubility of HTTA in the aqueous phase is much higher ($K_{d(\mathrm{HTTA})} = 4.5$). This, as well as the aqueous phase nitrate complexing of Np(IV), was ignored by Irving and Edgington in their work. The value of K_{AC} in cyclohexane would be much higher than in benzene (*32*).

It may not be worthwhile to continue this calculation further as the system becomes too complicated too btain any meaningful quantitative equilibrium constants for other species. However, it may be suggested that there is more than one species with nitrate participation in the extracted complexes. The extraction of a multiple number of species involving nitrate participation was further confirmed by some more solvent extraction work. Figure 6 presents the K_d values obtained as a function of [HTTA] at a fixed [TBP] in different ranges of [TBP] and [HTTA]. As the values of the slopes obtained range between 0.5 and 4.0, it is reasonable to infer that species involving from 0 to 4 molecules of HTTA are present in extractable complexes. Figure 7 presents the data on the variation of K_d as a function of [TBP] at constant [HTTA] in several ranges of [HTTA] and [TBP]. The values of the slopes obtained

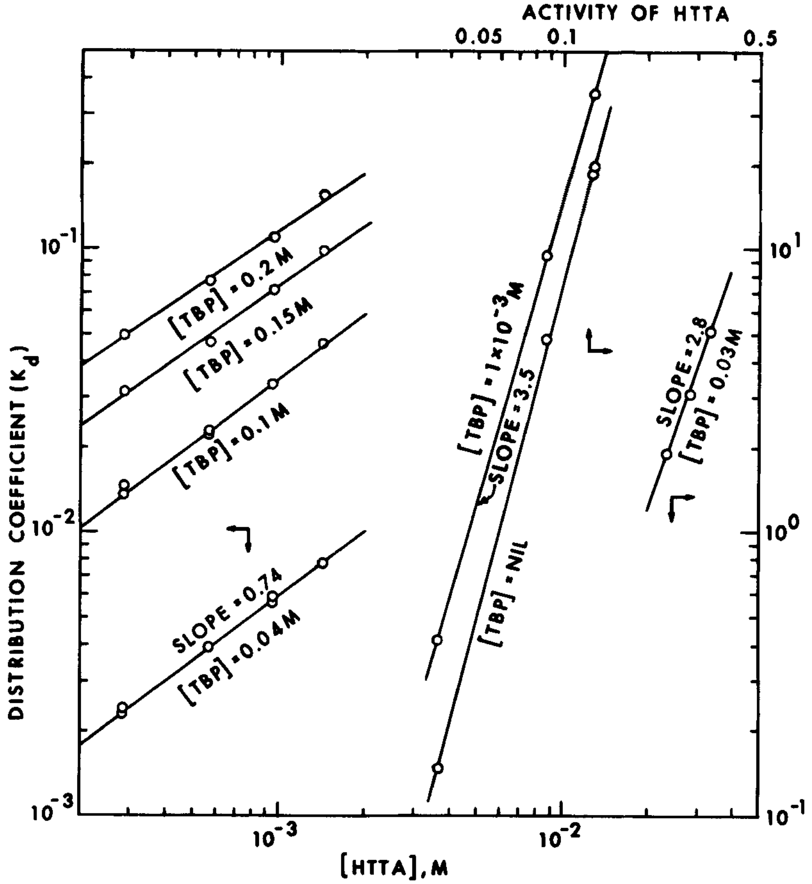

FIG. 6. Variation of distribution coefficient of Np(IV) with HTTA concentration at fixed TBP concentration (extracted from 1.0 M nitric acid).

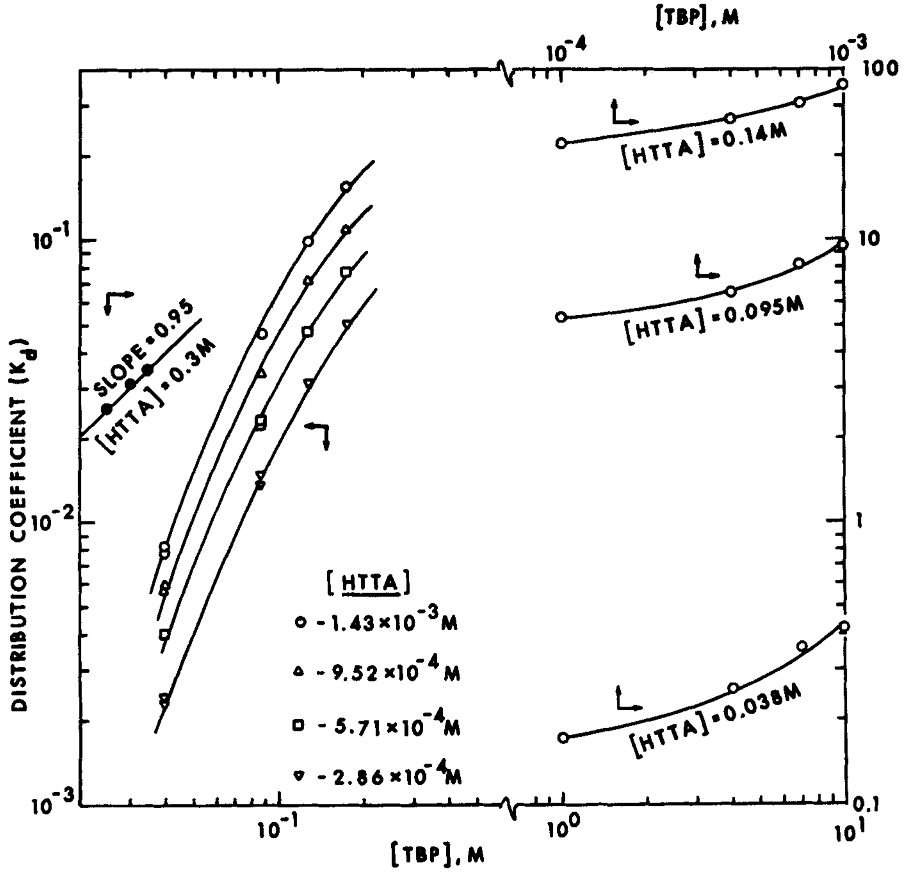

FIG. 7. Variation of distribution coefficient of Np(IV) with TBP concentration at fixed HTTA concentration (extracted from 1.0 *M* nitric acid).

lie between 0 and 2, which suggests that species involving 0, 1, or 2 molecules of TBP are present in the extractable complexes.

The variation of K_d of Np(IV) at constant ionic strength and $[H^+]$ but varying $[NO_3^-]$ is shown in Fig. 8. The values of the slopes vary from ~0.5 to 3.0, thereby showing the number of nitrate ions involved in the species to vary from 0 to 3. The data on the variation of K_d with $[H^+]$ at constant ionic strength and $[NO_3^-]$ are also included in Fig. 8. In the concentration range investigated, the slopes of these curves vary from 0 to −3, thereby indicating that 0 to 3 molecules of HTTA are involved in the formation of extractable species. To sum up, the data in Figs. 6, 7, and 8 suggest that a number of species with composition $Np(NO_3)_{4-x}(TTA)_x yTBP$, where $x = 0, 1, 2, 3$, or 4, and $y = 0, 1$, or 2, are involved in the extraction from nitric acid medium.

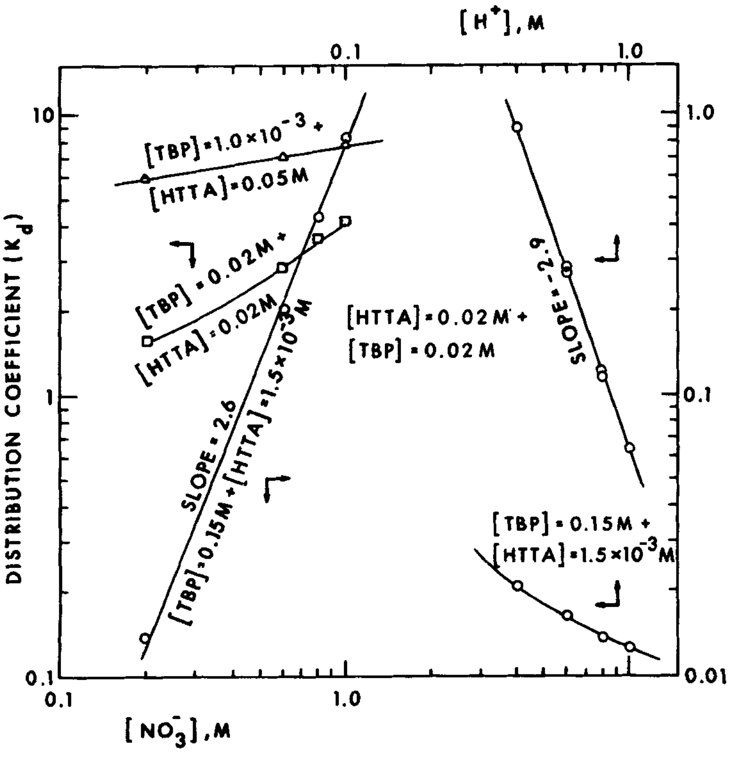

FIG. 8. Variation of distribution coefficient of Np(IV) with nitrate ion concentration and hydrogen ion concentration.

TABLE 5

Summary of the Concentration Equilibrium Constants. Solvent: Benzene, Temperature = 25 °C

Equilibrium	log *K*	Ref.
$Np^{4+}_{(aq)} + 4HTTA_{(org)} \rightleftarrows Np(TTA)_{4(org)} + 4H^{+}_{(aq)}$	5.57	This work
$Np^{4+}_{(aq)} + 4HTTA_{(org)} + TBP_{(org)} \rightleftarrows Np(TTA)_4 \cdot TBP_{(org)} + 4H^{+}_{(aq)}$	8.34	This work
$Np^{4+}_{(aq)} + 3HTTA_{(org)} + HNO_{3(aq)} + TBP_{(org)} \rightleftarrows Np(NO_3)(TTA)_3 \cdot TBP_{(org)} + 4H^{+}_{(aq)}$	7.30	This work
$Np(TTA)_{4(org)} + TBP_{(org)} \rightleftarrows Np(TTA)_4 \cdot TBP_{(org)}$	2.75	This work
$Np(TTA)_{4(org)} + TBP \cdot HNO_{3(org)} \rightleftarrows Np(NO_3)(TTA)_3 \cdot TBP_{(org)} + HTTA_{(org)}$	1.73	This work
$Th(TTA)_{4(org)} + TBP_{(org)} \rightleftarrows Th(TTA)_4 \cdot TBP_{(org)}$	4.7	*32*

The values of the equilibrium constants obtained in the present work are summarized in Table 5. A value of the equilibrium constant reported for Th(IV) obtained (*32*) in benzene is included in Table 5. The higher value observed for Th(IV) as compared to that for Np(IV) is expected from the general observation (*32*, *33*) that as the stability of the metal chelate decreases, the stability of the adduct increases.

Spectrophotometric Studies

The absorption spectra of Np(IV) extracted from 1.0 *M* nitric acid medium into 1.0 *M* TBP, 0.2 *M* HTTA, and 0.1 *M* TBP + 0.1 *M* HTTA, all in benzene, are shown in Fig. 9. They are the respective spectra of $Np(NO_3)_4 \cdot 2TBP$, $Np(TTA)_4$, and a mixed complex with some nitrate participation. The differences between the three spectra with respect to absorption maxima as well as intensities are quite apparent. The spectra obtained similarly with 1.0 *M* TBP + 0.05 *M* HTTA and 0.1 *M* TBP + 0.5 *M* HTTA are shown in Fig. 10. Thus the three spectra obtained with different compositions of TBP and HTTA differ very much within themselves as well as from those which are identified with the species $Np(NO_3)_4 \cdot 2TBP$, $Np(TTA)_4$, and $Np(TTA)_4 \cdot TBP$. Thus these spectra suggest that these probably are of the species $Np(NO_3)_{4-x}(TTA)_x y TBP$ with $x = 1, 2,$ or 3, and $y = 1$ or 2. It is interesting to note that the intensities of these mixed complexes are higher compared to those formed with TBP or HTTA alone. Another interesting feature is that these spectra are reproduced when different amounts of HTTA in benzene are added to the TBP extract of Np(IV) from nitric acid, which again confirms that the complexes do contain nitrate and HTTA as ligands.

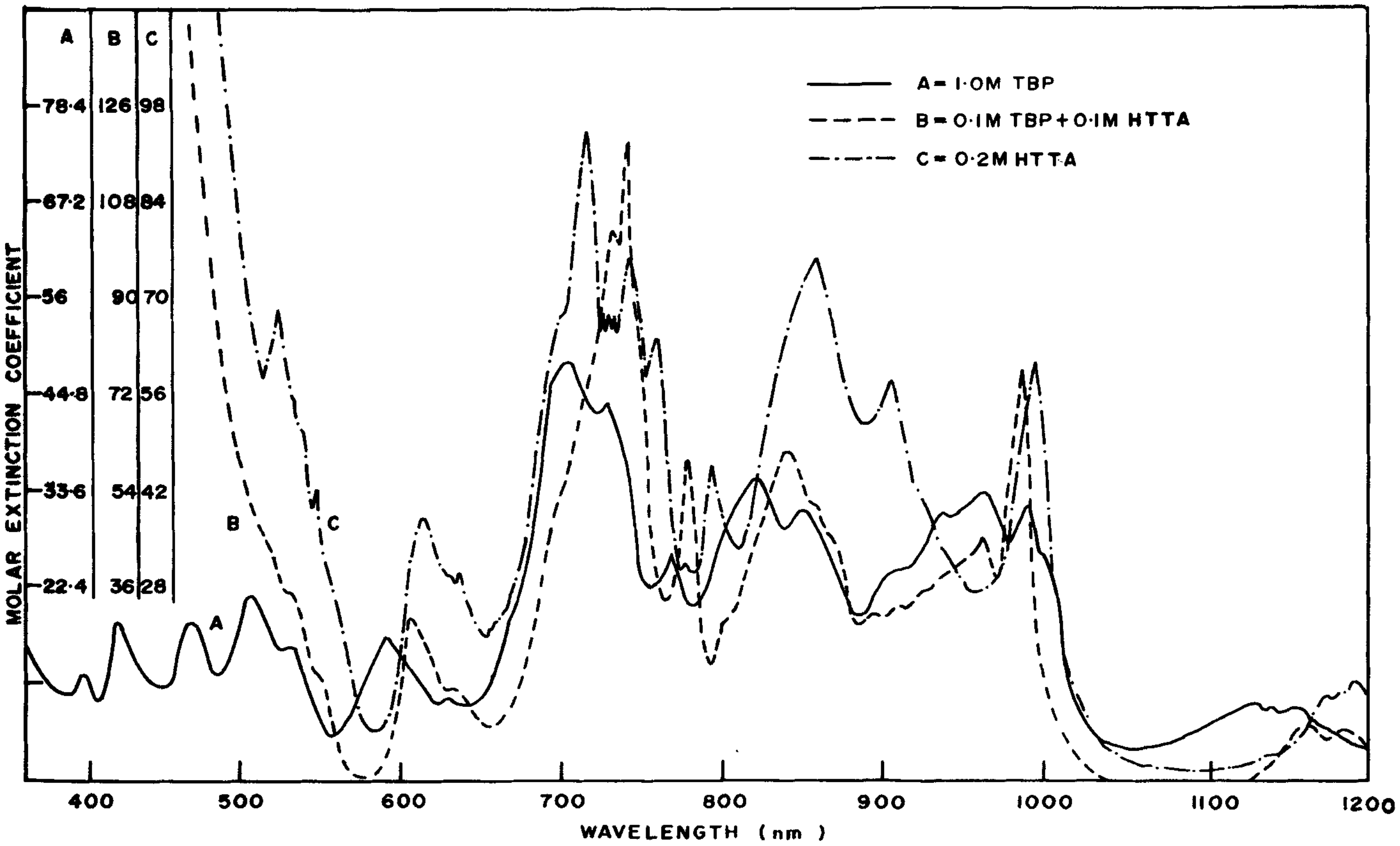

FIG. 9. Absorption spectra of Np(IV) extracted from 1.0 *M* nitric acid into (A) 1.0 *M* TBP in benzene, (B) 0.1 *M* TBP + 0.1 *M* HTTA in benzene, and (C) 0.2 *M* HTTA in benzene.

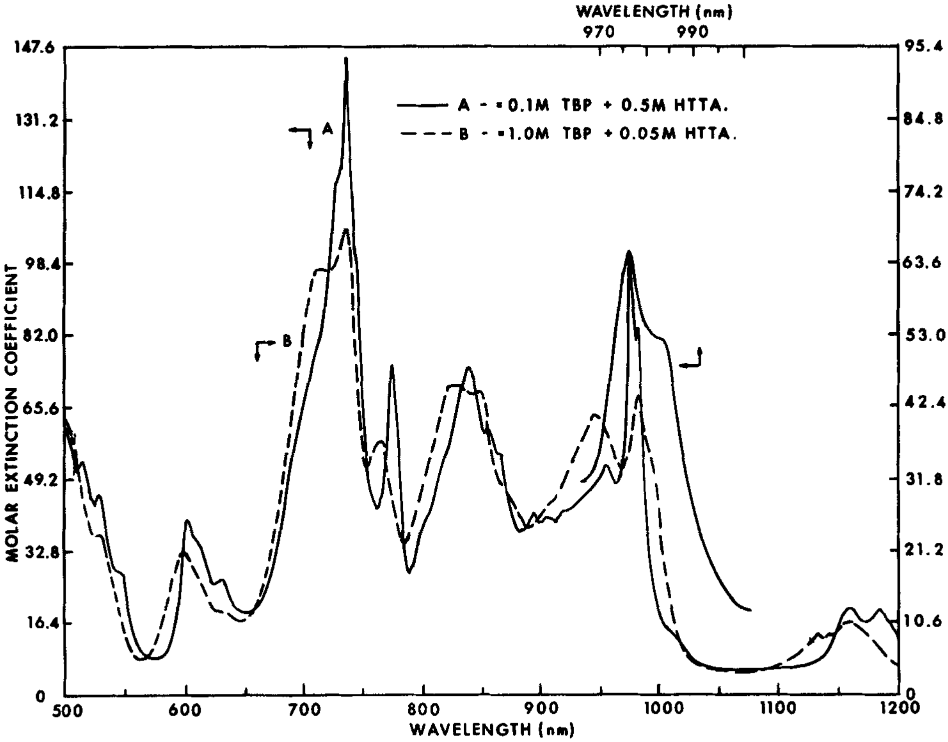

FIG. 10. Absorption spectra of Np(IV) extracted from 1.0 *M* nitric acid into (A) 0.1 *M* TBP + 0.5 *M* HTTA in benzene, and (B) 1.0 *M* TBP + 0.05 *M* HTTA in benzene.

Spectra were also reproduced when TBP pre-equilibrated with nitric acid was added to a HTTA extract of Np(IV). Unless more spectral work is done, it is difficult to assign each of the absorption spectra observed as representative of a definite species.

APPENDIX

Derivation of Eq. (13)

$$K_d^x = \frac{[\mathrm{Np(TTA)_4}] + [\mathrm{Np(TTA)_4 \cdot TBP}]}{[\mathrm{Np^{+4}}]} \qquad \text{(a)}$$

$$K_{d(\mathrm{A})}^x = \frac{[\mathrm{Np(TTA)_4}]}{[\mathrm{Np^{+4}}]} \qquad \text{(b)}$$

$$K_{d(\mathrm{AB})}^{x} = \frac{[\mathrm{Np(TTA)_4 \cdot TBP}]}{[\mathrm{Np}^{+4}]} \tag{c}$$

where x is the fraction of HTTA when [HTTA] + [TBP] = constant = C. From Eqs. (a), (b), and (c) it follows that

$$K_d^x = K_{d(\mathrm{A})}^{x} + K_{d(\mathrm{AB})}^{x} \tag{13}$$

Derivation of Eq. (14)

It follows from Eq. (12) that

$$K_{d(\mathrm{AB})}^{x} = K_{\mathrm{AB}}[\mathrm{H}^+]^{-4}[\mathrm{HTTA}]^4[\mathrm{TBP}] \tag{d}$$

where x is the fraction of HTTA when [HTTA] + [TBP] = constant = C. Substituting the values of [HTTA] and [TBP] from Eqs. (6), (7), and (8), one gets

$$K_{d(\mathrm{AB})}^{x} = K_{\mathrm{AB}}[\mathrm{H}^+]^{-4}C^5x^4(1-x) \tag{e}$$

Rearranging Eq. (e),

$$\frac{K_{d(\mathrm{AB})}^{x}}{x^4(1-x)} = K_{\mathrm{AB}}[\mathrm{H}^+]^{-4}C^5 \tag{f}$$

At a constant acidity, $K_{d(\mathrm{AB})}^{x}/x^4(1-x)$ would remain constant. This constant is designated as $K_{d(\mathrm{AB})}$. Thus

$$K_{d(\mathrm{AB})} = \frac{K_{d(\mathrm{AB})}^{x}}{x^4(1-x)} = K_{\mathrm{AB}}[\mathrm{H}^+]^{-4}C^5 \tag{14}$$

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REFERENCES

1. J. G. Cunninghame, P. Scargill, and H. M. Willis, UKAEA Report, AERE C/M 215 (1954).

2. H. Irving and D. N. Edgington, *J. Inorg. Nucl. Chem.*, *15*, 158 (1960).

3. H. Irving and D. N. Edgington, *Ibid.*, *20*, 321 (1961).

4. H. Irving and D. N. Edgington, *Ibid.*, *21*, 169 (1961).

5. H. L. Finston and E. Gnizi, in *Solvent Extraction Research* (A. S. Kertes and Y. Marcus, eds.), Wiley-Interscience, New York, 1969, p. 333.

6. T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem.*, *29*, 1457 (1967).
7. E. C. Cox, Jr., and M. W. Davis, Jr., *Sep. Sci.*, *8*, 205 (1973).
8. J. G. Hayden, I. H. Gerow, and M. W. Davis, Jr., *Ibid.*, *9*, 337 (1974).
9. I. H. Gerow, J. G. Hayden, K. Gaggar, and M. W. Davis, Jr., *Ibid.*, *12*, 511 (1977).
10. V. V. Ramakrishna, S. K. Patil, L. Krishna Reddy, and A. S. Reddy, *J. Inorg. Nucl. Chem.*, In Press.
11. V. V. Ramakrishna, S. K. Patil, L. Krishna Reddy, and A. S. Reddy, *J. Radioanal. Chem.*, In Press.
12. T. V. Healy, *J. Inorg. Nucl. Chem.*, *19*, 314 (1961).
13. F. L. Moore, *Anal. Chem.*, *29*, 941 (1957).
14. A. J. Fischman, H. L. Finston, and D. E. Goldberg, *J. Inorg. Nucl. Chem.*, *35*, 2497 (1973).
15. R. A. Day, Jr., and R. W. Stoughton, *J. Am. Chem. Soc.*, *72*, 5662 (1950).
16. K. Alcock, S. S. Grimley, T. V. Healy, J. Kennedy, and H. A. C. McKay, *Trans. Faraday Soc.*, *52*, 39 (1956).
17. R. F. Buchanan, J. P. Hughes, J. J. Hines, and C. A. A. Bloomquist, *Talanta*, *6*, 173 (1960).
18. E. L. King and W. H. Reas, *J. Am. Chem. Soc.*, *73*, 1804 (1951).
19. P. R. Vasudeva Rao, V. V. Ramakrishna, and S. K. Patil, To Be Published.
20. J. C. Sullivan and J. C. Hindman, *J. Am. Chem. Soc.*, *76*, 5931 (1954).
21. S. K. Patil and V. V. Ramakrishna, *J. Inorg. Nucl. Chem.*, *35*, 3333 (1973).
22. S. V. Bagawde, V. V. Ramakrishna, and S. K. Patil, *Ibid.*, *38*, 2085 (1976).
23. I. J. Gal and R. M. Nikolic, *Ibid.*, *28*, 563 (1966).
24. T. V. Healy and J. R. Ferraro, *Ibid.*, *24*, 1449 (1962).
25. T. Taketatsu and C. V. Banks, *Anal. Chem.*, *38*, 1524 (1966).
26. T. Taketatsu and N. Toriumi, *Bull. Chem. Soc. Jpn.*, *41*, 1275 (1968).
27. T. Taketatsu and N. Toriumi, *J. Inorg. Nucl. Chem.*, *31*, 2235 (1969).
28. T. Taketatsu and N. Ohkura, *Bull. Chem. Soc. Jpn.*, *44*, 2430 (1971).
29. A. Ramanujam, M. N. Nadkarni, V. V. Ramakrishna, and S. K. Patil, *J. Radioanal. Chem.*, *42*, 349 (1977).
30. K. Alcock, G. F. Best, E. Hesford, and H. A. C. McKay, *J. Inorg. Nucl. Chem.*, *6*, 328 (1958).
31. T. V. Healy, *Ibid.*, *19*, 328 (1961).
32. T. V. Healy, in *Solvent Extraction Research* (A. S. Kertes and Y. Marcus, eds.), Wiley-Interscience, New York, 1969, p. 257.
33. H. M. N. H. Irving, in *Solvent Extraction Chemistry* (D. Dyrssen, J. O. Liljenzin and J. Rydberg, eds.), North-Holland, Amsterdam, 1967, p. 90.

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