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Solvent Extraction and Spectrophotometric Studies on Synergistic Extraction of Plutonium(IV) by Mixtures of Thenoyltrifluoroacetone (HTTA) and Tri-*n*-butylphosphate (TBP) in Benzene

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Abstract

The synergistic extraction of Pu(IV) from perchloric acid solutions into mixtures of thenoyltrifluoroacetone (HTTA) and tri-*n*-butylphosphate (TBP) in benzene was investigated by solvent extraction methods. The adduct responsible for synergism was found to be $Pu(TTA)_4 \cdot TBP$. The adduct formation between $Pu(TTA)_4$ and TBP in the benzene phase was also investigated by spectrophotometry. The equilibrium constants for the equilibria involved were obtained both by solvent extraction and by spectrophotometric methods.

Several studies on synergistic extraction of actinide ions by mixtures of a chelating agent and a neutral donor (S) have been reported in the literature, and these data are covered in excellent reviews (*1–4*) on synergistic extraction. A limited number of such studies, however, have been devoted to the extraction of tetravalent actinides (*5–9*). The only studies reported (*6*) on the synergistic extraction of Np(IV) and Pu(IV) were

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carried out from nitric acid medium where mixed metal–nitrate–TTA–neutral donor species were involved. No data on the adduct formation of the type $M(TTA)_4S_x$ in the extraction of Np(IV) or Pu(IV) were reported though such a species was found in Th(IV) extraction (*5*, *7*). While studying the crystal structure of $Th(TTA)_4 \cdot TOPO$ adduct, Liepoldt et al. (*10*, *11*) observed that similar adducts of Zr(IV) and Hf(IV) could not be prepared.

We have initiated a program on synergistic extraction of tetravalent actinides from different aqueous media into mixtures of HTTA and neutral donors. Recently the work on the extraction of Np(IV) has been reported (*12*). In continuation of this, synergistic extraction of Pu(IV) from perchloric acid into mixtures of HTTA and TBP has been studied and the results obtained are reported here. The adduct formation between Pu $(TTA)_4$ and TBP, responsible for synergism, was also investigated by spectrophotometry, and these results are included here.

EXPERIMENTAL

Materials

Plutonium, which was mainly ^{239}Pu, was purified by anion exchange in nitric acid medium and its radiochemical purity was ascertained by alpha spectrometry. HTTA supplied by E. Merck, West Germany, was dried under vacuum over phosphorus pentoxide for several hours (*13*). Benzene solution of HTTA was preequilibrated with dilute perchloric acid for a few hours to allow hydration of HTTA (*14*). TBP was purified by the method described by Alcock et al. (*15*). Tetraheptylammonium chloride (THACl) was obtained from Serva International, Heidelberg, and used as such. Ammonium monovanadate of GR quality was obtained from E. Merck, West Germany. Scintillation grade naphthalene, PPO, and POPOP were used for making the liquid scintillator solutions. AR dioxane was purified (*16*) prior to use. Laboratory reagent grade di-2-ethyl hexyl phosphoric acid, obtained from B.D.H., England, was used as such. All other chemicals used were of analytical reagent grade.

Procedure

Plutonium in nitric acid medium was adjusted to Pu(IV) with hydrogen peroxide (*17*), the excess of which was subsequently destroyed by heating. The oxidation state of Pu(IV) was then ascertained by using the HTTA extraction method (*18*).

For solvent extraction work, Pu(IV) in perchloric acid was prepared (*18*) by extracting ~1 mg of Pu(IV) from 2.0 ml of 0.5 *M* nitric acid into an equal volume of 0.05 *M* THACl in xylene and then stripping the extracted Pu(IV) into 2.0 ml perchloric acid. From this stock suitable dilutions were made to get a plutonium concentration in the range of ~5 μg/ml and perchloric acid concentration as required. By this procedure the concentration of nitrate in the aqueous phase was limited to $<5 \times 10^{-4}$ *M*, the influence of which was considered negligible. About 10^{-4} *M* of vanadium(V) was kept as a holding oxidant for Pu(IV) (*19*). Aliquots (3.0 ml) of Pu(IV) in perchloric acid were equilibrated with an equal volume of the benzene phase containing mixtures of HTTA and TBP in the desired composition. The equilibration was done for 1 hr in a thermostated waterbath kept at 25 ± 0.1 °C. The solutions were allowed to settle, and suitable aliquots (50 to 250 μl) from both phases were pipetted into vials containing 5 ml of liquid scintillator solutions. The organic phase alpha disintegrations were assayed using a toluene-based liquid scintillator (*20*) and those of the aqueous phase by using a dioxane-based liquid scintillator (*21*). No quenching was found for the aliquots added in either case. The oxidation state of the plutonium remaining in the aqueous phase at the end of equilibration was checked using the HTTA extraction method (*18*) and was found to remain unchanged. All the experiments were done in triplicate, and agreement in the distribution coefficient (K_d) values was usually better than ±2%. The material balance was also found to be good.

The equilibrium value of the organic phase HTTA concentration was calculated by knowing its initial concentration and using $K_d = 40$ (*22*) for its distribution between benzene and dilute acid. The aqueous phase HTTA concentration was assayed in studies on the interaction of HTTA and TBP in benzene by measuring its absorbance at 292 nm with perchloric acid as the blank and using the molar extinction coefficient value of 7875 M^{-1} cm^{-1} (*19*). Free TBP in the organic phase was assumed as equal to its initial concentration, and the interaction between HTTA and TBP in the organic phase was not considered except where such a study was made.

Macroconcentrations of Pu(IV) in perchloric acid were prepared by coulometric reduction of plutonium to Pu(III) followed by coulometric oxidation of Pu(III) to Pu(IV). Suitable amounts of Pu(IV) in perchloric acid were then extracted from perchloric acid into mixtures of HTTA and TBP in benzene, and the absorption spectra of the organic extracts were recorded using a Cary-14 recording spectrophotometer with benzene as the blank.

For the study of adduct formation between $Pu(TTA)_4$ and TBP in benzene by spectrophotometry, macroconcentrations of Pu(IV) in nitric acid were extracted from ~0.5 *M* nitric acid into 0.1 *M* HTTA in benzene such that the HTTA was almost saturated with Pu(IV). The benzene solution of $Pu(TTA)_4$ thus obtained was subsequently diluted using TBP in benzene to give several solutions which were identical in Pu(IV) concentration (1.503×10^{-3} *M*) but differed in their TBP concentrations. The absorption spectra of these solutions were recorded at different scanning speeds by using 5.0 cm cells and with benzene as the blank. The records obtained with a scanning speed of 2.5 Å/sec were used for quantitative calculations. The concentration of plutonium in the organic solutions was assayed by liquid scintillation counting.

RESULTS AND DISCUSSION

Solvent Extraction Studies

The extraction of Pu(IV) from perchloric acid medium into a benzene solution of HTTA is given by (*23*) the equilibrium represented by

$$Pu^{4+}_{(aq)} + 4HTTA_{(org)} \overset{K_A}{\rightleftharpoons} Pu(TTA)_{4(org)} + 4H^{+}_{(aq)} \tag{1}$$

The equilibrium constant (expressed as its concentration quotient), K_A, for the equilibrium represented by Eq. (1) is

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

The square brackets represent concentration terms. If the distribution coefficient value of Pu(IV) when it is distributed between perchloric acid and a benzene solution of HTTA is denoted by $K_{d(A)}$, it can be shown that

$$K_{d(A)} = \frac{[Pu(TTA)_4]_{(org)}}{[Pu^{4+}]_{(aq)}} \tag{3}$$

as it is known that $Pu(TTA)_4$ is the only Pu(IV) species extracted by benzene solution of HTTA from a perchloric acid medium. It is assumed that under the extraction conditions used, hydrolysis (*24*, *25*) and aqueous HTTA complexing of Pu(IV) (*26*) are negligible. Substituting Eq. (3) in Eq. (2),

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

The extraction, though poor, of Pu(IV) from perchloric acid medium into a solution of TBP may be given (*27*) by the equilibrium represented by

$$\mathrm{Pu^{4+}_{(aq)}} + 4\mathrm{ClO^-_{4(aq)}} + 2\mathrm{TBP_{(org)}} \overset{K_B}{\rightleftharpoons} \mathrm{Pu(ClO_4)_4 \cdot 2TBP_{(org)}} \tag{5}$$

However, the extraction of Pu(IV) from dilute perchloric acid into a dilute benzene solution of TBP is practically negligible (*27*). Thus when Pu(IV) is extracted from perchloric acid into mixtures of HTTA and TBP in benzene, the extracted species may be either $\mathrm{Pu(TTA)_4}$ alone or the adducts of $\mathrm{Pu(TTA)_4}$ and TBP:

$$\mathrm{Pu(TTA)_{4(org)}} + n\mathrm{TBP_{(org)}} \overset{\beta_{(\mathrm{AB})_n}}{\rightleftharpoons} \mathrm{Pu(TTA)_4} \cdot n\mathrm{TBP_{(org)}} \tag{6}$$

The equilibrium constant for the equilibrium represented by Eq. (6) is designated as $\beta_{(\mathrm{AB})_n}$, where n refers to number of TBP molecules associated with the adduct formed, and is given by

$$\beta_{(\mathrm{AB})_n} = \frac{[\mathrm{Pu(TTA)_4} \cdot n\mathrm{TBP}]_{(\mathrm{org})}}{[\mathrm{Pu(TTA)_4}]_{(\mathrm{org})}[\mathrm{TBP}]^n_{(\mathrm{org})}} \tag{7}$$

When adduct formation occurs, the extraction of Pu(IV) from perchloric acid into mixtures of HTTA and TBP in benzene can be represented by the following equilibrium in addition to the one shown in Eq. (1):

$$\mathrm{Pu^{4+}_{(aq)}} + 4\mathrm{HTTA_{(org)}} + n\mathrm{TBP_{(org)}} \overset{K_{(\mathrm{AB})_n}}{\rightleftharpoons} \mathrm{Pu(TTA)_4} \cdot n\mathrm{TBP_{(org)}} + 4\mathrm{H^+_{(aq)}} \tag{8}$$

The equilibrium constant $K_{(\mathrm{AB})_n}$ is given by

$$K_{(\mathrm{AB})_n} = \frac{[\mathrm{Pu(TTA)_4} \cdot n\mathrm{TBP}]_{(\mathrm{org})}[\mathrm{H^+}]^4_{(\mathrm{aq})}}{[\mathrm{Pu^{4+}}]_{(\mathrm{aq})}[\mathrm{HTTA}]^4_{(\mathrm{org})}[\mathrm{TBP}]^n_{(\mathrm{org})}} \tag{9}$$

$$= K_{d(\mathrm{AB})_n} \cdot [\mathrm{H^+}]^4_{(\mathrm{aq})}[\mathrm{HTTA}]^{-4}_{(\mathrm{org})}[\mathrm{TBP}]^{-n}_{(\mathrm{org})} \tag{10}$$

where

$$K_{d(\mathrm{AB})_n} = \frac{[\mathrm{Pu(TTA)_4} \cdot n\mathrm{TBP}]_{(\mathrm{org})}}{[\mathrm{Pu^{4+}}]_{(\mathrm{aq})}} \tag{11}$$

is the distribution coefficient of Pu(IV) due to the adduct formed. As both the equilibria represented by Eqs. (1) and (8) are simultaneous, for the extraction of Pu(IV) into mixtures of HTTA and TBP the observed distribution coefficient of Pu(IV), $K_{d(\mathrm{S})}$, is given by

$$K_{d(\mathrm{S})} = K_{d(\mathrm{A})} + K_{d(\mathrm{AB})_n} \tag{12}$$

The results obtained for the extraction of Pu(IV) from 2.0 *M* perchloric acid medium into a benzene phase with constant TBP concentration and varying HTTA concentration are shown in Fig. 1. The slope of the $\log K_{d(\mathrm{S})}$ vs $\log [\mathrm{HTTA}]_{(\mathrm{org})}$ plot obtained is +3.7, which is quite close to +4, and this suggests that four TTA ions are associated with the extracted complexes, in conformity with Eqs. (4) and (10). The slightly lower than expected value of the slope could be due to interaction between HTTA and TBP (*1*, *28*, *29*). The results obtained for the extraction of Pu(IV) from perchloric acid medium into a benzene phase with constant HTTA concentration and varying TBP concentration are given in Table 1. It is clear from these data that there is enhancement in the extraction of Pu(IV) when TBP is added to HTTA, and this must be due to the extraction of adducts as shown in Eq. (8). The values of $K_{d(\mathrm{AB})_n}$ were calculated using Eq. (12) and are included in this table. From Eq. (10) it follows that at constant $[\mathrm{H}^+]_{\mathrm{aq}}$ and $[\mathrm{HTTA}]_{\mathrm{org}}$ the plot of $\log K_{d(\mathrm{AB})_n}$ vs $\log [\mathrm{TBP}]$ would be a straight line with slope *n*, the number of TBP molecules associated with the adduct. Such plots are shown in Fig. 2. It is seen from Fig. 2 that the slopes are initially ~1 and then progressively decrease with increasing TBP concentration. This decrease can be attributed either to an interaction between HTTA and TBP in the benzene phase, thereby causing a decrease in the equilibrium values of $[\mathrm{HTTA}]_{(\mathrm{org})}$ and $[\mathrm{TBP}]_{(\mathrm{org})}$, or to the presence of increased amounts of water with increasing TBP concentration, which results in the destruction of the adduct (*3*) or both. As decreasing the concentration of both HTTA and TBP would decrease both these effects to some extent, the data were also obtained employing lower concentrations of both HTTA and TBP. The results obtained are given in Table 2. The $K_{d(\mathrm{AB})_n}$ values obtained from these data are shown in Fig. 3. It is seen that the slopes of the log–log plots are around unity, thereby showing that the value of *n* in Eqs. (7)–(10) is unity. The data presented in Figs. 1 and 3 thus reveal that the adduct complex extracted is $\mathrm{Pu(TTA)_4 \cdot TBP}$. From Eqs. (4), (6), and (10) it can be shown that

$$K_{d(\mathrm{AB})_n}/K_{d(\mathrm{A})} = \beta_{(\mathrm{AB})_n} \cdot [\mathrm{TBP}] \tag{13}$$

Using the data presented in Table 2 and the relation given by Eq. (13), the values of $\beta_{(\mathrm{AB})_n}$ were calculated and are included in Table 2. It is seen that the values obtained at both acidities are quite close.

Alternatively, $\beta_{(\mathrm{AB})_n}$ can be determined by Job's method of continuous variations, applied to solvent extraction systems by Gal and Nikolic (*30*). In this method the total concentration of HTTA and TBP together was held constant, and the $K_{d(\mathrm{S})}$ values are obtained as a function of the

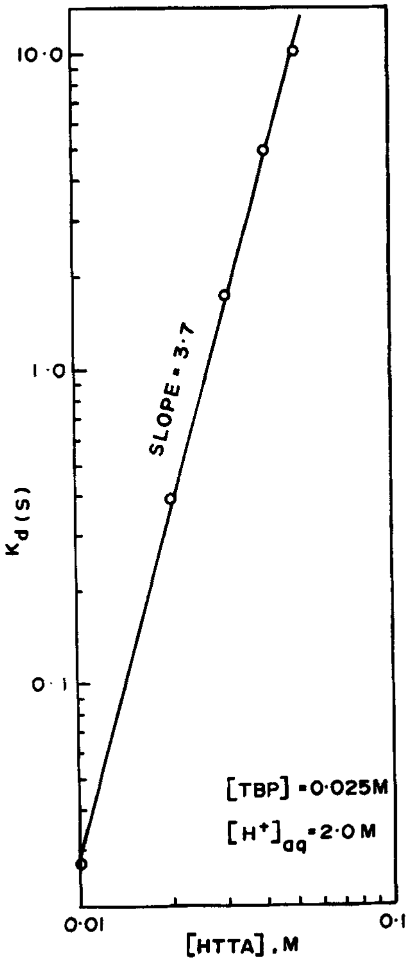

FIG. 1. Variation of distribution coefficient ($K_{d(s)}$) of Pu(IV) with HTTA concentration in the presence of TBP.

TABLE 1

Variation of the Distribution Coefficient of Pu(IV) with TBP Concentration[a]

[TBP] (M)	$K_{d(S)}$		$K_{d(AB)_n}$	
	A	B	A	B
0[b]	3.03	0.467	—	—
0.01	3.94	0.674	0.910	0.207
0.02	4.68	0.880	1.65	0.413
0.03	5.08	0.968	2.05	0.501
0.04	5.66	1.06	2.63	0.593
0.05	5.78	1.19	2.75	0.723

[a] A: $[H^+]_{(aq)} = 1.0\,M$; $[HTTA]_{(org)} = 0.02\,M$. B: $[H^+]_{(aq)} = 2.0\,M$; $[HTTA]_{(org)} = 0.025\,M$.

[b] At [TBP] = 0, $K_{d(S)} = K_{d(A)}$.

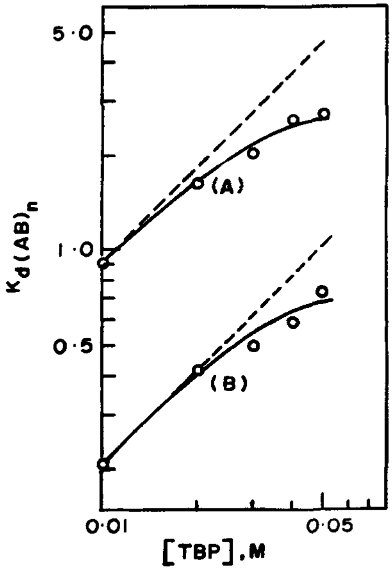

FIG. 2. Variation of $K_{d(AB)_n}$ with TBP concentration in the presence of HTTA. A: $[H^+]_{aq} = 1.0\,M$; $[HTTA]_{org} = 0.02\,M$. B: $[H^+]_{aq} = 2.0\,M$; $[HTTA]_{org} = 0.025\,M$.

TABLE 2

Variation of the Distribution Coefficient of Pu(IV) with TBP Concentration: $[HTTA]_{(org)} = 0.0125\ M$[a]

[TBP] (*M*)	$K_{d(S)}$		$K_{d(AB)}$		$\beta_{(AB)}$	
	A	B	A	B	A	B
0[b]	0.575	0.0308	—	—	—	—
0.002	0.624	0.0341	0.0490	0.0033	42.6	53.6
0.004	0.680	0.0366	0.105	0.0058	45.7	47.1
0.006	0.716	0.0406	0.141	0.0098	40.9	53.0
0.008	0.766	0.0424	0.191	0.0116	41.5	47.1
0.010	0.819	0.0444	0.244	0.0136	42.4	44.2

[a] A: $[H^+]_{(aq)} = 1.0\ M$. B: $[H^+]_{(aq)} = 2.0\ M$.
[b] At [TBP] = 0, $K_{d(S)} = K_{d(A)}$.

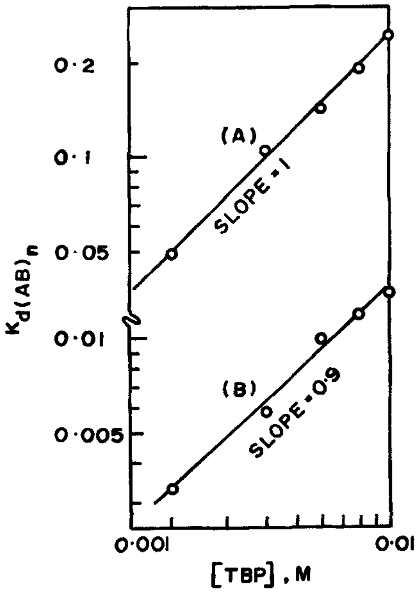

FIG. 3. Variation of $K_{d(AB)_n}$ with TBP concentration in the presence of HTTA. A: $[H^+]_{aq} = 1.0\ M$; $[HTTA]_{org} = 0.0125\ M$. B: $[H^+]_{aq} = 2.0\ M$; $[HTTA]_{org} = 0.0125\ M$.

fraction of either HTTA or TBP concentration. Thus, if

$$[\mathrm{HTTA}]_{(\mathrm{org})} + [\mathrm{TBP}]_{(\mathrm{org})} = \text{constant} = C \tag{14}$$

and

$$[\mathrm{HTTA}]_{(\mathrm{org})} = xC \tag{15}$$

where x is the fraction of [HTTA], it follows that

$$[\mathrm{TBP}]_{(\mathrm{org})} = (1 - x)C \tag{16}$$

If we denote the $K_{d(\mathrm{S})}$ obtained as a function of x as $K^x_{d(\mathrm{S})}$ to differentiate the same from the one so far used, it follows that

$$K^x_{d(\mathrm{S})} = K^x_{d(\mathrm{A})} + K^x_{d(\mathrm{AB})_n} \tag{17}$$

where $K^x_{d(\mathrm{A})}$ is the contribution to $K^x_{d(\mathrm{S})}$ due to extraction of the complex $\mathrm{Pu(TTA)_4}$ when the fraction of [HTTA] is x and $K^x_{d(\mathrm{AB})}$ is the contribution to $K^x_{d(\mathrm{S})}$ due to extraction of the adduct $\mathrm{Pu(TTA)_4(TBP)}_n$ when the fractions of [HTTA] and [TBP] are x and $(1 - x)$, respectively. It follows from Eq. (4), due to fourth power dependence of $K_{d(\mathrm{A})}$ on [HTTA] when $[\mathrm{H}^+]$ = constant, that

$$K^x_{d(\mathrm{A})} = K_{d(\mathrm{A})} \cdot x^4 \tag{18}$$

where

$$K_{d(\mathrm{A})} = K^x_{d(\mathrm{S})} \qquad \text{when} \quad x = 1 \tag{19}$$

Similarly, from Eq. (10), due to fourth power dependence on [HTTA] and nth power dependence on [TBP] of $K_{d(\mathrm{AB})_n}$, it follows that

$$K^x_{d(\mathrm{AB})_n} = K_{d(\mathrm{AB})_n} \cdot x^4 (1 - x)^n \tag{20}$$

Substituting the values of [HTTA] and [TBP] from Eqs. (15) and (16) in Eq. (10), it follows that

$$K_{(\mathrm{AB})_n} = K^x_{d(\mathrm{AB})_n} \cdot [\mathrm{H}^+]^4 x^{-4} \cdot C^{-4} (1 - x)^{-n} \cdot C^{-n} \tag{21}$$

$$= \frac{K^x_{d(\mathrm{AB})_n}}{x^4 (1 - x)^n} \cdot [\mathrm{H}^+]^4 \cdot C^{-(4+n)} \tag{22}$$

$$= K_{d(\mathrm{AB})_n} \cdot [\mathrm{H}^+]^4 \cdot C^{-(4+n)} \tag{23}$$

from which $K_{(\mathrm{AB})_n}$ can be calculated by knowing the values of $[\mathrm{H}^+]$, C, and n.

The results obtained for the extraction of Pu(IV) from perchloric acid into benzene solutions with HTTA and TBP of varying composition are presented in Tables 3–5. Tables 3 and 4 present data where the organic phase [HTTA] + [TBP] was held constant while the aqueous phase acidity differed, and Tables 4 and 5 present data where the aqueous phase acidity was held constant while the organic phase composition [HTTA] + [TBP] differed. From Job's relation *(30)* it follows that for the maximum value of $K^x_{d(\mathrm{AB})_n}$,

$$\frac{m}{n} = \frac{x_{\max}}{(1 - x_{\max})} \tag{24}$$

where *m* and *n* are the numbers of molecules of HTTA and TBP, respectively, associated with the adduct. From the data presented in Tables 3–5,

TABLE 3

Distribution Coefficient Data of Pu(IV) Obtained with Simultaneous Variation of [HTTA] and [TBP]: [HTTA] + [TBP] = 0.025 *M*; $[\mathrm{H}^+]_{(\mathrm{aq})} = 1.0\ M$

x^a	$K^x_{d(\mathrm{S})}$	$K^x_{d(\mathrm{A})}$	$K^x_{d(\mathrm{AB})}$	$K_{d(\mathrm{AB})}$
1	8.58	8.58	—	—
0.9	6.61	5.63	0.98	14.9
0.8	4.58	3.51	1.07	13.1
0.7	3.08	2.06	1.02	14.2
0.6	1.79	1.11	0.68	13.1
0.5	0.977	0.536	0.441	14.1
0.4	0.439	0.220	0.219	14.3
0.3	0.154	0.0695	0.0845	14.9
0.2	0.0317	0.0137	0.018	14.1

[a] x = fraction of [HTTA].

TABLE 4

Distribution Coefficient Data of Pu(IV) Obtained with Simultaneous Variation of [HTTA] and [TBP]: [HTTA] + [TBP] = 0.025 *M*; $[\mathrm{H}^+]_{(\mathrm{aq})} = 2.0\ M$

x^a	$K^x_{d(\mathrm{S})}$	$K^x_{d(\mathrm{A})}$	$K^x_{d(\mathrm{AB})}$	$K_{d(\mathrm{AB})}$
1	0.433	0.433	—	—
0.9	0.320	0.284	0.036	0.549
0.8	0.234	0.177	0.057	0.696
0.7	0.145	0.104	0.041	0.569
0.6	0.0863	0.0561	0.0302	0.583
0.5	0.0458	0.0271	0.0187	0.598
0.4	0.0206	0.0111	0.0095	0.619
0.3	0.00720	0.00351	0.00369	0.651

[a] x = fraction of [HTTA].

TABLE 5

Distribution Coefficient Data of Pu(IV) Obtained with Simultaneous Variation of [HTTA] and [TBP]: [HTTA] + [TBP] = 0.05 M; $[H^+]_{(aq)} = 2.0\ M$

x^a	$K^x_{d(S)}$	$K^x_{d(A)}$	$K^x_{d(AB)}$	$K_{d(AB)}$
1	6.16	6.16	—	—
0.9	4.94	4.04	0.90	13.7
0.8	3.71	2.52	1.19	14.5
0.7	2.58	1.48	1.10	15.3
0.6	1.64	0.80	0.84	16.2
0.5	0.869	0.385	0.484	15.5
0.4	0.394	0.158	0.236	15.4

[a] x = fraction of [HTTA].

it is seen that the maximum value of $K^x_{d(AB)_n}$ is reached when $x_{\max}/(1 - x_{\max}) = 0.8/0.2 = 4$. As it was shown that $m = 4$ (from Fig. 1), it follows that $n = 1$. The values of $K_{d(AB)}$ calculated from Eqs. (17)–(20) are included in Tables 3–5. The remarkable constancy of $K_{d(AB)}$ obtained as a function of x in each case confirms that there is only one adduct formed. By substituting average value of $K_{d(AB)}$ in Eq. (23), the values of $K_{(AB)}$ were calculated and are given in Table 6 along with the values of K_A and $\beta_{(AB)}$. The value of $\beta_{(AB)}$ was obtained from the relation

$$\beta_{(AB)} = K_{(AB)}/K_A \tag{25}$$

which can be derived from Eqs. (1), (6), and (8). The same values calculated

TABLE 6

Summary of the Values of the Concentration Equilibrium Constants: Temperature = 25 °C

Source of the data	log K_A	log K_{AB}	log β_{AB}
Table 2[a]	7.37	9.00	1.63
Table 2[b]	7.31	9.00	1.69
Table 3	7.34	9.16	1.82
Table 4	7.25	9.00	1.75
Table 5	7.20	8.89	1.69
Table 9	—	—	1.89

[a] $[H^+] = 1.0\ M$.
[b] $[H^+] = 2.0\ M$.

from the data given in Table 2 are also included in Table 6 for comparison. The agreement among all the values is quite satisfactory.

Interaction of HTTA and TBP in Benzene

The results presented in Table 1 and Fig. 2 suggested that there might be some interaction between HTTA and TBP in the benzene phase. In order to study this interaction, distribution of HTTA between benzene and 1.0 *M* perchloric acid was studied as a function of the organic TBP concentration. The results obtained are given in Table 7. Time of equilibration for these studies was kept as 3, 4, and 5 hr, and all the timings gave the same equilibrium data. The data presented in this table show that though the interaction is weak, it is significant. Assuming the following equilibrium for the interaction (*3*)

$$[\mathrm{HTTA}]_{\mathrm{org}} + [\mathrm{TBP}]_{\mathrm{org}} \overset{K_{\mathrm{HT}}}{\rightleftharpoons} [\mathrm{HTTA\cdot TBP}]_{\mathrm{org}} \tag{26}$$

the value of the equilibrium constant, K_{HT}, given by

$$K_{\mathrm{HT}} = \frac{[\mathrm{HTTA\cdot TBP}]_{\mathrm{org}}}{[\mathrm{HTTA}]_{\mathrm{org}}[\mathrm{TBP}]_{\mathrm{org}}} \tag{27}$$

was calculated and included in Table 7. Using the value of $K_{\mathrm{HT}} = 2.87$, data presented in Table 1 and Fig. 2 show that the decrease in the values of the slopes with increasing TBP concentration is mainly due to this interaction rather than destruction of synergism, if any.

TABLE 7

Variation of the Distribution Coefficient of HTTA with TBP Concentration: Initial $[\mathrm{HTTA}]_{(\mathrm{org})} = 0.0128$ *M*; $[\mathrm{H}^+]_{(\mathrm{aq})} = 1.0$ *M*; Solvent–Benzene; Temperature = 25 °C

[TBP] (*M*)	$K_{d(\mathrm{T})}$	K_{HT}
0	39.4	—
0.001	39.4	—
0.005	39.4	—
0.010	39.4	—
0.050	44.9	2.89
0.100	51.4	3.17
0.500	88.7	2.54

Spectrophotometric Studies

The absorption spectra of Pu(IV) extracted from either dilute perchloric acid or dilute nitric acid into 0.1 *M* HTTA in benzene are identical with each other, and this shows that the complex species of Pu(IV) extracted into HTTA in benzene is the same irrespective of the aqueous medium employed for extraction. This species is known to be $Pu(TTA)_4$. When increasing amounts of TBP in benzene were added to an HTTA extract of Pu(IV), the absorption spectra showed changes up to a certain concentration of TBP and then remained unaltered at higher TBP concentrations. Typical changes in the spectra are shown in Fig. 4. It is clearly seen from this figure that all the spectra coincide at several well-defined isobestic points, thereby indicating the presence of only two complex species of

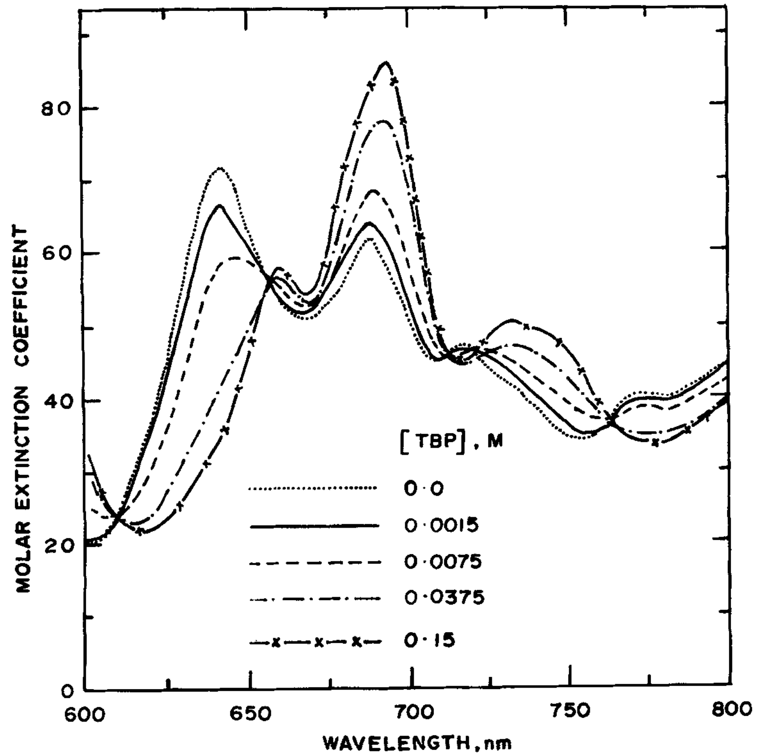

FIG. 4. Changes in the absorption spectra of HTTA extract of Pu(IV) with concentration of TBP added. $[Pu(IV)]_{org} = 1.503 \times 10^{-3}$ *M*.

TABLE 8

Variation of Extinction Coefficient of Pu(IV) Extracted into HTTA in Benzene as a Function of Concentration of TBP Added: $[\mathrm{Pu(IV)}]_{\mathrm{org}} = 1.503 \times 10^{-3}$ *M*

		Molar extinction coefficients ($\bar{E}$, in nm) at	
$[\mathrm{TBP}]_{\mathrm{total}}$ (*M*)	$[\mathrm{TBP}]_{\mathrm{org}}$: $[\mathrm{Pu(IV)}]_{\mathrm{org}}$	642	692
0.0[a]	0	71.2	60.5
0.0015	1	65.9	63.2
0.0030	2	65.2	65.2
0.0075	5	58.8	67.2
0.0150	10	53.9	73.2
0.0375	25	43.9	78.5
0.0750	50	38.6	81.8
0.150[b]	100	35.9	85.2

[a] $\bar{E} = E_1$ when [TBP] = 0.

[b] $\bar{E} = E_2$ when $[\mathrm{TBP}]_{\mathrm{total}}/[\mathrm{Pu(IV)}]_{\mathrm{total}} \simeq 100$.

Pu(IV). It can be concluded from the data obtained by solvent extraction that these are $\mathrm{Pu(TTA)_4}$ and $\mathrm{Pu(TTA)_4 \cdot TBP}$. The extinction coefficient data for two selected wavelengths, which are wide apart and where the changes in the absorbance with TBP added are maximum, are summarized in Table 8. Using these data the values of $\beta_{(\mathrm{AB})}$ were calculated by the method used by Graddon and Walton (*31*), using the relation given by

$$\beta_{(\mathrm{AB})} = \frac{(E_1 - \bar{E})}{(\bar{E} - E_2)[\mathrm{TBP}]_{\mathrm{free}}} \tag{28}$$

where E_1 = molar extinction coefficient of $\mathrm{Pu(TTA)_4}$

E_2 = molar extinction coefficient of $\mathrm{Pu(TTA)_4 \cdot TBP}$

$\bar{E}$ = observed average molar extinction coefficient when both species are present

and

$$[\mathrm{TBP}]_{(\mathrm{free})} = [\mathrm{TBP}]_{(\mathrm{added})} - [\mathrm{Pu(TTA)_4 \cdot TBP}]$$
$$= [\mathrm{TBP}]_{(\mathrm{added})} - [\mathrm{Pu(IV)}]_{(\mathrm{total})} \times \frac{(E_1 - \bar{E})}{(E_1 - E_2)} \tag{29}$$

The interaction between HTTA and TBP is ignored for these calculations because [HTTA] was kept low. The absorption spectrum of Pu(IV) extract, in the absence of any TBP added, was considered to be due to $\mathrm{Pu(TTA)_4}$

TABLE 9

Summary of the $\beta_{(AB)}$ Values Obtained by Spectrophotometry

$[TBP]_{total}$ (M)	$\beta_{(AB)}$ obtained by using the $\bar{E}$ values (in nm) at	
	642	692
0.0015	139[a]	91.9
0.0030	74.7	86.6
0.0075	77.7	52.5
0.0150	67.2	74.4
0.0375	94.0	73.8
0.0750	164[a]	85.0
Average	78.4	77.4

[a] Not taken for calculating the average value.

alone and used to calculate E_1 values at the desired wavelengths. Similarly, the absorption spectrum of the extract when TBP was added was such that $[TBP]_{(total)}/[Pu(IV)]_{(total)} \simeq 100$ was assumed to be that of $Pu(TTA)_4 \cdot TBP$ only and used to calculate E_2 values at required wavelengths. This assumption is reasonably valid as further increase in the $[TBP]_{(total)}/[Pu(IV)]_{(total)}$ ratio did not show any measurable changes in the absorption spectra. The values of $\beta_{(AB)}$ calculated from absorption spectra are summarized in Table 9. It can be seen that the agreement in the $\beta_{(AB)}$ values obtained by using the data for different wavelengths is satisfactory, the average value being $\beta_{(AB)} = 78$. Further, the values of $\beta_{(AB)}$ obtained by solvent extraction and spectrophotometry are also in reasonable agreement with each other.

Some absorption spectra of Pu(IV) were recorded by directly extracting Pu(IV) from perchloric acid solutions into mixtures of HTTA and TBP in benzene. These spectra were identical to those given in Fig. 4 when the organic phase composition was the same. This confirms that there is no additional species of Pu(IV) in the organic phase other than the two suggested species.

From spectrophotometric observations it has been reported (*1*) that in metal/β-diketone/neutral donor synergistic systems the adduct breaks up, resulting in the formation of a metal chelate, probably hydrated, when an excess of water-equilibrated neutral donor is added to the organic solution containing the adduct. In the present work, however, even when a large excess [1000-fold with respect to Pu(IV)] of water-saturated TBP was added to the HTTA extract of Pu(IV) in benzene, the spectrum was the same as that of the adduct, thereby indicating that there is no destruction of the adduct. It is likely that the complex $Pu(TTA)_4$ is coordinatively saturated with a coordination number of 8. TBP, however, being a stronger donor than H_2O, may be able to cause sufficient reorientation of the complex to make it 9-coordinated or an 8-coordinate with the opening of one of the chelating rings to accommodate TBP. The latter may be less probable since it would involve considerable loss of chelation energy (*2*, *33*). Recently it has been reported (*34*) that several such complexes of Th(IV) exhibit 9-coordination, and hence similar Pu(IV) complexes are expected to have the same coordination. It is probable that Pu(IV) is extracted into HTTA as the 9-coordinate hydrate (viz., $Pu(TTA)_4 \cdot H_2O$) and that TBP is exchanged for H_2O in the adduct formation, thus keeping the 9-coordination unaltered. However, the failure to observe any significant changes in the absorption spectrum by adding excess water-equilibrated TBP does not seem to support this view.

A comparison of $\beta_{(AB)}$ values for the formation of the adduct $M(TTA)_4 \cdot TBP$ of tetravalent actinides in benzene reveals that they follow the order Th(IV) (*3*) > U(IV) (*35*) > Np(IV) (*12*) > Pu(IV). This is in conformity with the observation that the stability of the adduct decreases with increasing stability of the chelate as reported (*2*) by Irving.

SYMBOLS

$K_{d(A)}$	$\dfrac{[Pu(TTA)_4]_{(org)}}{[Pu^{4+}]_{(aq)}}$
$K_{d(AB)_n}$	$\dfrac{[Pu(TTA)_4 \cdot n TBP]_{(org)}}{[Pu^{4+}]_{(aq)}}$
$K_{d(S)}$	$\dfrac{[Pu(TTA)_4]_{(org)} + [Pu(TTA)_4 \cdot n TBP]_{(org)}}{[Pu^{4+}]_{(aq)}}$ $= K_{d(A)} + K_{d(AB)_n}$
K_A	$\dfrac{[Pu(TTA)_4]_{(org)}[H^+]^4_{(aq)}}{[Pu^{4+}]_{(aq)}[HTTA]^4_{(org)}}$
$K_{(AB)_n}$	$\dfrac{[Pu(TTA)_4 \cdot n TBP]_{(org)}[H^+]^4_{(aq)}}{[Pu^{4+}]_{(aq)}[HTTA]^4_{(org)}[TBP]^n_{(org)}}$
$\beta_{(AB)_n}$	$\dfrac{[Pu(TTA)_4 \cdot n TBP]_{(org)}}{[Pu(TTA)_4]_{(org)}[TBP]^n_{(org)}}$ $= \dfrac{K_{(AB)_n}}{K_A}$

C	$[\text{HTTA}]_{(\text{org})} + [\text{TBP}]_{(\text{org})}$ $= \text{constant}$
x	concentration fraction of HTTA when the sum of concentrations of HTTA and TBP was kept constant
$K^{x}_{d(\text{S})}$	distribution coefficient of Pu(IV), when $[\text{HTTA}]_{(\text{org})} = xC$ and $[\text{TBP}]_{(\text{org})} = (1 - x)C$
$K^{x}_{d(\text{A})}$	the contribution to $K^{x}_{d(\text{S})}$ due to the extraction of the complex Pu(TTA)_4 $= K_{d(\text{A})} \cdot x^4$
$K^{x}_{d(\text{AB})_n}$	the contribution to $K^{x}_{d(\text{S})}$ due to the extraction of the adduct $\text{Pu(TTA)}_4(\text{TBP})_n$ $= K_{d(\text{AB})_n} \cdot x^4 \cdot (1 - x)^n$
K_{HT}	$\dfrac{[\text{HTTA}\cdot\text{TBP}]_{(\text{org})}}{[\text{HTTA}]_{(\text{org})}[\text{TBP}]_{(\text{org})}}$

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