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Synergistic Extraction of Th(IV) by Mixtures of HTTA and TBP in Benzene

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Abstract

Extraction of Th(IV) from dilute perchloric acid medium by mixtures of HTTA and TBP in benzene medium was studied. The species $Th(TTA)_4 \cdot TBP$ was found responsible for the observed synergism. Equilibrium constants for the extraction equilibria involved are $\log K_A = 2.25$, $\log K_{AB} = 6.88$, and $\log \beta_{AB} = 4.63$.

INTRODUCTION

Synergistic extraction of actinide ions by mixtures of a β-diketone and a neutral donor has been studied extensively (*1*). A limited number of such studies, however, have been devoted to the extraction of tetravalent actinides (*2–4*). In the extraction of Th(IV) by mixtures of thenoyltrifluoroacetone (HTTA) and tri-*n*-butylphosphate (TBP) in cyclohexane, Healy (*3*) appears to have ignored the aqueous phase solubility of HTTA. With cyclohexane as the diluent, the aqueous phase solubility of HTTA is quite appreciable (*5*, *6*). Consequently the extraction data require corrections due to changes in the concentration of HTTA in the organic phase as well as the complexing of Th(IV) by HTTA in the aqueous phase. In similar studies by Sekine and Dyrssen using chloroform and carbon tetra-

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chloride as diluents, the presence of Th(IV) species of the type $Th(TTA)_4 \cdot HTTA$ was indicated. The diluent used is known to have a pronounced effect on synergism. No data on the synergistic extraction of Th(IV) using benzene as diluent have been obtained although Newman (*7*) as well as Sekine and Dyrssen (*4*) have reported the equilibrium constants, estimating them from Healy's data (*8*).

However, such estimates may not be reliable since they involve assumptions of limited validity. In continuation of our work on tetravalent actinides (*9–12*), the synergistic extraction of Th(IV) by mixtures of HTTA and TBP from aqueous perchlorate medium was studied by two methods and the results obtained are reported in the present paper.

EXPERIMENTAL

Materials

^{234}Th was separated from nuclear pure uranium by LaF_3 coprecipitation. The LaF_3 containing ^{234}Th was dissolved in nitric acid in the presence of $Al(NO_3)_3$ followed by $La(OH)_3$ precipitation using NaOH. $La(OH)_3$ was dissolved in 2 *M* nitric acid and ^{234}Th was purified by amine extraction (*13*). HTTA was obtained from E. Merck, Germany, and kept under vacuum over P_2O_5 for several hours. Benzene solution of HTTA was preequilibrated with dilute perchloric acid for several hours. TBP was purified by the method of Alcock et al. (*14*). All the other reagents used were of AR grade.

Procedure

A stock solution of Th(IV) was made in 0.10 *M* perchloric acid. Benzene solutions of HTTA and TBP of required concentrations were made. Equal volumes (3 ml each) of the aqueous perchloric acid (0.1 *M*) containing Th(IV) and the desired organic phase were pipetted into stoppered tubes and equilibrated for 45 minutes in a thermostated water bath kept at 25 ± 0.1°C. Two milliliter aliquots of each phase were then pipetted out for the assay of thorium using a well-type NaI(Tl) detector. All the measurements were done in triplicate, and the agreement in the distribution ratio (D'_M) values obtained was in general within ±3%. Aqueous phase HTTA concentration was estimated spectrophotometrically by measuring its absorbance at 292 nm.

RESULTS AND DISCUSSION

Extraction of Th(IV) from dilute perchloric acid by HTTA in benzene is given by

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

The corresponding equilibrium constant K_A is given by

$$K_A = \frac{[Th(TTA)_4][H^+]^4}{[Th^{4+}][HTTA]^4} = D_{M(A)} \cdot \frac{[H^+]^4}{[HTTA]^4} \tag{2}$$

$$D_{M(A)} = \frac{[Th(TTA)_4]}{[Th^{4+}]} = D'_{M(A)} \cdot F \tag{3}$$

where $D'_{M(A)} = [Th(TTA)_4]/[Th(IV)]$, the observed distribution ratio of Th(IV), and

$$F = 1 + \sum_1^n \beta_n \left\{\frac{[HTTA]_{(aq)}}{[H^+]_{(aq)}}\right\}^n$$

is the factor due to the aqueous phase complexing of Th(IV) by TTA, assuming that perchlorate ion complexing of Th(IV) is not significant. With benzene as the solvent such a correction, though small at lower concentrations of HTTA ($\leqslant 0.02$ *M*), becomes appreciable at higher concentrations. Assuming that $Th(TTA)^{3+}$ is the predominant complex present in the aqueous phase and using the value of $\beta_1 = 16$ (*15*) for the equilibrium,

$$Th^{4+}_{(aq)} + HTTA_{(aq)} \overset{\beta_1}{\rightleftharpoons} Th(TTA)^{3+}_{(aq)} + H^{+}_{(aq)}$$

the factor F was evaluated and used wherever necessary. Figure 1 shows the $D_{M(A)}$ values thus obtained at varying concentrations of HTTA. The fourth power dependency observed of the log $D_{M(A)}$ values on log [HTTA] is in conformity with Eq. (1) and suggests that the extracted complex is $Th(TTA)_4$.

On the other hand, Th(IV) is poorly extracted by TBP from perchlorate media and its extraction by TBP alone, under the conditions used in the present work, is negligible. Thus when a mixture of HTTA and TBP is employed for the extraction of Th(IV), the observed enhancement in the extraction may be explained by assuming the following additional equi-

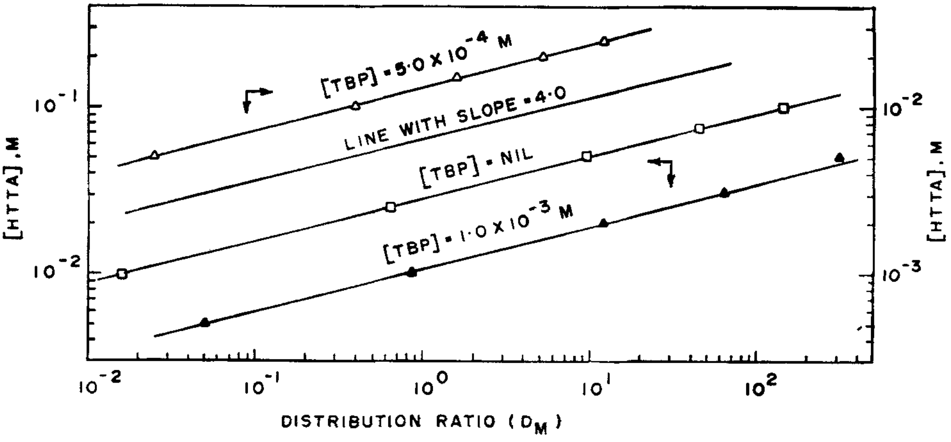

FIG. 1. Variation of the distribution ratio of Th(IV) with HTTA concentration.

librium:

$$\mathrm{Th}^{4+}_{(aq)} + 4\mathrm{HTTA}_{(org)} + Y\mathrm{TBP}_{(org)} \overset{K_{AB}}{\rightleftharpoons} \mathrm{Th(TTA)_4}\cdot Y\mathrm{TBP}_{(org)} + 4\mathrm{H}^{+}_{(aq)} \tag{4}$$

The equilibrium constant K_{AB} can be given as

$$K_{AB} = \frac{[\mathrm{Th(TTA)_4}\cdot Y\mathrm{TBP}][\mathrm{H}^+]^4}{[\mathrm{Th}^{4+}][\mathrm{HTTA}]^4[\mathrm{TBP}]} = D_{M(AB)}\frac{[\mathrm{H}^+]^4}{[\mathrm{HTTA}]^4[\mathrm{TBP}]} \tag{5}$$

where

$$D_{MA(B)} = D'_{M(AB)}\cdot F \quad \text{and} \quad D'_{M(AB)} = [\mathrm{Th(TTA)_4}\cdot Y\mathrm{TBP}]/[\mathrm{Th(IV)}] \tag{6}$$

The variation of D_M ($= D'_M \cdot F$ where D'_M is the observed overall distribution ratio) with [HTTA] was studied at constant [TBP] and [$\mathrm{HClO_4}$], and the results obtained are included in Fig. 1. The slopes of +4 observed for [HTTA] dependence suggest that 4TTA ions are associated with the extracted species, even in the presence of TBP. The variation of $D'_{M(AB)}$ ($= D'_M - D'_{M(A)}$) was studied as a function of [TBP] at constant [HTTA] and [$\mathrm{HClO_4}$], and the data obtained are given in Table 1. The linear plots (Fig. 2) have slopes close to unity, thereby suggesting that one TBP molecule is associated with the extracted species of Th(IV). Thus the complex responsible for synergism has the composition $\mathrm{Th(TTA)_4}\cdot\mathrm{TBP}$ (i.e., $Y = 1$ in Eq. 5). Healy and Ferraro (*16*), who have investigated the synergistic species in Th(IV)–HTTA–TBP–benzene system by absorption

TABLE 1

Variation of the Distribution Ratio of Th(IV) with TBP Concentration: $\mu = [H^+] = 0.1\ M$

No.[a]	[TBP] × 10^3 M	D'_M	$D'_{M(AB)}$	$\beta_{AB} \times 10^{-4}$
1	0	0.232	—	—
2	0.2	2.49	2.26	4.87
3	0.4	4.55	4.32	4.65
4	0.6	6.53	6.30	4.52
5	0.8	9.26	9.03	4.86
6	1.0	11.1	10.9	4.68
7	0	0.0164	—	—
8	2.0	1.58	1.56	4.77
9	4.0	2.91	2.89	4.41
10	6.0	4.14	4.12	4.19
11	8.0	5.26	5.24	4.00
12	10.0	6.71	6.69	4.08

[a] [HTTA] = 0.02 M for Nos. 1–6 and 0.01 M for Nos. 7–12.

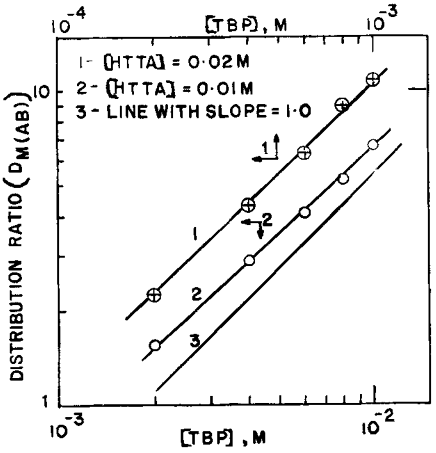

FIG. 2. Variation of the distribution ratio of Th(IV) with TBP concentration.

spectral method, have also reported the same species. From Eqs. (2), (5), and (6) it can be shown that

$$\frac{K_{AB}}{K_A} = \frac{D'_{M(AB)}}{D'_{M(A)}}[\mathrm{TBP}]^{-1} = \beta_{AB} \tag{7}$$

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

$$\mathrm{Th(TTA)_{4(org)}} + \mathrm{TBP_{(org)}} \overset{\beta_{AB}}{\rightleftharpoons} \mathrm{Th(TTA)_4TBP_{(org)}} \tag{8}$$

Using the data given in Table 1, the values of β_{AB} were calculated using Eq. (7) and are included in Table 1. The values of β_{AB} decrease with increasing [TBP] when the [HTTA] and [TBP] used are comparable. This could be mainly due to the interaction between HTTA and TBP (*10*). When due corrections were made, the β_{AB} values were then found to remain constant, the average value being 4.68×10^4. The extraction data were also obtained at much lower concentrations of TBP, where the corrections due to interaction between HTTA and TBP may be neglected, and they are included in Table 1. The values of β_{AB} calculated from these data are reasonably constant, thus supporting the validity of the assumptions. The average value of β_{AB} thus obtained is 4.72×10^4 which is in excellent agreement with that estimated and given above. The values of K_A, K_{AB}, and β_{AB} thus obtained are given in Table 2.

Synergistic extraction of Th(IV) was also studied by Job's method as applied to two-phase systems by the procedure adopted by Gal and Nikolic (*17*). For this, the distribution data were obtained by keeping the

TABLE 2

Summary of the Equilibrium Constants: Solvent-Benzene

Aqueous medium	Log K_A	Log K_{AB}	Log β_{AB}	Refs.
0.10 *M* $HClO_4$[a]	2.25	6.92	4.67	This work
[b]	2.25	6.87	4.62	This work
[c]	2.25	6.84	4.59	This work
0.10 *M* HCl	1.00	5.70	4.7	*7*
	—	—	7.2	*4*
1.0 *M* $NaClO_4$ (0.1 *M* $[H^+]$)	1.38	—	—	*18*
$\mu = 2.0$	1.34	—	—	*19*

[a] Data from Table 1.
[b] Data from Table 3.
[c] Data from Table 4.

total concentration of HTTA + TBP constant and varying the fraction of each component. The D'_M values thus obtained are shown in Fig. 3. At both the concentrations studied, 0.01 and 0.02 *M*, the maximum $D'_{M(AB)}$ value was obtained when the ratio of [HTTA]/[TBP] = 8/2 = 4/1, thus giving the composition of the extracted species to be $Th(TTA)_4 \cdot TBP$. This is in conformity with the conclusions reached earlier. If x is the fraction of [HTTA] when [HTTA] + [TBP] = C, it follows that [HTTA] = xC and [TBP] = $(1 - x)C$. By substituting these values for [HTTA] and [TBP] and $Y = 1$ in Eq. (5), it follows that

$$K_{AB} = D_{M(AB)} \cdot [H^+]^4 x^{-4} (1 - x)^{-1} C^{-5} \tag{9}$$

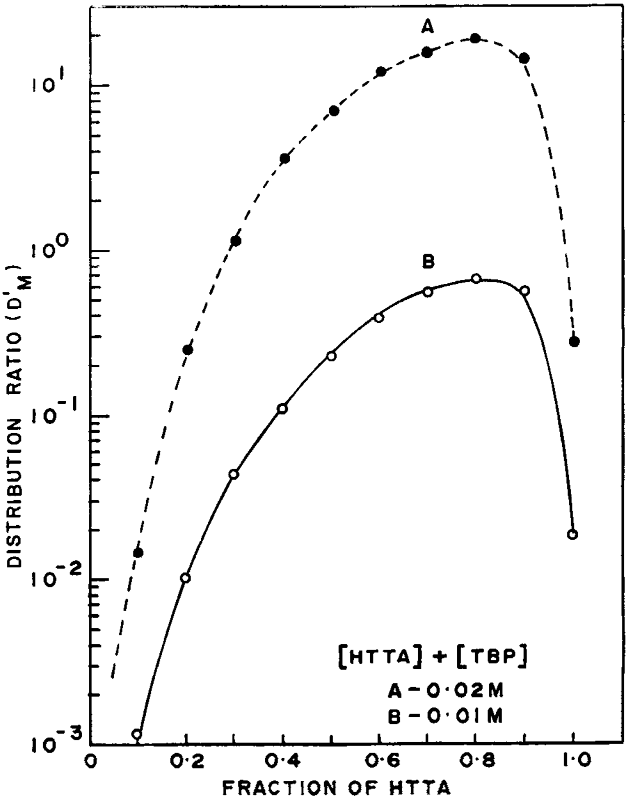

FIG. 3. Variation of distribution ratio of Th(IV) with fraction of [HTTA] when [HTTA] + [TBP] is constant.

Rearranging Eq. (9):

$$D_{\mathrm{M(AB)}} \cdot x^{-4}(1-x)^{-1} = K_{\mathrm{AB}}[\mathrm{H}^+]^{-4}C^5 = D \qquad (10)$$

where D is a constant as $[\mathrm{H}^+]$ and C are constants. The values of D'_{M}, $D'_{\mathrm{M(AB)}}$, and D thus obtained for $C = 0.01\ M$ are given in Table 3 and for $C = 0.02\ M$ are given in Table 4. The constancy of the values of D obtained in both cases confirms the validity of Eq. (10). Using the average

TABLE 3

Data on the Distribution Ratio of Th(IV) as a Function of Simultaneous Variation of [HTTA] and [TBP]. Aqueous pH = 0.10 M; $\mathrm{HClO_4}$; [HTTA] + [TBP] = 0.10 M

x	D'_{M}	$D'_{\mathrm{M(AB)}}$	D
1	0.0182	—	—
0.9	0.552	0.540	8.23
0.8	0.644	0.637	7.78
0.7	0.525	0.521	7.23
0.6	0.379	0.377	7.27
0.5	0.222	0.221	7.07
0.4	0.107	0.107	6.97
0.3	0.0434	0.0430	7.58
0.2	0.0101	0.0097	7.58
0.1	0.00114	0.00069	7.67
0	0.00056	—	—

TABLE 4

Data on the Distribution Ratio of Th(IV) as a Function of Simultaneous Variation of [HTTA] and [TBP]. Aqueous pH = 0.10 M; [HTTA] + [TBP] = 0.02 M $\mathrm{HClO_4}$

x	D'_{M}	$D'_{\mathrm{M(AB)}}$	D
1	0.268	—	—
0.9	14.3	14.2	216
0.8	18.7	18.6	226
0.7	15.4	15.4	213
0.6	11.8	11.8	227
0.5	6.93	6.91	221
0.4	3.63	3.62	236
0.3	1.15	1.14	202
0.2	0.245	0.245	191
0.1	0.0146	0.0146	162
0	0.00004	—	—

values of D and Eq. (9), the values of K_{AB} were obtained and are included in Table 2. It is seen that all the values obtained by the two methods are in good agreement. Estimated values reported in the literature are included in this table for comparison.

It is seen from the data given in Table 2 that K_A values depend on the composition of the aqueous phase used. The values of K_A for 0.1 M $HClO_4$ or HCl may not differ very much, and hence the value of $K_A = 10$ used by Newman (*7*) appears to be too low. Furthermore, the estimated value of K_{AB} is also much lower than that obtained in the present work. Although the β_{AB} value reported by him is close to that obtained in the present work, such an agreement is fortuitous. The estimated value of β_{AB} by Sekine and Dyrssen (*4*) is too high, and it is not clear from their paper how the estimation was done. To understand the effects of aqueous media and organic solvents on K_A, K_{AB}, and β_{AB}, more work is now in progress.

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