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Synergistic Extraction of Np(IV) by Mixtures of HTTA and TBP in Chloroform

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Abstract

Extraction of Np(IV) from perchloric acid medium by chloroform solutions of HTTA and TBP was studied. The species $\text{Np}(\text{TTA})_4 \cdot \text{TBP}$ was found to be mainly responsible for the observed synergism. Equilibrium constants for the extraction equilibria involved were obtained.

INTRODUCTION

Compared to metal ions in other oxidation states, synergistic solvent extraction of tetravalent ions by mixtures of β -diketones and neutral donors has not received much attention. We have recently initiated studies on the extraction of tetravalent actinides by mixtures of thenoyltrifluoroacetone (HTTA) with several neutral donors and reported some results on the extraction of Th(IV) (1, 2), U(IV) (3-6), Np(IV) (7, 8), and Pu(IV) (9, 10). In continuation of these studies the results obtained on the extraction of Np(IV) from perchloric acid medium by chloroform solutions of HTTA and tri-*n*-butylphosphate (TBP) are reported here. The effect of diluents on the synergistic extraction of tetravalent actinides is also discussed.

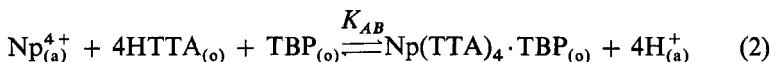
EXPERIMENTAL

All the materials used in this work were the same as those described earlier (7, 8). Analar chloroform was washed thoroughly with water before

use. Chloroform solutions of HTTA were preequilibrated with dilute perchloric acid for several hours. The procedure for the measurement of distribution ratios of Np(IV) was the same as described earlier (7, 8).

RESULTS AND DISCUSSION

The extraction of Np(IV) from perchloric acid by HTTA and mixtures of HTTA and TBP may be represented, respectively, by the following equilibria:



The subscripts (a) and (o) refer to aqueous and organic media, respectively. The equilibrium constants K_A and K_{AB} are given by

$$K_A = \frac{[\text{Np}(\text{TTA})_4][\text{H}^+]^4}{[\text{Np}^{4+}][\text{HTTA}]^4} = D_A \frac{[\text{H}^+]^4}{[\text{HTTA}]^4} \quad (3)$$

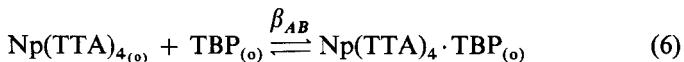
where $D_A = [\text{Np}(\text{TTA})_4]_{(o)}/[\text{Np}^{4+}]_{(a)}$ is the distribution ratio of Np(IV) with HTTA alone as the extractant, and

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

where $D_{AB} = D - D_A$, and D is the measured distribution ratio of Np(IV) with a mixture of HTTA and TBP as the extractant. It follows from Eqs. (3) and (4) that

$$\frac{K_{AB}}{K_A} = \frac{D_{AB}}{D_A[\text{TBP}]} = \beta_{AB} \quad (5)$$

where β_{AB} is the equilibrium constant for the equilibrium shown in



Distribution ratios of Np(IV) obtained as a function of concentration of HTTA at constant aqueous phase acidity (1.0 M HClO_4) using chloroform as diluent are plotted in Fig. 1. The logarithmic plot of D_A against $[\text{HTTA}]$ has a slope of 4.0 in accordance with Eq. (3), but a plot of similar data obtained in the presence of TBP has a slightly lower slope. This could be due to partial extraction of an additional species, such as $[\text{Np}(\text{TTA})_3(\text{TBP})_n]^+ \text{ClO}_4^-$. Distribution ratios of Np(IV) obtained as a

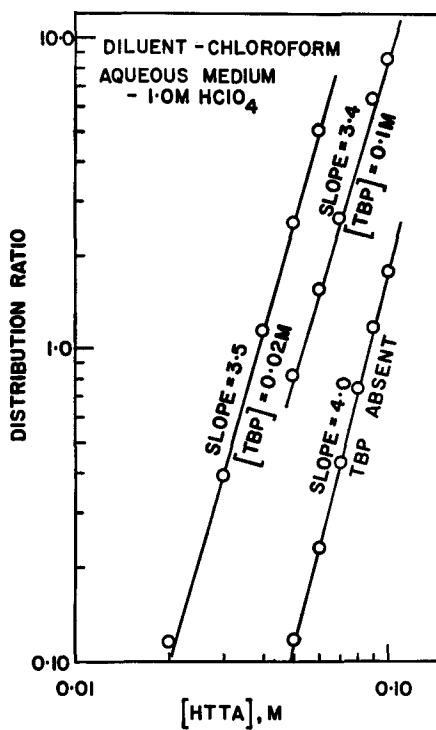


FIG. 1. Variation of the distribution ratio of Np(IV) with concentration of HTTA.

function of hydrogen ion concentration at constant ionic strength (1.0 M) and at constant HTTA concentration are plotted in Fig. 2. The slopes obtained, both in the absence and presence of TBP, are quite close to -4.0 in accordance with the predictions of Eqs. (3) and (4).

Data on the variation of the distribution ratio of Np(IV) with TBP concentration at constant HTTA concentration are given in Table 1. The plot of D_{AB} versus [TBP] (Fig. 3) has a slope of +1 in accordance with Eq. (4), suggesting that one molecule of TBP is associated with the adduct. The β_{AB} values are calculated from these data using Eq. (5) and are included in Table 1. The values obtained at a particular concentration of HTTA are reasonably constant though they differ to a small extent from those obtained at another concentration of HTTA. An average of $\beta_{AB} = 44$ was taken from these data. Using $K_A = 1.83 \times 10^4$, obtained from several values of the distribution ratios of Np(IV) with HTTA alone, the value of $K_{AB} = 8.05 \times 10^5$ was calculated using Eq. (5). The calculation of K_{AB} by the Job's method was also attempted using the

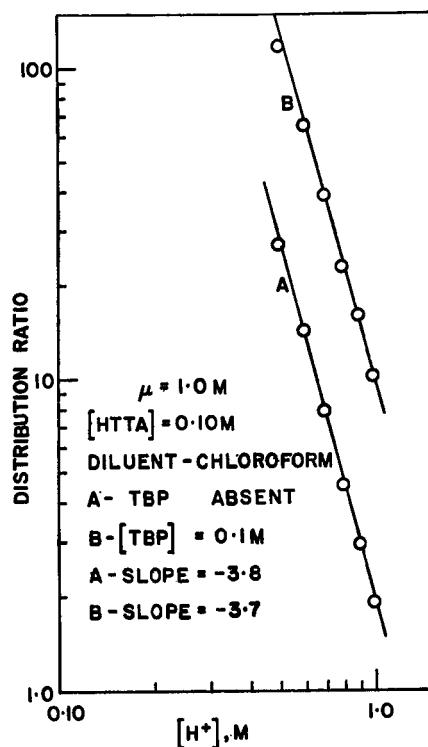


FIG. 2. Variation of the distribution ratio of Np(IV) with hydrogen ion concentration.

TABLE I
Variation of the Distribution Ratio of Np(IV) with TBP Concentration
(aqueous phase: 1.0 M HClO_4)

[TBP] <i>M</i>	[HTTA] = 0.05 <i>M</i>			[HTTA] = 0.10 <i>M</i>		
	<i>D</i>	D_{AB}	β_{AB}	<i>D</i>	D_{AB}	β_{AB}
0	0.124	—	—	1.82	—	—
0.02	0.244	0.120	48.4	3.33	1.51	41.5
0.04	0.369	0.245	49.4	4.65	2.83	38.9
0.06	0.504	0.380	51.1	6.33	4.51	41.3
0.08	0.618	0.494	49.8	7.18	5.36	36.8
0.10	0.756	0.632	51.0	8.36	6.54	35.9

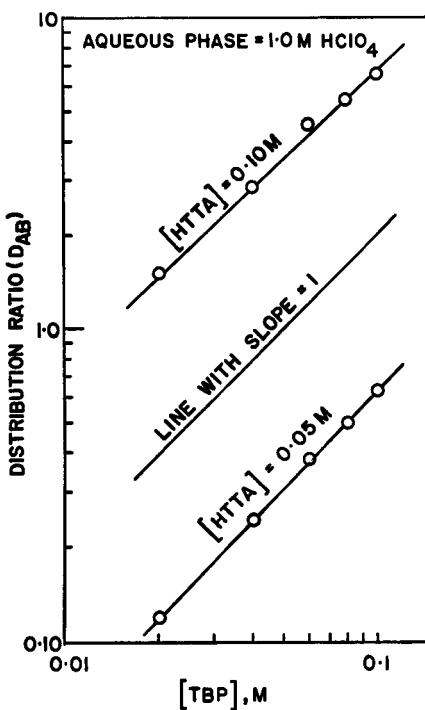


FIG. 3. Variation of the distribution ratio of Np(IV) with concentration of TBP.

TABLE 2

Data for the Distribution Ratio of Np(IV) with Simultaneous Variation of [HTTA] and [TBP] ($[HTTA] + [TBP] = 0.10\text{ M}$; aqueous phase = 1.0 M HClO_4)

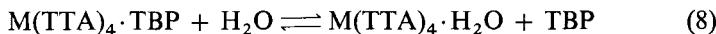
x	D	D_{AB}	$D_{AB}/x^4(1 - x)$
1	1.73	—	—
0.9	1.60	0.465	7.09
0.8	1.32	0.611	7.46
0.7	1.03	0.615	8.54
0.6	0.712	0.488	9.41
0.5	0.447	0.339	10.9
0.4	0.251	0.207	13.5
0.3	0.125	0.111	19.6

procedures adopted by Gal and Nikolic (11). In this method, data on the distribution ratios of Np(IV) were obtained by keeping the total concentration of HTTA and TBP constant and varying the fractions of the two components. Thus, if $[HTTA] + [TBP] = C$ and $[HTTA] = xC$, it follows that $[TBP] = (1 - x)C$. By incorporating these values in Eq. (4), it follows that

$$K_{AB} = \frac{D_{AB}}{x^4(1 - x)} \frac{[H^+]^4}{C^5} \quad (7)$$

The data obtained using $C = 0.1 M$ are given in Table 2. The values of $D_{AB}/x^4(1 - x)$ increase slightly with decreasing values of x . This increase may be due to the extraction of an additional species apart from $Np(TTA)_4 \cdot TBP$, whose contribution to the extraction probably increases with increasing TBP concentration. Assuming that the extraction of the additional species will be negligible when $[TBP] \rightarrow 0$, the value of $D_{AB}/x^4(1 - x) = 6.8$ was obtained by extrapolating the values given in Table 2 to $x = 1$. Using this value, $K_{AB} = 6.8 \times 10^5$ was calculated from Eq. (7). This value is quite close to that obtained earlier. The additional species that seems to be involved in the extraction may be of the type $[Np(TTA)_3(TBP)_n]^+ClO_4^-$. In the extraction of lanthanides by mixtures of HTTA and TOPO using polar diluents such as dichloromethane, 1,2-dichloroethane, or nitrobenzene, it was established (12) that the predominant species extracted is $[Ln(TTA)_2(TOPO)_5]^+ClO_4^-$. Our earlier spectrophotometric studies (7) on the extraction of Np(IV) by mixtures of HTTA and TBP in nitrobenzene also revealed that the predominant species extracted is not $Np(TTA)_4 \cdot TBP$. More work is necessary to establish the stoichiometry of the mixed adduct involved in the extraction by using polar diluents such as chloroform.

The equilibrium constant values obtained in the present work are summarized in Table 3 along with literature values for the extraction of tetravalent actinides by mixtures of HTTA and TBP. The synergistic extraction of tetravalent actinides is very much dependent on the diluent used and follows the order cyclohexane > benzene > chloroform. This order is the same as that reported by Healy for extraction of Th(IV). Healy attributed the diluent effect to the change in water content of the organic phase with the diluent used (13). If the water present in the organic phase interacts with the adduct to result in the metal chelate



such an interaction is expected to depend very much on the metal ion present in the adduct. From the data presented in Table 3, the ratio of the β_{AB} values in different diluents, obtained for a given metal ion, remains

TABLE 3
Summary of Equilibrium Constants (aqueous phase = 1.0 M HClO₄;
temperature = 25°C)

M ⁺⁴	Diluent	log K _A	log K _{AB}	log β _{AB}	Ref.
Np	Chloroform	4.26	5.88	1.62	This work
	Benzene	5.57	8.34	2.75	7
	Cyclohexane	6.14	10.45	4.31	8
Pu	Benzene	7.34	9.06	1.72	9
	Cyclohexane	7.74	11.11	3.37	10
Th	Chloroform	1.00	4.24	3.24	2 ^a
	Benzene	2.25	6.89	4.63	1 ^a
	Cyclohexane	2.73	8.80	6.07	2 ^a
U	Benzene	5.42	8.46	3.04	3

^aAqueous phase = 0.1 M HClO₄.

roughly constant irrespective of the metal ion involved. Thus it is doubtful whether the change in content of water, which is too poor a donor to replace TBP in the adduct, of the organic phase causes the observed differences in synergism with diluents. More work is required to elucidate the mechanism.

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