

## Spectrophotometric studies on the formation of adducts involved in the extraction of U(VI) by mixtures of HTTA with some neutral extractants

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**Abstract.** The adduct formation of  $\text{UO}_2(\text{TTA})_2$  with the neutral donors TBP, DBBP and TOPO, in benzene, was investigated spectrophotometrically and it was found that each of these donors form a 1 : 1 adduct with  $\text{UO}_2(\text{TTA})_2$ . It was also shown spectrophotometrically that the adduct  $\text{UO}_2(\text{TTA})_2 \cdot \text{S}$  can also be formed, in the organic medium according to the equilibrium,  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{S} + 2\text{HTTA} + \text{S} \rightleftharpoons \text{UO}_2(\text{TTA})_2 \cdot \text{S} + 2(\text{HNO}_3 \cdot \text{S})$

**Keywords.** Solvent extraction ; synergism ;  $\text{UO}_2(\text{TTA})_2$ -neutral donor adducts.

### 1. Introduction

Synergic solvent extraction of U(VI) by mixtures of thenoyltrifluoroacetone (HTTA) in combination with various neutral extractants (S) was studied by several workers. It was inferred that the adduct formation responsible for the observed synergism occurs in the organic phase and the composition of the adducts and their formation constants were estimated from the extraction data. No work, however, was reported on such adduct formation studies, directly in organic media. The adduct formation between copper chelates and neutral donors (Graddon and Watton 1961 ; Walker and Li 1965 ; Dyrssen and Petkovic 1965) and between U(IV) (Ramakrishna *et al* 1980 ; Patil *et al* 1979 ; Patil and Ramakrishna 1979), Np (IV) (Patil *et al* 1981a) and Pu(IV) (Ramakrishna *et al* 1979 ; Patil *et al* 1980b ; Patil *et al* 1981d) chelates and neutral donors, in organic media, has been successfully demonstrated by using spectrophotometric methods. In the present work the adduct formation between  $\text{UO}_2(\text{TTA})_2$  and the neutral donors tri-*n*-butyl-phosphate (TBP), di-*n*-butyl-*n*-butylphosphonate (DBBP) and tri-*n*-octyl phosphine oxide (TOPO), in benzene, was investigated spectrophotometrically and the results are reported here.

In the extraction of U(VI) by mixtures of HTTA and TBP, from nitric acid medium, it was reported (Irving and Edgington 1960) that the observed syner-

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gism was due to the formation of the adducts  $\text{UO}_2(\text{TТА})_2$ , TBP and  $\text{UO}_2(\text{NO}_3)_2 \cdot \text{TТА} \cdot \text{TBP}$ . In a reinvestigation of that work (Patil *et al* 1981c) no evidence for the presence of the latter mixed adduct could be found. It was therefore, felt interesting to study the nature of the equilibrium between  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$  and  $\text{UO}_2(\text{TТА})_2 \cdot \text{TBP}$  in the organic phase and see whether any mixed  $\text{NO}_3$ —TТА adduct is formed. Such systems involving the donors TBP and DBBP were investigated spectrophotometrically and the results are included here.

## 2. Experimental

### 2.1. Materials

Analar grade uranyl nitrate hexahydrate was obtained from M/s BDH Chemicals Ltd., England. TBP was obtained from M/s Monsanto chemicals USA, and was purified (Alcock *et al* 1956). DBBP was obtained from M/s K and K labs USA and was purified (Healy *et al* 1977). TOPO and HTTA (M/s E. Merck, West Germany) were kept under vacuum, for a few hours, before use.

The compound  $\text{UO}_2(\text{TТА})_2$  was prepared (Prasad 1963) by mixing alcoholic solutions of uranyl nitrate and HTTA, the former slightly in excess over the stoichiometric ratio, and then precipitating  $\text{UO}_2(\text{TТА})_2$  by addition of excess water. The precipitate was washed thoroughly with alcohol-water mixture and vacuum dried, in a desiccator, over  $\text{P}_2\text{O}_5$ . The m.p. ( $212^\circ\text{C}$ ) and DTA curve of the compound were in agreement with the reported (Prasad 1963) data. Stock solutions of  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$  and  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{DBBP}$  in benzene were prepared by equilibrating 0.10 M TBP in benzene and 0.10 M DBBP in benzene respectively, with solid uranyl nitrate hexahydrate. The solutions were analysed for their uranium concentration which was found to be 0.05 M in each case and this is in agreement with the formulae given. Benzene solutions of  $\text{TBP} \cdot \text{HNO}_3$  and  $\text{DBBP} \cdot \text{HNO}_3$  were prepared by equilibrating the donors with required quantities of conc. nitric acid. All other chemicals used were of Analar grade.

### 2.2. Procedure

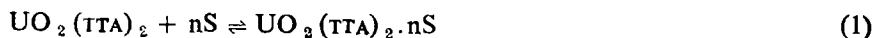
For studying the equilibria between  $\text{UO}_2(\text{TТА})_2$  and the neutral donors (S) several solutions of a fixed concentration of  $\text{UO}_2(\text{TТА})_2$  with varying concentrations of neutral donor under investigation were prepared. The absorption spectra of these solutions were recorded, in the visible region, using Cary—14 recording spectrophotometer employing 10 cm path length cells. The neutral donors, at the concentrations used, were not found to absorb, in the wavelength region studied.

For studying the equilibria involving  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{S}$ , several solutions  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{S}$  with varying concentrations of HTTA and S were made and their absorption at a few fixed wavelengths was recorded. The same equilibria were also studied by following the absorption of a number of solutions of  $\text{UO}_2(\text{TТА})_2$  containing different amounts of S and  $\text{S} \cdot \text{HNO}_3$ .

### 3. Results

#### 3.1. Adduct formation between $\text{UO}_2(\text{TTA})_2$ and S

The formation of adducts between  $\text{UO}_2(\text{TTA})_2$  and a neutral donor S can be represented as



The absorption spectrum of  $\text{UO}_2(\text{TTA})_2$  and the changes caused to it by addition of different amounts of TOPO (figure 1) showed the presence of isosbestic points suggesting that there are only two absorbing species present in the system viz.,  $\text{UO}_2(\text{TTA})_2$  and an adduct of it with TOPO. The plots of the change in absorbance, at fixed wavelengths, with  $[\text{TOPO}] / [\text{U(VI)}]$  (figure 2) showed that the absorption data correspond with the formation of a 1:1 adduct between  $\text{UO}_2(\text{TTA})_2$  and TOPO. The spectral data did not give any indication regarding the formation of any higher adducts though the formation of  $\text{UO}_2(\text{TTA})_2 \cdot 2 \text{TOPO}$  (Healy 1961a) or  $\text{UO}_2(\text{TTA})_2 \cdot 3 \text{TOPO}$  (Healy 1961b) were reported from extraction studies and that of  $\text{UO}_2(\text{TTA})_2 \cdot 3 \text{TOPO}$  was reported (Ferraro and Healy 1962) from structural studies. Similar spectral data obtained with DBBP and TBP showed that the adducts formed are, respectively,  $\text{UO}_2(\text{TTA})_2 \cdot \text{DBBP}$  and  $\text{UO}_2(\text{TTA})_2 \cdot \text{TBP}$ .

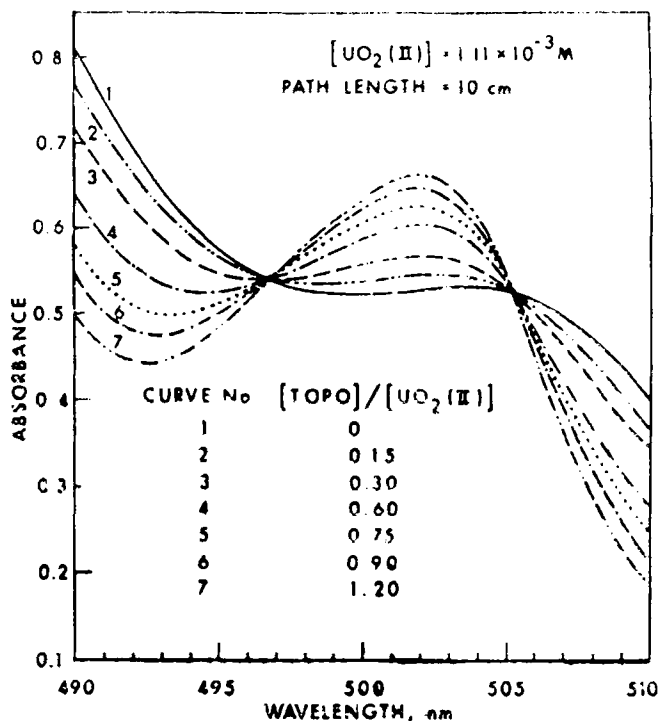


Figure 1. Absorption spectra of benzene solutions of  $\text{UO}_2(\text{TTA})_2$  and the changes caused to it by the addition of TOPO.

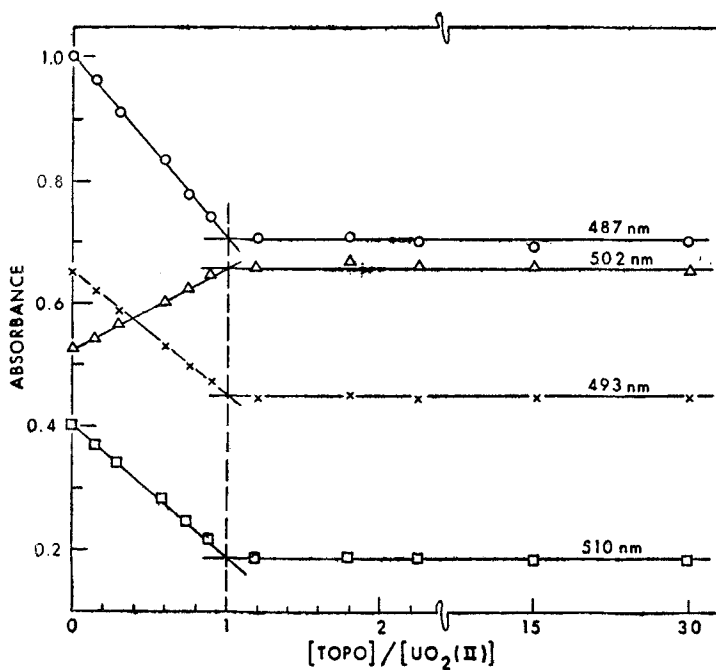


Figure 2. Variation of the absorbance value of U (VI) with  $[TOPO]/[U(VI)]$ .

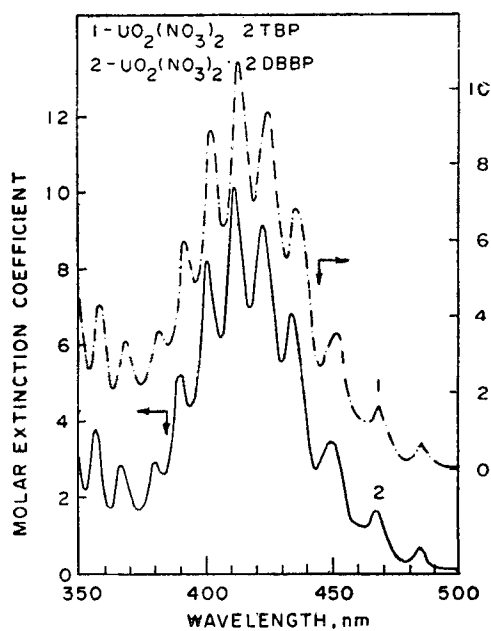


Figure 3. Absorption spectra of  $UO_2(NO_3)_2 \cdot 2TBP$  and  $UO_2(NO_3)_2 \cdot 2DBBP$  in benzene.

3.2. Equilibria involving  $UO_2(NO_3)_2 \cdot 2S$  and  $UO_2(TTA)_2 \cdot S$ 

The absorption spectra of  $UO_2(NO_3)_2 \cdot 2TBP$  and  $UO_2(NO_3)_2 \cdot 2DBBP$ , in benzene are shown in figure 3. The spectra are identical to one another and their molar extinction coefficient values, in the wavelength region shown, are much lower as compared to those observed for  $UO_2(TTA)_2$  or  $UO_2(TTA)_2 \cdot S$ . When different amounts of HTTA were added to a solution of  $UO_2(NO_3)_2 \cdot 2TBP$ , in presence of excess but constant (TBP), the extinction coefficient values continuously increased finally reaching a constant. The latter constant value was the same as that of  $UO_2(TTA)_2 \cdot TBP$ , observed earlier, thereby indicating complete conversion of  $UO_2(NO_3)_2 \cdot 2TBP$  to  $UO_2(TTA)_2 \cdot TBP$ . From the data obtained (table 1) the constant  $\beta$  for the equilibrium represented by equation



was calculated as given below.

The equilibrium constant  $\beta$  is given by

$$\beta = [UO_2(TTA)_2 \cdot TBP] [TBP \cdot HNO_3]^2 / [UO_2(NO_3)_2 \cdot 2TBP] [HTTA_2]^2 [TBP] \quad (3)$$

when a given absorption spectrum is due to a mixture of two absorbing species the observed molar extinction coefficient,  $E$ , at a particular wavelength, can be given by the relation,

$$EC = E_1 C_1 + E_2 C_2 \quad (4)$$

In the present case, the total concentrations ( $C$ ) of the absorbing uranyl ion is given by

$$C = C_1 + C_2 \quad (5)$$

Table 1. Spectrophotometric data concerning the equilibrium,  $UO_2(NO_3)_2 \cdot 2TBP + 2HTTA + TBP \xrightleftharpoons{\beta} UO_2(TTA)_2 \cdot TBP + 2(TBP \cdot HNO_3)$

$$[U(VI)] = 6.3 \times 10^{-4} \text{ M.}$$

[TBP] M × 10	[HTTA] M × 10 <sup>3</sup>	E at, (nm)			β at, (nm)		
		430	440	450	430	440	450
0.101	6.24	881	560	400	0.31	0.31	0.29
0.101	3.12	590	373	270	0.26	0.26	0.26
0.198	3.12	643	421	314	0.35	0.22	0.25
0.0513	6.24	714	437	302	0.24	0.20	0.18
	E <sub>1</sub>	6	5	3			
	E <sub>2</sub>	1446	915	665			

here  $C_1$  and  $C_2$  are the concentrations and  $E_1$  and  $E_2$  are the molar extinction coefficients of  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$  and  $\text{UO}_2(\text{HTTA})_2 \cdot \text{TBP}$ , respectively. From the observed  $E$  values it can be shown from (4) and (5) that

$$C_1 = C(E_2 - E)/(E_2 - E_1) \quad (6)$$

$$\text{and } C_2 = C(E - E_1)/(E_2 - E_1) \quad (7)$$

If one denotes the total concentrations of TBP, HTTA and  $\text{TBP} \cdot \text{HNO}_3$  respectively as  $a$ ,  $b$  and  $d$  and their equilibrium concentrations respectively as  $a_1$ ,  $b_1$  and  $d_1$ , it follows from (2) that,

$$a_1 = a - c_2 - 2C_1 \quad (8)$$

$$b_1 = b - 2C_2 \quad (9)$$

$$\text{and } d_1 = d - 2C_2 \quad (10)$$

The equilibrium constant  $\beta$ , represented by (3) can now be rewritten as

$$\beta = c_2 \cdot d_1^2 / c_1 \cdot b_1^2 \cdot a_1 \quad (11)$$

The values of  $\beta$ , thus obtained using the data, at different wavelengths, and at different concentrations of TBP and HTTA are included in table 1. From these an average value of  $\beta = 0.26 \pm 0.05$  was obtained for equation (2).

The equilibrium represented by (2) was also studied in reverse by the addition of different amounts of  $\text{TBP} \cdot \text{HNO}_3$  to a solution of  $\text{UO}_2(\text{HTTA})_2$  in excess TBP and recording the spectral changes. The data obtained are given in table 2 and from these data the equilibrium constant  $\beta^*$  ( $=1/\beta$ ) was calculated and the values of  $\beta^*$  are also included in table 2, the average value being  $\beta^* = 3.1 \pm 0.5$ . The value of  $d_1$  for these calculations is given by,

$$d_1 = d - 2C_1 \quad (12)$$

Table 2. Spectrophotometric data concerning the equilibrium,  $\text{UO}_2(\text{HTTA})_2 \cdot \text{TBP} + 2(\text{TBP} \cdot \text{HNO}_3) \rightleftharpoons \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP} + 2\text{HTTA} + \text{TBP}$ .

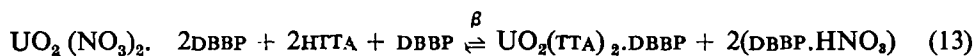
$$[\text{U(VI)}] = 5.79 \times 10^{-4} \text{ M}, [\text{TBP} \cdot \text{HNO}_3] = 1.844 \times 10^{-3} \text{ M}.$$

[TBP] M × 10 <sup>2</sup>	[HTTA] M × 10 <sup>3</sup>	E at, (nm)			β* = 1/β at, (nm)		
		430	440	450	430	440	450
1.50	7.56	320	192	117	2.8	3.2	4.3
1.50	14.0	583	364	244	2.7	2.8	3.4
2.75	7.56	451	278	183	2.8	2.9	3.6
1.38	7.56	825	520	356	2.5	2.2	3.6
2.75 <sup>(a)</sup>	14.0	730	456	307	2.8	2.9	3.6
	$E_1$	6	5	3			
	$E_2$	1446	915	665			

(<sup>a</sup>)  $(\text{TBP} \cdot \text{HNO}_3) = 9.22 \times 10^{-4} \text{ M}$ .

It can be seen that the values of  $\beta$  obtained by approaching the equilibrium, represented by (2), either way are in good agreement with one another.

Similar results obtained in the study of the equilibrium



are given in table 3, for which an average value of  $\beta = 0.48 \pm 0.05$  was obtained. This equilibrium was also confirmed by approaching it in a reverse way as described above for TBP.

#### 4. Discussion

This study, thus supports the conclusion arrived at from solvent extraction work that synergism in the extraction of U(VI) by mixtures of HTTA and a neutral donor is due to the formation of an adduct between the metal chelate and the neutral donor, in the organic phase. Besides, it is established that there exists an equilibrium between the synergic adduct and the neutral donor complex of the metal salt, which, in fact, decides the extent of synergism when metal ion is extracted from an aqueous medium from which the neutral donor alone is able to extract the metal ion. The present study did not reveal the presence of and mixed adduct such as  $\text{UO}_2(\text{NO}_3)(\text{TTA}) \cdot \text{TBP}$  and, thus, is in agreement with the recent extraction studies (Patil *et al* 1981c). The absence of such a mixed adduct in these systems is surprising since a number of such mixed  $\text{NO}_3\text{-TTA-S}$  adducts were shown to be formed in the extraction of trivalent lanthanides (Cox and Davis 1973; Cunninghame *et al* 1954; Gerow *et al* 1977; Hayden *et al* 1974; Irving and Edgington 1961b) as well as trivalent (Cox and Davis 1973; Irving and Edgington 1961b; Ramanujam *et al* 1981) and tetravalent (Irving and Edgington 1961a; Patil *et al* 1980c; Patil *et al* 1981b) actinides from nitrate media. Thus the lack of formation of such a mixed adduct by uranyl ion can probably be ascribed only to limitations due to structural factors. Recent

Table 3. Spectrophotometric data concerning the equilibrium,  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{DBBP} + 2\text{HTTA} + \text{DBBP} \stackrel{\beta}{\rightleftharpoons} \text{UO}_2(\text{TTA})_2 \cdot \text{DBBP} + 2(\text{DBBP} \cdot \text{HNO}_3)$ .  
 $[\text{U(VI)}] = 6.25 \times 10^{-4} \text{ M}$

[DBBP] M	[HTTA] M $\times 10^3$	E at, (nm)			$\beta$ at, (nm)		
		420	430	440	420	430	440
0.101	0.625	322	216	144	0.44	0.48	0.55
0.101	1.25	510	344	226	0.43	0.47	0.52
0.101	1.56	590	396	260	0.43	0.47	0.51
0.101	3.13	876	592	384	0.38	0.43	0.46
0.0513	3.13	768	512	332	0.56	0.47	0.50
0.0263	3.13	644	436	280	0.45	0.50	0.51
	$E_1$	7	6	6			
	$E_2$	1952	1280	816			

work on synergic extraction of Np(VI) (Patil *et al* 1980a) has also shown that  $\text{NpO}_2(\text{NO}_3)$  (TIA).TBP is not involved in the extraction. It would be interesting to know what factors prevent the formation of such mixed species in case of hexavalent actinides and much work is needed to throw light on this aspect.

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