

Spectrophotometric study of the formation of adducts between $U(TTA)_4$ and some neutral organo sulphoxide donors

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Abstract. Adduct formation between $U(TTA)_4$ and neutral organosulphoxide donors dibenzyl sulphoxide (DBSO), dimethyl sulphoxide (DMSO), dihexyl sulphoxide (DHSO) and dioctylsulphoxide (DOSO) was studied by spectrophotometry. Each of these donors form a 1 : 1 adduct with $U(TTA)_4$. The adduct formation constants ($\log \beta_{AB}$) were calculated from spectral changes and were found to be 3·10 (DBSO), 3·23 (DMSO), 3·62 (DHSO) and 3·64 (DOSO).

Keywords. Solvent extraction ; synergism ; $U(TTA)_4$; neutral donor adducts.

1. Introduction

The synergism in the extraction of metal ions from aqueous media by organic solvents containing a mixture of a betadiketone (HA) and a neutral donor (S) is mainly due to the formation of adducts in the organic medium between the metal betadiketonate and the neutral donor. This is especially true when the aqueous and the organic media used are such that the neutral donor alone is not capable of extracting the metal ion to a significant extent. Among tetravalent actinides, formation of such adducts have been reported for thorium, uranium, neptunium and plutonium. The adduct formation constants are usually estimated from the solvent extraction data. Such data, however, can be obtained directly from spectral changes accompanying the adduct formation and we have earlier reported such results on $U(IV)$ (Patil *et al* 1979a; Patil and Ramakrishna 1979b; Ramakrishna *et al* 1980), $Np(IV)$ (Sajun *et al* 1981) and $Pu(IV)$ (Ramakrishna *et al* 1979; Patil *et al* 1980). In continuation of these studies, the adduct formation between $U(TTA)_4$ (TTA—thenoyltrifluoroacetone ligand) and the neutral organosulphoxide donors DBSO, DMSO, DHSO and DOSO, in benzene, has been investigated and the results are reported here.

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2. Experimental

2.1. Materials

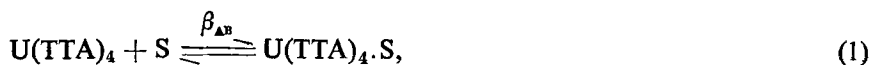
The compound $U(TTA)_4$ was prepared as described (Ramakrishna *et al* 1980). The sulphoxides were prepared and purified (Mohanty and Reddy 1975). HTTA was obtained from M/s. E. Merck, Germany and used after drying over P_2O_5 . Analar benzene was used as such.

2.2. Procedure

The experimental procedure used was the same as described (Patil *et al* 1979a). Benzene solutions of $U(TTA)_4$, in the presence of ten-fold excess of HTTA, and suitable concentration of the desired neutral donor (S) were prepared so as to get solutions having varying ratios of (S)/(U(IV)) but the same concentration of U(IV). Absorption spectra of these solutions were recorded using a Cary 14 spectrophotometer.

3. Results and discussion

The absorption spectrum of $U(TTA)_4$ and the changes caused to it by the addition of different amounts of DMSO are shown in figure 1. Similar changes were observed with other sulphoxides as well. The presence of well-defined isosbestic points in the spectra shown in figure 1 suggests that there are only two absorbing species in the system, obviously, $U(TTA)_4$ and its adduct $U(TTA)_4 \cdot S$, in analogy with the adducts reported using the organo phosphorus donors. Following the same procedure as reported earlier, the adduct formation reaction can be written as



for which the equilibrium constant is given by

$$\beta_{AB} = \frac{[U(TTA)_4 \cdot S]}{[U(TTA)_4][S]} = \frac{(E_1 - E)}{(E - E_2)[S]} \quad (2)$$

where

$$[S] = [S]_{total} - \frac{(E_1 - E) \times C}{(E_1 - E_2)} \quad (3)$$

where C = the total concentration of U(IV), E_1 = molar extinction coefficient of $U(TTA)_4$ alone, E_2 = molar extinction coefficient of $U(TTA)_4 \cdot S$ alone and E = molar extinction coefficient of the mixture.

The absorption spectrum of $U(TTA)_4$ obtained in the absence of any added S was used to get the value of E_1 at the desired wavelength. The value of E_2 was derived from the spectrum when (S)/(U(IV)) is high so that any further increase in this ratio did not cause any observable change in the spectrum, thereby suggesting the almost complete conversion of $U(TTA)_4$ to its adduct. Typical data giving the absorbance values and the values of β_{AB} calculated from them, with the donor DMSO are given in table 1. A summary of the adduct formation constant values obtained in this work are given in table 2 alongwith the literature data,

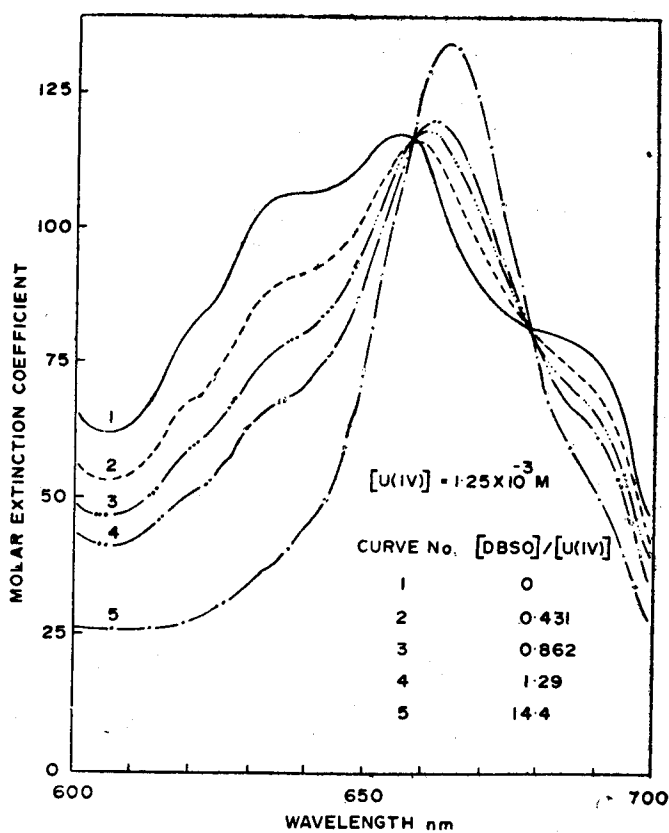


Figure 1. Absorption spectra of $U(TTA)_4$ with varying (DBSO).

Table 1. Spectrophotometric data on the adduct formation between $U(TTA)_4$ and DBSO in benzene.

$$[U(IV)] = 1.25 \times 10^{-3} M$$

$[DBSO]/[U(IV)]$		Molar extinction coefficient (E) at nm			$\log \beta_{AB}$ at, nm		
		570	580	590	570	580	590
0	(E_1)	176	125	88
14.4	(E_2)	103	58	29	—
0.431		158	108	73	3.18	3.16	3.15
0.862		146	98	64	3.08	3.08	3.09
1.29		135	88	54	3.14	3.13	3.16
1.72		130	83	51	3.09	3.08	3.08
2.15		127	80	48	3.06	3.04	3.04
2.87		120	76	44	3.10	3.03	3.04

Table 2. Summary of the β_{AB} values for the formation of 1 : 1 adducts between $U(TTA)_4$ and neutral donors in benzene.

Neutral donor	$\log \beta_{AB}$
Tri- <i>n</i> -octyl phosphine oxide (TOPO)	6.23
Tri phenyl phosphine oxide (TPPO)	4.72
Di- <i>n</i> -butyl butyl phosphonate (DBBP)	4.04
Dicotyl sulphoxide (DOSO)	3.64
Dihexyl sulphoxide (DHSO)	3.62
Dimethyl sulphoxide (DMSO)	3.23
Dibenzyl sulphoxide (DBSO)	3.10
Tri- <i>n</i> -butyl phosphate (TBP)	3.04
Tri-iso octyl thio phosphate (TIOTP)	1.04
Methyl-iso butyl ketone (MIBK)	0.1

The β_{AB} values of the sulphoxide adducts of $U(TTA)_4$ are seen to follow the increasing order that DBSO < DMSO < DHSO < DOSO which is in conformity with their expected basicity values (Nikitin *et al* 1976). The structures of these adducts are expected to be identical to those discussed earlier, with uranium atom having a coordination number of nine in them (Patil *et al* 1979c).

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