

Absorption spectral studies on the adduct formation between $U(TTA)_4$ and some neutral donors†

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Abstract. Synergism in solvent extraction of metal ions is known to be due to adduct formation which occurs in the organic phase. The adduct formation between $U(TTA)_4$ and different neutral donors was studied by spectrophotometry. Spectral changes were used to calculate adduct formation constants (β) and values of $\log \beta$ obtained for different donors.

Keywords. Synergism; $U(TTA)_4$; neutral donor adducts.

1. Introduction

Synergism observed in the extraction of the tetravalent actinides into organic solvents containing a mixture of a β -diketone and a neutral donor, is attributed to the adduct formation between metal β -diketonate and the neutral donor. The adduct formation is usually studied by solvent extraction methods. As the adduct formation occurs in the organic phase and as the metal chelates and their adducts with neutral donors have distinct absorption spectra, spectrophotometric methods can be employed for studying the same. The stoichiometry and the formation constants of the resulting adducts can be calculated from the absorption spectral data. Such studies for the adduct formation of $U(TTA)_4$ with various monodentate neutral donors have been reported recently (Patil *et al* 1979; Patil and Ramakrishna 1979; Ramakrishna *et al* 1980; Ramanujan *et al* 1982; Bullock and Sweatman 1982). In continuation the present work was carried out to study the influence of the variation of the side chains in the monodentate neutral phosphate donors on the adduct formation constant. The monodentate donors studied are tri-butylethylphosphate (ТБЕР), tris-2-ethylhexylphosphate (ТЕНР), tridichloropropylphosphate (ТДСРР) and triisobutylphosphate (ТІВР). Also the absorption spectral studies on the adduct formation between $U(TTA)_4$ and bidentate neutral donors *viz* dibutyl N-N-diethyl carbamoyl methylene phosphonate (DBDECMP), bipyridyl and *o*-Phenanthroline have been carried out to determine the stoichiometry and the coordination in the adducts formed.

2. Experimental

2.1 Materials

$U(TTA)_4$ was prepared as described in literature (Prasad and Baskin 1966). Thenoyltrifluoroacetone (HTTA) and *o*-Phenanthroline were obtained from M/s

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E Merck, Germany. TBEP, TEHP, TDCPP and TIBP were obtained from Tenneco Organic Ltd., Bristol. Bipyridyl was obtained from BDH, England. DBDECMP was obtained from Richmond Organics, USA.

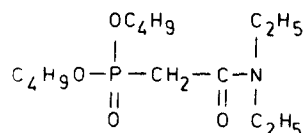
2.2 Procedure

Weighed amounts of $U(TTA)_4$ and HTTA were dissolved in benzene to get a solution of $U(TTA)_4$ with ten-fold excess of HTTA. Stock solutions of suitable concentration of the desired neutral donors (S) were prepared by dissolving a weighed amount of the donor in benzene. Solutions for recording the spectra were obtained by adding different aliquots of the donor stock solution to a fixed volume of $U(TTA)_4$ solution and finally making up to a constant volume, in each case with benzene. Thus the U(IV) concentration in all the solutions was held constant while the concentration of the neutral donor was varied. Absorption spectra of these solutions in the visible region were recorded on CARY-14 spectrophotometer using benzene as the blank. HTTA and the neutral donors used do not absorb in this wavelength region. The absorbance values recorded at a few different wavelengths were used for the calculation of the adduct formation constants.

3. Results and discussion

3.1 Bidentate donors

$U(TTA)_4$ forms a 1:1 adduct with most of the monodentate neutral donors giving a nine-coordinated species. The adduct formation of $U(TTA)_4$ with a bidentate donor was studied to see whether a 10-coordinated species would be formed. Three bidentate donors *viz* DBDECMP, *o*-phenanthroline and bipyridyl were chosen for this study. When *o*-phenanthroline was added to the solution of $U(TTA)_4$, the colour of the solution changed and the absorption values continuously decreased with time. The solution finally became yellow which suggested the oxidation of U(IV) to U(VI). The addition of bipyridyl also resulted in the oxidation of U(IV) to U(VI). The oxidation of U(IV) is apparently a consequence of the stronger adduct forming tendency of these neutral donors with $UO_2(TTA)_2$ than with $U(TTA)_4$. Hence the studies were restricted to DBDECMP which did not cause the oxidation of $U(TTA)_4$. The structure of DBDECMP has been shown below:



The spectral changes of $U(TTA)_4$ on the addition of various amounts of DBDECMP are shown in figure 1. The changes are similar to those observed with all other monodentate donors. This indicated that DBDECMP behaves as a monodentate donor during adduct formation with $U(TTA)_4$.

The monoadduct formation equilibrium is given as (S = neutral donor),



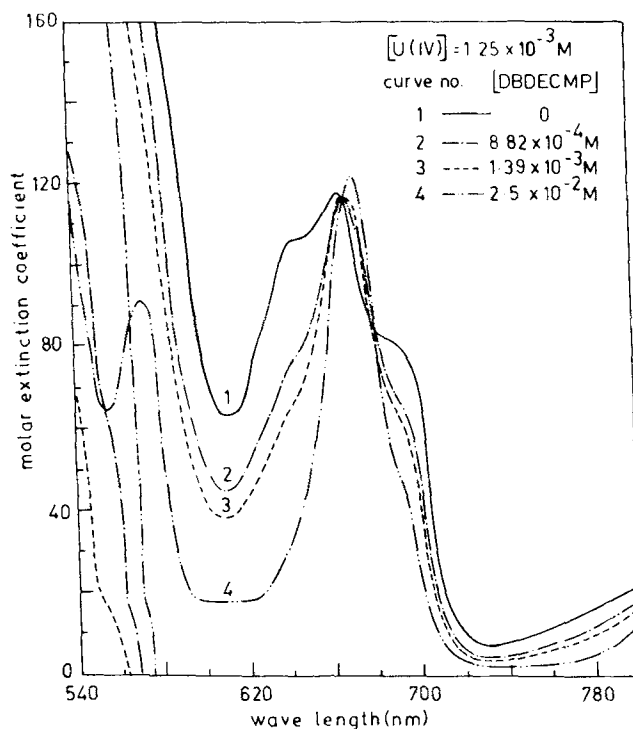


Figure 1.

The adduct formation constant (β) can be written as

$$\beta = \frac{[U(\text{TTA})_4 \cdot S]}{[U(\text{TTA})_4][S]_{\text{free}}} = \frac{(E_1 - E)}{(E - E_2)[S]_{\text{free}}}, \quad (2)$$

where E_1 , E_2 and E are molar extinction coefficients of $U(\text{TTA})_4$, $U(\text{TTA})_4 \cdot S$ and their mixture, respectively, at a particular wavelength. The concentration of free neutral donor $[S]_{\text{free}}$ is given by

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

where C is the total concentration of $U(\text{IV})$. The value of E_2 at the desired wavelength was obtained from the absorbance of $U(\text{TTA})_4$ in the presence of a large excess of the donor and it was assumed that $U(\text{TTA})_4$ was completely converted to $U(\text{TTA})_4 \cdot S$. This assumption was confirmed as no change was seen in the spectrum on further increasing the donor concentration. From the known values of E_1 , E_2 , E , C and $[S]_{\text{total}}$ the β values are calculated. Table 1 gives the β values calculated for DBDECMP at various concentrations of donor and at different wavelengths. The magnitude of the average β value ($\log \beta = 3.2$) is of the same order as that of a monodentate phospho-donor such as TBP. This is in confirmation with our earlier conclusion obtained from the spectral changes *viz* that this donor behaves as a monodentate donor towards $U(\text{TTA})_4$.

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

[DBDECMP]	Molar extinction coefficient							
	(E) at wavelength (nm)				log β at wavelength (nm)			
[U(NTA) ₄]	560	570	580	590	560	570	580	590
0 (E_1)	264	177	128	90	—	—	—	—
80 (E_2)	85	86	44	20	—	—	—	—
0.7	193	146	96	63	3.25	3.07	3.18	3.18
0.9	178	146	93	61	3.25	2.88	3.05	3.07
1	170	133	85	54	3.28	3.16	3.22	3.21
1.2	160	128	81	51	3.26	3.15	3.20	3.19
1.5	148	121	74	46	3.24	3.14	3.21	3.14

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

Table 2. β -values with different donors.

Donor (S)	log β
TDCPP	1.3
TBEP	2.3
TEHP	2.8
TIBP	3.0

3.2 Monodentate donors

In continuation of earlier work four additional neutral monodentate donors were taken up for study. The spectral changes on the addition of each of these donors to $U(NTA)_4$ were similar to monoadduct spectra. For TDCPP and TIBP the β values were calculated from the spectral data as described for DBDECMP. Such calculation however was not possible with TEHP and TBEP as obtaining E_2 values required the use of higher concentrations of these donors which induced partial oxidation of U(IV) in the solution. Hence an alternative method (Hershenson *et al* 1953), which does not require the knowledge of E_2 for β calculation, was used. The method used involves the following expression which is obtained on rearranging (2):

$$[S]_{\text{free}}/(E_1 - E) = 1/\beta(E_2 - E_1) + [S]_{\text{free}}/(E_2 - E_1). \quad (4)$$

The plot of $[S]_{\text{free}}/(E_1 - E)$ vs $[S]_{\text{free}}$ will give a straight line and slope/intercept will give the β values. To use this method $[S]_{\text{total}}$ was taken as an initial approximation of $[S]_{\text{free}}$. The corrected $[S]_{\text{free}}$ was calculated iteratively from the plot and using the expression:

$$[S]_{\text{free}} = [S]_{\text{total}} - (E_1 - E) \cdot C \cdot \text{slope}. \quad (5)$$

With TEHP and TBEP only 3 iterations were required to reach constant $[S]_{\text{free}}$ values. β values were calculated from the plot using corrected $[S]_{\text{free}}$ values. Table 2 summarises the β values obtained for the four donors. The constants with the donors TIBP and TBEP

(TBP data taken from literature) were found to be the same thus suggesting that the iso-group has not offered any steric hindrance to the donor. Substitution of the chloro group in the side-chain (TDCPP) has lowered the adduct stability appreciably by lowering the basicity of the donor.

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