

Synergism in the extraction of uranium in presence of antipyrine

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Abstract. Synergism in the extraction of uranium(VI) has been studied in the presence of a mixture of antipyrine and β -diketones like benzoyltrifluoroacetone, trifluoroacetylacetone and furoyltrifluoroacetone. The nature of the extracted species has been ascertained from the variation of $\log D$ with pH and the concentrations of the extractants. The equilibrium constants for the synergistic species have been evaluated taking into account the protonation and partition coefficient of antipyrine.

Keywords. Synergism; uranium; β -diketones; antipyrine.

1. Introduction

Synergism in the extraction of metals has generally been studied in the presence of β -diketones in combination with alkylphosphorus esters like TBP or TOPO and to a lesser extent, with alkylphosphoric acids (Marcus and Kertes 1969; Sekine and Hasegawa 1977). The use of other donors has been comparatively meagre. We have made a systematic study on the use of other synergists like sulphoxides and nitrogen donors in the extraction of rare earths (More and Sudersanan 1980; Sudersanan and Sundaram 1981). The present work is part of our efforts in the use of other nitrogen and oxygen donors to assess their potentialities for use as donors.

Antipyrine, a substituted pyrazolone is of considerable importance in medicine. In addition, it can be considered as a starting material for other acyl substituted pyrazolones which are attracting attention for use in extraction as β -diketones. It is therefore of interest to study the role of antipyrine as an extractant and synergist. The influence of protonation and partition coefficient of antipyrine will be of interest in understanding the role of these factors on synergism. The influence of terminal group of β -diketones has also been studied systematically to understand the correlation between the stability of the adduct and the nature of participating ligands. The results are presented in this paper.

2. Experimental

2.1 Chemicals

Antipyrine (Magenta Chemicals, Bombay; BPC quality) was used as a solution in water. Solutions of benzoyltrifluoroacetone, trifluoroacetylacetone and furoyltrifluoroacetone (K and K Labs., USA) were prepared in CCl_4 , used as a diluent. Other chemicals were of analytical grade.

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2.2 Extraction studies

Extraction experiments were carried out by equilibrating 10 ml of the aqueous phase, containing uranium, antipyrine, sodium chloride, to maintain the ionic strength at 0.5, and HCl to maintain the pH, with an equal volume of the organic phase containing the β -diketone. The two phases were equilibrated at $25 \pm 1^\circ\text{C}$ using a thermostated mechanical shaker for about 4 hr, the time being sufficient for equilibration. The phases were separated and the pH of the aqueous phase was measured using a Beckman Expandomatic SS-2 pH meter. Eight ml of the organic phase was equilibrated with an acidic solution (~ 0.4 M in HCl) containing 0.5 M sodium chloride to strip uranium into the aqueous phase. The two aqueous phases were then estimated for uranium.

2.3 Estimation of uranium

Uranium was estimated spectrophotometrically using pyridylazoresorcinol (PAR). The solution containing uranium was evaporated to dryness and was then dissolved in about 4 ml of water. One ml of 0.1 M EDTA, 1 ml of solution containing 200 μg of PAR and 2 ml of 10% (V/V) ammonia were added and the solution made up to 10 ml. The optical density was measured at 540 nm with water as blank and was corrected for absorption due to the reagents alone.

2.4 Partition coefficient of antipyrine

The partition coefficient of antipyrine (APY) was determined by equilibrating an aqueous solution of APY with an equal volume of CCl_4 and determining the concentrations in the two phases by volumetry (Garratt 1964). APY was estimated by treating with iodine dissolved in about 2 g of sodium iodide to convert it to its iodo derivative. After 20 min. when the reaction was over, excess iodine was titrated, after dissolving iodo antipyrine in chloroform or CCl_4 with sodium thiosulphate using freshly prepared starch as indicator. The partition coefficient P_{APY} , was determined to be 0.12.

2.5 Dissociation constant of APY

The dissociation constant of APY K_a , was determined to be $10^{-1.38}$ by the pH-titration technique (Irving and Rossotti 1954). The protonation constant was utilised to correct for the association of protons with APY.

3. Results and discussion

Extraction of uranium was studied in the presence of antipyrine and β -diketones with a view to investigate the effect of terminal groups of the β -diketone.

3.1 Uranium-benzoyltrifluoroacetone-APY system

The distribution ratio D was measured as a function of pH and concentrations of benzoyltrifluoroacetone, HBFA and APY. The plots of $\log D$ as a function of pH, $\log [\text{HBFA}]_0$ and $\log [\text{APY}]_{\text{tot}}$ are presented in figure 1. The first two plots resulted in straight lines having a slope of about two while the plot of $\log D$ vs $\log [\text{APY}]_{\text{tot}}$ resulted

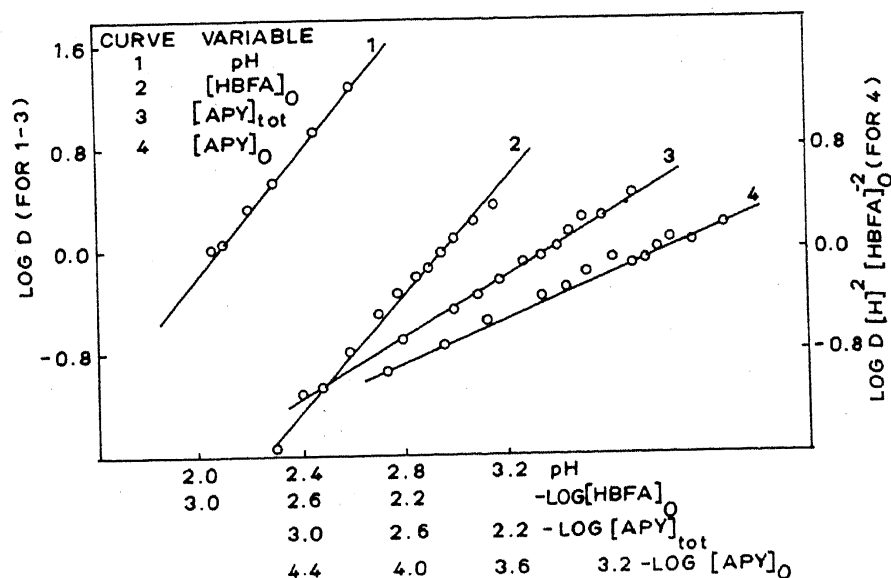
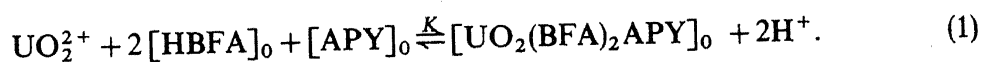


Figure 1. $\text{UO}_2\text{-HBFA-APY-CCl}_4$: log-log plots.

in a straight line with slope about one. Hence the extraction mechanism can be written as



The association of APY with protons and its partition into the organic phase were taken into account in calculating the concentration of APY in the organic phase using the relation

$$[\text{APY}]_{\text{tot}} = [\text{APY}]_0 + \frac{[\text{APY}]_0}{P_{\text{APY}}} + \frac{K_a^{-1}[\text{H}][\text{APY}]_0}{P_{\text{APY}}} \quad (2)$$

The equilibrium constant K for the extraction reaction was calculated from

$$K = D[\text{H}]^2 [\text{HBFA}]_0^{-2} [\text{APY}]_0^{-1} \quad (3)$$

In order to correct for the variations of pH in the measurements, $\log D [\text{H}]^2 [\text{HBFA}]_0^{-2}$ was plotted as a function of $\log [\text{APY}]_0$, which resulted in a straight line of slope 1, in agreement with the above equation. The equilibrium constant was also calculated and is presented graphically in figure 3.

3.2 Uranium-trifluoroacetylacetone-APY system

Extraction of uranium by APY was also studied in the presence of another fluorinated β -diketone, viz. trifluoroacetylacetone, HTFA. The distribution ratio was measured as a function of pH and concentrations of HTFA and APY. The concentration of APY in the organic phase was calculated, as mentioned earlier and that of HTFA was also corrected for the partition to the aqueous phase, the partition coefficient being 0.646 (Sekine *et al* 1973).

The plot of $\log D$ vs pH resulted in a straight line with a slope of 2.5 when no correction was applied for the concentration of APY in the organic phase. However, with the corrected values of $[\text{APY}]_0$, as a result of change in pH, the slope was close to two

indicating the influence of protonation on the apparent values of slope. The plot of $\log D$ vs $\log [\text{HTFA}]_0$ resulted in a slope of 2 indicating the extracted species to contain two molecules of TFA. The plot of $\log D$ vs $\log [\text{APY}]_0$ could not be made due to the change in pH and hence the variation of pH was considered (figure 2) by plotting $\log D$ vs $[\text{H}]^2$ vs $\log [\text{APY}]_0$. This resulted in a curve but could be approximated by a line with a slope of one corresponding to the coordination of one molecule of APY. The extraction mechanism could be written for the formation of $\text{UO}_2 (\text{TFA})_2 \text{APY}$ and the equilibrium constant was also calculated (figure 3).

The $\log K$ values however decreased, from an almost constant value, with increasing concentrations of APY, as shown in figure 3. A similar behaviour was also observed in

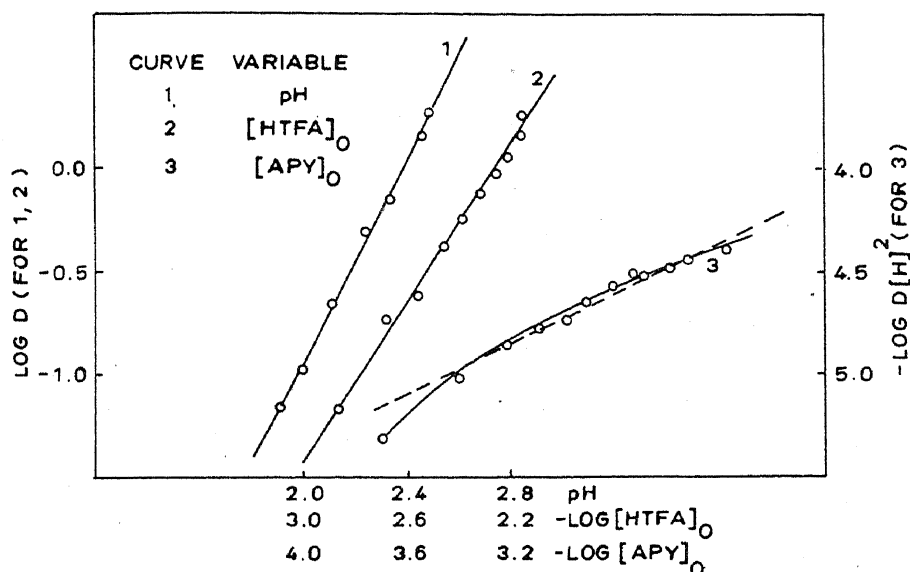


Figure 2. UO_2 -HTFA-APY- CCl_4 : log-log plots.

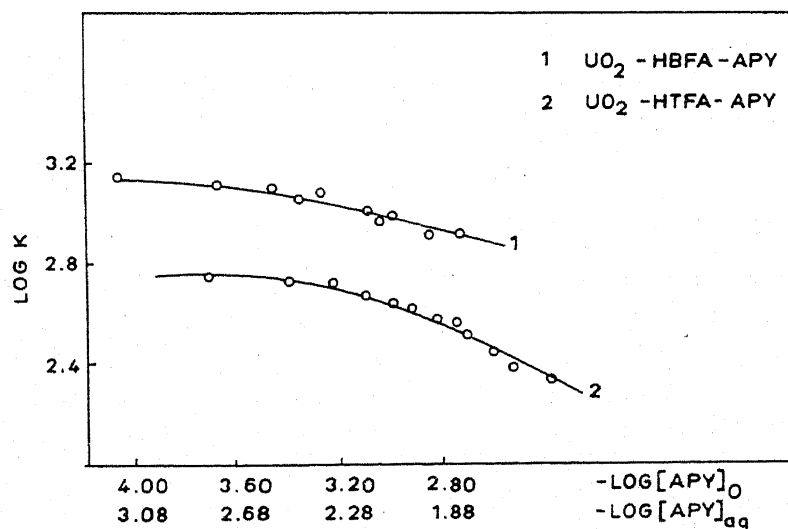


Figure 3. Variation of $\log K$ with $[\text{APY}]$.

HBFA system indicating the variation to be due to similar effects in both the cases. The decrease in the equilibrium constant may be attributed to the formation of UO_2APY complexes in the aqueous phase. The concentration of UO_2APY increases with increasing concentrations of APY, thereby causing an apparent decrease in the equilibrium constant. The data were therefore analysed by a method similar to that of aqueous phase complexes by the method of competitive reactions (Connick and Mc Vey 1949; Sudersanan and Sundaram 1976). It can be shown that

$$\frac{D_0}{D} - 1 = \left(\frac{K_0}{K} - 1 \right) = \beta'_1 [\text{APY}] + \beta'_2 [\text{APY}]^2 + \dots \quad (4)$$

where D_0 and D refer to the distribution ratios in the absence and presence of APY, K_0 and K refer to the corresponding apparent equilibrium constants and β 's refer to the stability constants of uranium APY complexes in the aqueous phase. It was found that the value of β'_1 calculated from

$$\beta'_1 = \left(\frac{K_0}{K} - 1 \right) / [\text{APY}] \quad (5)$$

was nearly constant at $10^{1.6}$ indicating the predominance of UO_2APY species. This value should however be considered only as approximate since other factors may also influence the results. The formation of uranium-antipyrine complexes was also indicated qualitatively by the appearance of a yellow colour on addition of antipyrine to uranium solutions.

3.3 Uranium-furoyltrifluoroacetone-APY systems

Extraction of uranium in the presence of APY and furoyltrifluoroacetone, HFTA, occurred at a lower pH (~ 1.8) where extraction by either HFTA or APY alone was negligible and the enhancement in extraction could be attributed to the formation of a synergistic species.

The plots of $\log D$ vs pH, $\log [\text{HFTA}]_0$ and $\log [\text{APY}]_0$, resulting in straight lines having slopes of 2.1, 2.2 and 1.2 respectively, indicated the extraction of $\text{UO}_2(\text{FTA})_2\text{APY}$. The concentration of HFTA was corrected for the transfer of the extractant to the aqueous phase using the value of 5.75 for the partition coefficient (Sudersanan and Sundaram 1978).

It was observed, in this case also, that the value of the equilibrium constant varied with the concentration of APY and hence the average $\log K$ value was taken as $10^{3.4}$. The nature of the adduct remained unchanged and only the numerical value of the equilibrium constant varied with a change in the β -diketone.

Table 1. Values of equilibrium constants for uranium- β -diketone-antipyrine adducts.

β -diketone	pK of β -diketone	$\log P_{\text{HA}}$	$\log K$
HBFA	6.01	2.47	3.15
HTFA	6.09	-0.19	2.75
HFTA	5.87	0.76	3.40

$\log P_{\text{APY}} = -0.92$; Diluent: CCl_4 .

The equilibrium constants for the various systems reported here are summarised in table 1. The effect of terminal groups of the β -diketones on synergism can be interpreted on the basis of the electron withdrawing effects of the β -diketones. In fluorinated β -diketones, the presence of electron withdrawing groups, lowers the electron density at the enol group (ring) so that the electron density at the metal is reduced. The metal ion can, therefore, form a stronger adduct with the neutral donors which are usually electron donors. The results obtained in the present case agree with the above postulates.

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