Synergism in the extraction of uranium (VI) by a mixture of oxine and β-diketones

R K MALHOTRA†, M SUDERSANAN and A K SUNDARAM*

Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India.
†Atomic Minerals Division, Begumpet, Hyderabad 500 016, India

Abstract. Extraction of uranium (VI) in presence of a mixture of oxine and β-diketones, viz, benzoyltrifluoroacetone, trifluoroacetylacetone, thenoyltrifluoroacetone and furoyltrifluoroacetone was studied. Extraction was found to be higher than that for oxine or β-diketone alone and the loss of uranium due to precipitation by oxine was eliminated completely. The synergistic species was found to be a mixed chelate and the nature of the species and equilibrium constant were evaluated. A correlation between the two phase stability constants and dissociation constants and partition coefficients of the β-diketones was also established.

Keywords. Synergism; uranium (VI) extraction; oxine; β-diketones.

1. Introduction

Synergism in the extraction of uranium by oxine is of interest since it takes place mainly from chloroform media and the extracted species has been postulated (Vogel 1968) as a self-adduct $[UO_2(OX)_2 \cdot HOX]$, unlike the formation of mixed chelates in the case of β-diketones. Extraction of uranium by oxine was very poor from carbon tetrachloride. Investigation of mixed complex formation with other chelates was taken up to study the solubilisation of uranium in the presence of oxine. The formation of adducts by oxine could also lead to synergism of a larger magnitude than in the case of mixed chelates.

2. Experimental

A solution of uranium was prepared from uranyl sulphate (Uranium Extraction Division, BARC). Oxine (BDH, AR), benzoyltrifluoroacetone, trifluoroacetylacetone and furoyltrifluoroacetone (K and K Labs) and thenoyltrifluoroacetone (Koch Light Lab) were used as solutions in carbon tetrachloride (E. Merck GR). The pH of the solution was adjusted with dilute hydrochloric acid or acetic acid-sodium acetate buffer, the concentration of acetic acid was maintained at 0·02 M.

Studies were carried out at 25 ± 1°C at an ionic strength of 0·5 maintained with sodium chloride. Extraction experiments and the method of estimation of uranium have been described earlier (Malhotra et al 1984).

---

* To whom all correspondence should be addressed.

3. Results and discussion

Extraction of uranium (VI) was studied using a mixture of oxine and β-diketones like benzoyltrifluoroacetone (HBFA), furoyltrifluoroacetone (HFTA), thenoyltrifluoroacetone (HTTA) and trifluoroacetylacetone (HTFA) in order to investigate the influence of the terminal group of the β-diketone on synergism.

The concentration of β-diketone in the organic phase was calculated taking into account pK values and partition coefficients (Sekine *et al* 1973). Extraction by individual β-diketones was also investigated. Extraction due to oxine alone could not be studied in detail since extraction was poor at low pH whereas an increase in pH resulted in a gradual loss of metal due to precipitation. The studies were carried out similarly with various β-diketones and hence only the results in the case of HBFA are described.

3.1 *Uranium−HBFA−oxine system*

Extraction of uranium in the presence of a mixture of HBFA and oxine was found to be considerable and loss of uranium was eliminated completely due to the solubilisation of uranyl oxinate. Extraction was also much higher than that expected for HBFA alone. Such results have not been reported earlier and hence this system has been studied in detail to understand the nature of the complexes.

Experiments were carried out in the pH range of 2·6 to 3·9, keeping the concentrations of HBFA and HOX constant at 0·01 M each. The plot of log D *vs* pH resulted in a straight line (figure 1) with a slope of about 2·3. A higher value may be due to the association of oxine with the proton resulting in the formation of H_2OX and hence the extraction mechanism can be postulated as involving two molecules of hydrogen. The plot of log D $[H^+]^2$ *vs* log $[HBFA]_0$ at pH 3·5 to 3·6 and $[HOX]_{tot}$ equal to 0·01 M resulted in a straight line (figure 1) with a slope of about 1·3 indicating the replacement of some of the oxine molecules by HBFA in the formation of the mixed complex.
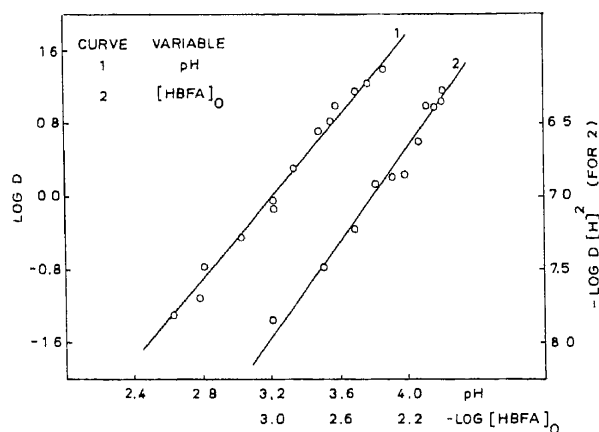

Figure 1. UO_2-HBFA-HOX: log-log plots.

Experiments were also carried out at a constant concentration of HBFA (0·01 M) and varying amounts of oxine. Since the pH varied during these studies (2·8–3·5) due to the association of protons with oxine, meaningful results could not be obtained from the plot of $\log D$ vs $\log [HOX]_0$ and hence correction for the association of oxine was made.

The concentration of HOX in the aqueous and organic phase were calculated from the partition coefficient (Leo *et al* 1971) of oxine (Log $P_{HOX} = 2\cdot06$) and the dissociation constants ($pK_1 = 5\cdot09$ and $pK_2 = 9\cdot62$) of oxine (Smith and Martell 1975).

The results indicated the formation of a mixed chelate in which part of HOX was replaced by the β-diketone. To investigate the nature of the extracted species, an analysis of the data based on the formation and extraction of mixed complexes was made (Sudersanan and Sundaram 1978; Pushparaja and Sudersanan 1981).

The distribution ratio, D, for the synergistic reaction can be written as

$$D = \frac{[UO_2(BFA)\cdot OX\cdot HOX]_0 + [UO_2(BFA)_2 HOX]_0}{[UO_2^{2+}]} \tag{1}$$

This can be written in terms of the equilibrium constants and on rearranging we get

$$\frac{D[H^+]^2}{[HOX]^3} = F_0 = K_{12}[L] + K_{21}[L]^2 \tag{2}$$

where $[L] = [HBFA]_0/[HOX]_0$. The function, F_0, calculated from all the data obtained at varying pH and concentrations of HBFA and HOX fitted in a single curve (figure 2) indicating the validity of the interpretations discussed earlier. The smooth curve was utilised for the calculation of equilibrium constants by a graphical method. The results are summarised in table 1.

3.2 *Uranium–HFTA/HTFA/HTTA–oxine systems*

Similar studies were made with other fluorinated β-diketones having varying partition coefficients. The plots of $\log \{D[H^+]^2/[HOX]_0^3\}$ vs $\log [L]$, obtained from the data at varying pH and concentrations of the two ligands are presented in figure 3 and were analysed for the nature of the extracted species and their equilibrium constants (table 1). The equilibrium constants for the mixed complexes are quite high, compared
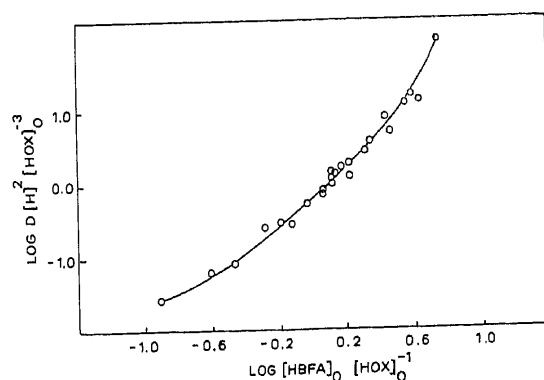

Figure 2. Plot of $\log F_0$ vs. $\log [HBFA]_0 [HOX]_0^{-1}$

Table 1. Correlation of equilibrium constants.

System	β-diketone pK	$\log P_{HA}$	$\log K$	$\log P_{mn}\beta_{mn}$	X
$UO_2(BFA)_2$ HOX	6·01	2·47	−0·43	16·53	8·48*
$UO_2(TTA)_2$ HOX	6·28	1·30	0·25	15·41	7·58
$UO_2(FTA)_2$ HOX	6·18	0·76	0·30	14·18	6·94
$UO_2(TFA)_2$ HOX	6·09	−0·19	−0·15	11·65	5·90
$UO_2(BFA)(OX)$ HOX	6.01	2·47	−0·86	19·30	10·08**
$UO_2(TTA)(OX)$ HOX	6·28	1·30	−0·15	19·11	9·63
$UO_2(FTA)(OX)$ HOX	6·18	0·76	0·30	18·92	9·31
$UO_2(TFA)(OX)$ HOX	6·09	−0·19	0·15	17·73	8·79

$pK_1 = 5·09$; $pK_2 = 9·62$; $\log P_{HA} = 2·06$ for oxine; $* X = \log P_{HA} + pK$; $** X = 1/2\{\text{Log } P_{HA} + pK + (\text{Log } P_{HA} + pK_2)_{HOX}\}$.
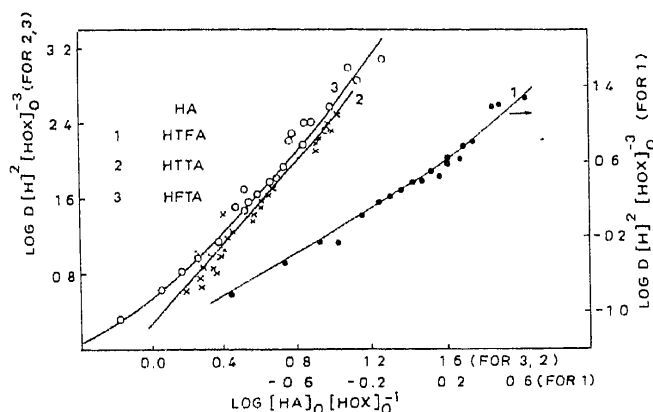
Figure 3. UO_2-HA-Oxine system: plot of $\log F_0$ vs. $\log [L]$

to that for β-diketones alone (which were of the order of 10^{-4} for HTFA and HBFA) since oxine behaves both as a chelating agent and a synergist and hence, the adduct formation with HOX leads to considerable stabilisation of uranium complexes. The values of K_{12} and K_{21} are almost of the same order of magnitude and small differences may be attributed to the relative stabilisation of complexes on the basis of electron distribution and reduced steric hindrance.

In our earlier studies on mixed complexes (Pushparaja and Sudersanan 1981), a correlation was observed between the stability constants of the complexes and the partition coefficients and dissociation constants of the ligands. The applicability of this correlation for the present case was investigated.

The values of $\log P_{21}\beta_{21}$ and $\log P_{12}\beta_{12}$, where P_{mn} and β_{mn} represent the partition coefficient and stability constant of the complex $[UO_2 A_m (OX)_{n-1} HOX]$ respectively, were calculated from the experimental values of K_{21}, K_{12} and the pK_a and P_{HA} of the ligands. The values are presented in table 1. A plot of $\log P_{mn}\beta_{mn}$ vs $[\log P_{HA} + pK]$ is presented in figure 4. All the points were on a single line and both the complexes could be interpreted on the basis of this correlation. The slope of the line was also found to be about two, in agreement with the slope expected on the basis of the correlation.
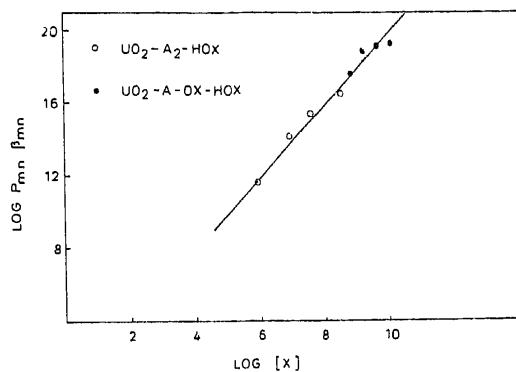
Figure 4. Correlation of equilibrium constants

$$\log P_{mn}\beta_{mn} = 2\left[\log P_{HA} + pK\right] + const. \tag{3}$$

where the values of $\log P_{HA}$ and pK were calculated as the geometric mean of the participating ligands.

This behaviour indicates the compatibility of the ligands in the inner coordination sphere and also the absence of any steric effect of the ligands on the stabilisation of the complexes. A similar behaviour may also be expected for other β-diketones provided the nature of the ligand does not change so grossly as to introduce other steric effects.

References

Leo A, Hansch C and Elkins D 1971 *Chem. Rev.* **71** 525

Malhotra R K, Sudersanan M and Sundaram A K 1984 *Proc. Indian Acad. Sci. (Chem. Sci.)* **93** 837

Pushparaja and Sudersanan M 1981 *J. Inorg. Nucl. Chem.* **43** 1371

Sekine T, Hasegawa Y and Ihara N 1973 *J. Inorg. Nucl. Chem.* **35** 3968

Smith R E and Martell A E 1975 *Critical stability constants* (New York: Plenum Press)

Sudersanan M and Sundaram A K 1978 *Proc. Indian Acad. Sci. (Chem. Sci.)*, **A87** 203

Vogel A I 1968 *A textbook of quantitative inorganic analysis* 3rd ed. (London: ELBS and Longmans) p. 539