Diluent Effects on Synergism in Extraction of Uranium(VI)

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Synergism in the extraction of uranium (VI) by a mixture of benzoyltrifluoroacetone and antipyrine from benzene, chloroform, hexane, cyclohexane and chlorobenzene media has been studied. The partition of antipyrine as well as its protonation has also been determined. The synergistic species changes from a monoadduct in the case of hexane, cyclohexane and benzene to a diadduct in the case of chloroform, whereas a mixture of mono- and di-adducts is obtained in chlorobenzene. A correlation of the nature of the species with the partition coefficient of antipyrine is observed as also between the partition coefficient and stability constant of the adduct with those of the participating ligands.

The influence of solvents on synergism is of considerable interest. It has been observed in the extraction of some neutral complexes that the partition coefficient of metal complexes can be correlated to that of the chelating agent by regular solution theory. In synergistic systems, the donor-organic diluent is also considered as an effective extractant rather than the donor alone. Further, the influence of solvents in extraction systems with donors having considerable solubility in water has not been investigated. The influence of solvents has therefore been studied on the extraction of uranium with a mixture of benzoyltrifluoroacetone and antipyrine and the results are presented in this paper.

Materials and Methods

A stock solution of uranyl sulphate (Uranium Metal Plant, BARC) was prepared in dil. hydrochloric acid and standardised gravimetrically. Benzoyltrifluoroacetone (K and K Labs) was used as a solution in the appropriate solvent. Antipyrine (Magenta Chemicals, BPC quality) was used as an aqueous solution. All other reagents were of analytical grade.

Extraction experiments were carried out by equilibrating the aqueous phase (10 ml) containing uranium, sodium chloride to adjust the ionic strength to 0.5, hydrochloric acid to maintain the pH and antipyrine with an equal volume of the organic phase containing benzoyltrifluoroacetone, for about 4 hr using a mechanical shaker at 25±1°C. After equilibration, the two phases were allowed to settle and the pH of the aqueous phase was measured using a Beckman Expandomatic SS-2-pH meter. The organic phase (8 ml) was equilibrated with an equal volume of hydrochloric acid containing 0.5 M sodium chloride to strip the uranium to the aqueous phase. The uranium content in both the phases was estimated spectrophotometrically at 540 nm using pyridylazoresorcinol as the reagent.

Results and Discussion

Extraction of uranium by a mixture of benzoyltrifluoroacetone (HBFA) and antipyrine (APY) was studied in benzene, chloroform, cyclohexane, hexane and chlorobenzene media.

Benzene medium

The distribution ratio was measured as a function of pH and concentrations of the extractants. The partition coefficient of HBFA being high, its concentration in the organic phase can be assumed to be equal to its initial concentration. The partition coefficient of APY was determined as 0.525 at an ionic strength of 0.5 maintained with sodium chloride. The concentration of APY was determined in the two phases by an iodometric method. The concentration of APY in the organic phase was calculated taking into account its protonation and partition to the aqueous phase using the relation (1)

\[
[\text{APY}]_{\text{tot}} = [\text{APY}]_0 \left(1 + \frac{1}{P_{\text{APY}}} + \frac{\beta_1 [H^+]}{P_{\text{APY}}} \right)
\]

where \(\beta_1\) represents the association constant (10\(^{-3}\)–3\(^{-3}\)), determined by the pH titration technique.

The plots of \(\log D\) versus \(pH\) and \(\log [\text{HBFA}]_0\) were linear with slopes = 2 (Fig. 1) indicating the pre-dominance of \(\text{UO}_2(\text{BFA})_2\text{APY}\). The plot of \(\log D[H^+]^2[\text{HBFA}]_0^{-2}\) versus \(\log [\text{APY}]_0\) gave a slope of 1.0 (Fig. 1). The equilibrium constant, \(K\), given by Eq. (2)

\[
K = D[H^+]^2[\text{HBFA}]^{-2}[\text{APY}]_0^{-1}
\]

was calculated as 10\(^{3}\)–3\(^{-6}\).
Chloroform medium

In order to investigate the effect of a solvent of hydrogen bonding type, extraction of uranium by HBFA and APY was studied in chloroform medium in a similar manner. The partition coefficient of APY was determined under the present experimental conditions as 25.0 which was quite high compared to the values obtained in other solvents.

The slopes of the plots of log \( D \) versus \( pH \) and log \([\text{HBFA}]_o\) were 2.0. The plot of log \( D \) versus log \([\text{APY}]_o\) gave a slope of 1.7. The slope was the same even after correction for the protonation of APY and indicated the formation of higher adducts, \( \text{UO}_2(\text{BFA})_3(\text{APY})_2 \) in addition to the monoadduct. Since the value was close to two the equilibrium constant was calculated for the diadduct as \( 10^{3.55} \) although the data showed some scatter due to the presence of both the adducts.

The results obtained in chloroform medium are of interest because of the formation of the second adduct. This may be attributed to the higher partition coefficient of APY resulting in an increased concentration in the organic phase, thereby favouring the formation of the second adduct.

Cyclohexane medium

The partition coefficient of antipyrine in cyclohexane was very low, hence it was present predominantly in the aqueous phase. Calculations, therefore, were made on the basis of the concentration of APY in the aqueous phase corrected for the protonated form, \( \text{APY} \) using the relation (3)

\[
[\text{APY}]_{\text{aq}}' = [\text{APY}]_{\text{aq}}' [H^+] k_a^{-1} \quad \ldots (3)
\]

In Eq. (3) \( k_a \) is the dissociation constant being equal to \( 10^{-3.35} \).

The plots of log \( D \) versus \( pH \), log \([\text{HBFA}]_o\) and log \([\text{APY}]_o\) uncorrected for small changes in \( pH \) were linear with slopes of 2.6, 2.1 and 1.1 respectively, indicating the formation of \( \text{UO}_2(\text{BFA})_3(\text{APY})_2 \). The plot of log \( D[\text{H}^+]^2[\text{HBFA}]_o^{-2} \) as a function of log \([\text{APY}]_{\text{aq}} \) gave a slope of 0.8. The extraction reaction can be written as

\[
\text{UO}_2^{2+} + 2[\text{HBFA}]_o + [\text{APY}]_{\text{aq}} \rightarrow \text{UO}_2(\text{BFA})_3(\text{APY})_2 + 2\text{H}^+ \quad \ldots (4)
\]

for which the equilibrium constant, \( K' \), is given by Eq. (5)

\[
K' = D[\text{H}^+]^2/[\text{HBFA}]_o [\text{APY}]_{\text{aq}} \quad \ldots (5)
\]

and is related to the equilibrium constant corresponding to the organic phase reaction by Eq. (6)

\[
K = D[\text{H}^+]^2/[\text{HBFA}]_o [\text{APY}]_o = K' / P_{\text{APY}} \quad \ldots (6)
\]

A plot of log \( K' \) versus log \([\text{APY}]_{\text{aq}} \) indicated a slight decrease in the value of \( K' \) probably due to the complexation of uranium with antipyrine thereby lowering the value. The value of log \( K' \) corrected for complexation with APY was taken as 1.42 corresponding to the asymptotic value. It is interesting to note that this effect is observed with solvents for which the partition coefficient of APY is low, i.e. when the concentration of APY in the aqueous phase is considerable.

Hexane medium

Hexane has been selected as an example of a straight chain hydrocarbon which does not normally dissolve polar compounds. The results are presented in Fig. 2. The partition coefficient of APY was too low to be determined accurately and hence its concentration in the aqueous phase was considered equal to the initial concentration after correcting for protonation. It was also observed that the solubility of the adduct was limited as indicated by the loss of metal at higher concentrations of the ligand or \( pH \). Hence the data were analysed from the results obtained at lower
Table 1—Values of Equilibrium Constants of Uranium-HBFA-Antipyrine Adducts

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$pK_{HA}=6.01$</th>
<th>$\log P_{HA}$</th>
<th>$\log P_{APY}$</th>
<th>$\log K$</th>
<th>$\log P_{\beta N}$</th>
<th>$\log X^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>2.66</td>
<td>-0.28</td>
<td>3.36</td>
<td>20.42</td>
<td>17.06</td>
<td></td>
</tr>
<tr>
<td>Chloroform</td>
<td>2.88</td>
<td>1.40</td>
<td>3.55+</td>
<td>24.13</td>
<td>20.58</td>
<td></td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>2.20</td>
<td>-</td>
<td>1.40†</td>
<td>17.82</td>
<td>16.42</td>
<td></td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>2.50</td>
<td>0.06</td>
<td>3.10</td>
<td>20.18</td>
<td>17.08</td>
<td></td>
</tr>
<tr>
<td>Hexane</td>
<td>1.82</td>
<td>very low</td>
<td>0.72‡</td>
<td>16.38</td>
<td>15.66</td>
<td></td>
</tr>
</tbody>
</table>

$\log X=2(\log P_{HA}+pK_{HA})+\log P_{APY}$

Values for diadduct

$K=\frac{\beta N}{K_{HA}/K_{PA}}$ and $\log X=2(\log P_{HA}+pK_{HA})$

concentrations and the plots indicated an adduct of the type $[\text{UO}_2(\text{BFA})_2\text{APY}]$. The plot of $D[H^+][\text{BFA}]_0^2$ versus $\log [\text{APY}]_{aq}$ also indicated the extraction of a monoadduct. The equilibrium constant $K'$ was calculated as $10^{-9}$. The results indicated a decrease in the value of $K'$ with antipyrine concentration.

**Chlorobenzene medium**

Chlorobenzene was selected as an example of a substituted benzene compound in order to study the substituent effects on the stability of the adduct. The partition coefficient of antipyrine was determined as 1.15. The plot of $\log D$ versus $\log [\text{BFA}]_0$ had a slope of 2.0. The plot of $D[H^+][\text{BFA}]_0^2$ versus $\log [\text{APY}]_0$ was a smooth curve indicating the presence of both $\text{UO}_2(\text{BFA})_2\text{APY}$ and $\text{UO}_2(\text{BFA})_2(\text{APY})_2$. The formation constants were obtained by the graphical extrapolation method as $1.35 \times 10^3$ and $1.30 \times 10^5$, respectively. Studies in chlorobenzene are of interest since two adducts are observed in this system.

**Effect of solvent on adduct formation**

It is of interest to compare the effect of solvents on the formation of adducts of uranium with HBFA and APY. The solubility of APY is quite low in hexane and increases in the order: hexane < cyclohexane < benzene < chlorobenzene < chloroform. In agreement with this, extraction is very poor in hexane whereas synergism is pronounced in other solvents. In cyclohexane and benzene only the monoadduct is formed whereas in chlorobenzene, with an increase in the solubility of APY, both the adducts are formed. In chloroform medium, where the donor is present predominantly in the organic phase, the diadduct formation is pronounced. Thus the composition of the adduct depends on the effective concentration of APY in the organic phase.

**Application of regular solution theory**

The equilibrium constants for the various adducts reported here are summarised in Table 1. A correlation between the partition coefficients of the adducts and those of the constituent groups was attempted in order to study the applicability of the regular solution theory for synergistic adducts. The stability constant, $\beta_N$, of the adduct can be described as

$$\beta_N = \frac{[\text{UO}_2(\text{BFA})_2\text{APY}]}{[\text{UO}_2(\text{BFA})_2][\text{APY}]}$$

and the partition coefficient as

$$P_N = \frac{[\text{UO}_2(\text{BFA})_2\text{APY}]}{[\text{UO}_2(\text{BFA})_2][\text{APY}]}$$

The value of $P_N\beta_N$ can be obtained from the limiting value of $\frac{D[\text{BFA}]^2[\text{APY}]}{[\text{BFA}][\text{APY}]}$ at low concentrations of $[\text{BFA}]^2[\text{APY}]$ or calculated from the equilibrium constants.

The partition coefficient and stability constant of the chelate can be correlated to those of the chelating agent as

$$\log P_N\beta_N = \log P_{HA} + \log P_{APY} + \text{const}$$

In the case of synergistic systems, the partition coefficient of APY has to be taken into account and the above equation can therefore be modified as

$$\log P_N\beta_N = \log P_{HA} + \log P_{APY} + \text{const} + \log P_{HA}$$

The $pK_{HA}$ value for HBFA has been taken as 6.01 and the $P_{HA}$ values are reported in Table 1. A plot of $\log P_N\beta_N$ as a function of $[2\log P_{HA} + \log P_{APY} + 2pK_{HA}]$ was made to confirm the validity of the above relation. A good correlation was obtained.

In the case of hexane and cyclohexane, the partition coefficient of APY was very low. Since the data on various solvents for the plot of $\log P_N\beta_N$ versus $[2\log P_{HA} + pK_{HA} + \log P_{APY}]$ fall on a single line, this was used for the evaluation of the partition coefficient of APY in hexane as $10^{-2.2}$ and in cyclohexane as $10^{-1.8}$. These values are of the expected order of magnitude and hence it may be assumed that the systems behave as expected on the basis of regular solution theory.
References


3 Healy T V, *Nucl Sci Engng*, 16 (1963) 413.


