CHAPTER-X

EXTRACTION OF THORIUM (IV) WITH MIXTURE OF 3-PHENYL-4-BENZOYL-5-ISOXAZOLONE AND NETURAL OXODONORS
10.1 Introduction

The extraction behaviour of metal ions using β-diketones has been studied extensively [6]. This class of ligands is fascinating because of their unique property of extracting metal ions from a wide range of acidities by the proper choice of substituents. Employing dioxouran(IV) as a typical metal ion, it has been shown by Batzar et al. [134], that lower the pK\textsubscript{a} value of the β-diketone, higher is the two-phase equilibrium constant of the binary extraction system as well as for the ternary (synergistic) extraction system. In view of the modest pK\textsubscript{a} value, favourable partition coefficient towards the organic phase and easy commercial availability, 2-thenylytrifluoroacetone (HTTA) is the most extensively used β-diketone for analytical applications. On the other hand, it has a few limitations such as slow kinetics, poor loading characteristics, photosensitive decomposition, hydrolysis under high pH conditions (pH > 7.0) and above all its inability to extract metal ions from strong acidic and complexing media. Pyrazolones and isoxazolones, on the other hand, have been found to be particularly effective analytical extractants for actinide ions from strong acidic as well as complexing media [146, 147] encountered at different stages of nuclear fuel cycle.

The much lower pK\textsubscript{a} values of these ligands arise due to the participation of the heterocyclic ring in electron delocalisation imparting additional resonance stabilization. Some recent reports
explain the better extractability of these ligands based on the O-O distance [148].

The present investigation involves the synergistic solvent extraction of Th\(^{4+}\) with mixture of 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) and neutral oxo-donor such as TBP and TOPO. Monodentate oxodonors chosen for the present study are well known fuel reprocessing reagent, tri-n-butyl phosphate (TBP), a strong basic extractant and tri-n-octyl phosphine oxide (TOPO), used for the recovery of uranium from phosphoric acid. The oxodonor covers a wide range of basicity (Table 10.1) represented by their acid uptake equilibrium constants [149]. Analytical application of HPBI for the separation of Th-234 radiotracer from natural uranium (99.3 % U-238) has been suggested.

Table-10.1: pK\(_a\) of \(\beta\)-diketone and pK\(_b\) of neutral oxodonors.

<table>
<thead>
<tr>
<th>β-diketone</th>
<th>O-O distance (Å)</th>
<th>pK(_a)</th>
<th>Neutral donor</th>
<th>pK(_b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPBI</td>
<td>2.9</td>
<td>1.25</td>
<td>TOPO</td>
<td>8.9</td>
</tr>
<tr>
<td>HPMBBP</td>
<td>2.7</td>
<td>3.91</td>
<td>TBP</td>
<td>0.17</td>
</tr>
<tr>
<td>HTTA</td>
<td>2.6</td>
<td>6.23</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
10.2 Experimental

Reagents:

Thorium stock solution:

Stock solution of thorium(IV) \( (1.0 \times 10^{-2} \text{ M}) \) was prepared in \( 1 \text{ M} \) HNO\(_3\) using the metal nitrate \( \text{Th(NO}_3\text{)}_4\cdot6\text{H}_2\text{O} \) and was diluted to the desired concentration for the extraction studies. The solution was standardised by a reported method [150].

3-Phenyl-4-benzoyl-5-isoxazolone (HPBI):

HPBI was prepared by the method of Korte and Storiko [113]. The detailed preparative method is given in Chapter-VIII.

Tri-n-butyl phosphate (TBP):

TBP was purified by the method of Alcock et al. [151].

Other reagents:

Arsenazo(III) procured from Merck was prepared by dissolving 25 mg of the reagent in 25 mL of distilled water. Extra pure grade xylene from E. Merck, proanalysis grade TOPO and sulfamic acid from B.D.H were used as such.

10.2.1 Solvent extraction procedure:

The aqueous phase (usually 1 mL) containing Th(IV) at the desired concentration of HNO\(_3\) was equilibrated with the
required organic phase (1 mL) containing the extractant. The equilibration was usually carried out for 1 hour in a thermostated water bath at 298±1 K. Subsequently the equilibration tubes were centrifuged, phases were separated and aliquots from the aqueous phase (200-400 μL) were assayed by spectrophotometry using a Beckmann DU-7 single beam spectrophotometer.

The equilibrium concentration of Th(IV) in the organic phase was determined by the difference in the initial and final Th concentration in the aqueous phase. Occasionally the organic phase containing thorium was stripped by 10 M HNO₃ and the metal concentration was estimated by the above method. An excellent agreement (± 2%) was observed between the Th concentration determined by these two methods.

10.2.2 Estimation of Thorium(IV):

Thorium was assayed spectrophotometrically using Arsenazo(III) which forms a stable chelate compound with the former [152]. Fig. 10.1 shows the visible spectra of Arsenazo(III) as well as its complex with Th(IV). Th(IV)-Arsenazo(III) complex colour was developed in 10 mL solution containing 1 mL of 0.1% Arsenazo(III) solution and varying concentration of thorium followed by the addition of 5 mL of 12 M HNO₃ and 1 mL of sulfamic acid 1 M. It may be noted that a resultant nitric acid concentration of 6 M was needed to obtain steady and reproducible O.D. value. The absorbance of the solution against a suitable blank
was measured at 660 nm. The molar extinction coefficient was determined as $1.0 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$.

10.3 Results and Discussion:

Extraction of Th(IV) by HPBI:

The extraction of Th(IV) by a HPBI is represented as

$$\text{Th}^{4+} + 4 \text{HPBI} \rightleftharpoons \text{Th(PBI)}_4^{(\text{org})} + 4\text{H}^+ \quad (1)$$

Applying the law of mass action, the extraction equilibrium constant, $K_{ex}$, can be expressed as:

$$K_{ex} = \frac{[\text{Th(PBI)}_4^{(\text{org})}] [\text{H}^+]^4}{[\text{Th}^{4+}] [\text{HPBI}]_4^{(\text{org})}} \quad (2)$$

Neglecting the complexation by the isoxazolone anion (PBI$^{-}$) in the aqueous phase the distribution ratio for the binary extraction system Th(IV)-HPBI from nitric acid medium is given by

$$D_0 = \frac{[\text{Th(PBI)}_4^{(\text{org})}]}{[\text{Th}]_{\text{aq}} (1+\Sigma \beta_i [\text{NO}_3^-]^i)} \quad (3)$$

where $\beta_i$ are the complex formation constants of Th$^{4+}$ with nitrate ion in aqueous phase ($\log \beta_1 = 0.1; \log \beta_2 = 0.8$) [153]. For the calculation of $K_{ex}$, the corrections for the aqueous complexation of nitrate ion have been incorporated. On rearrangement eqn. (2) becomes.
Fig. 10.1: Visible spectra of Th(IV)-Arsenazo(III) complex.

Fig. 10.2: Variation of log D with log[HPBI]; [HNO₃]=0.5 M.
\[ \log K_{\text{ex}} = \log D_0 + 4 \log [H^+] - 4 \log [\text{HPBI}] + \log [1+X] \]  

(4)

where \( X = \sum \beta_i [\text{NO}_3]^i \).

The variation of log D with log [HPBI] is linear with a slope of 3.89 ± 0.08 (Fig. 10.2) indicating that four molecules of the \( \beta \)-diketones are associated with the extracted species. The dependence of log D with log [hydrogen ion activity] is found to be -3.80±0.04 thereby suggesting the validity of eqn. (4).

These observations conform to the organic phase species Th(PBI)\(_4\).

Table 10.2 gives the extraction constant values. It is fascinating to note that extraction constant for the Th(IV)-HPBI system is much larger as compared to those with Th(IV)-HPMBP [154] and Th(IV)-HTTA [155] systems.

**Table-10.2:** Extraction constant of Th(IV)-HPBI, Th(IV)-HPMBP and Th(IV)-HTTA systems.

<table>
<thead>
<tr>
<th>( \beta )-diketones</th>
<th>( \log K_{\text{ex}} )</th>
<th>( \log K_{\text{syn}} ) (TOPO)</th>
<th>( \log K_{\text{syn}} ) (TBP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPBI</td>
<td>8.26</td>
<td>6.70</td>
<td>7.78, 2.28 *</td>
</tr>
<tr>
<td>HPMBP</td>
<td>7.32</td>
<td>-</td>
<td>5.49</td>
</tr>
<tr>
<td>HTTA</td>
<td>2.25</td>
<td>4.63</td>
<td>7.50</td>
</tr>
</tbody>
</table>

*In case of TOPO, two adduct formation constants for Th(PBI)\(_4\).TOPO and Th(PBI)\(_4\).2 TOPO respectively are reported.*
The log $K_{ex}$ value obtained in the present work is larger compared to that reported by Jyothi et al [136] log $K_{ex} = 6.92$ probably due to the use of diluents of different polarities in the two studies. The log $K_{ex}$ value increases in the order: Th(IV) < Np(IV) < Pu(IV) which follow their ionic potentials [142, 143, 156] Table-10.3.

Table-10.3: Two phase extraction constants of Th(IV), Np(IV) and Pu(IV) with HPBI and HTTA.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Ionic radii (Å)</th>
<th>log $K_{ex}$ (HTTA)</th>
<th>log $K_{ex}$ (HPBI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th(IV)</td>
<td>1.05</td>
<td>2.25$^a$</td>
<td>8.26$^c$</td>
</tr>
<tr>
<td>Np(IV)</td>
<td>0.98</td>
<td>5.75$^b$</td>
<td>11.41$^d$</td>
</tr>
<tr>
<td>Pu(IV)</td>
<td>0.96</td>
<td>7.32$^b$</td>
<td>12.85$^d$</td>
</tr>
</tbody>
</table>

a- ref. 155; b- ref. 157; c- Present work; d-ref. 143.

Extraction of Th(IV) with mixtures of HPBI and oxodonor.

The extraction of Th(IV) by HPBI and neutral donor may be represented as

$$Th^{4+}_{aq} + 4 \text{HPBI}_{org} + n.S_{org} \xrightleftharpoons[K_{syn,n}]{\text{syn,n}} \text{Th(HPBI)}_{4}S_{n(org)} + 4H^{+}_{aq} \quad (5)$$

where $n$ = the number of neutral donor attached.

The overall extraction constant ($K_{syn,n}$) is given by
The distribution ratio of the synergistic extraction system ($D$) is given by the following eqn.

$$D = \frac{[\text{Th(PBI)}_4 \cdot S]_{\text{org}} + [\text{Th(PBI)}_4 \cdot S]_{\text{org}} + ... + [\text{Th(PBI)}_4 \cdot S]_{\text{org}}}{[\text{Th}] (1 + \sum \beta_i [\text{NO}_3]^{i})} \quad \ldots \quad (7)$$

From eqn. (2), (6) and (7)

$$K_{\text{syn,n}} = \frac{(D-D_0)[H^+]^4 (1 + \sum \beta_i [\text{NO}_3]^{i})}{[\text{HPBI}]_{\text{org}}^4 [S]_{\text{org}}^n} \quad \ldots \quad (8)$$

Taking the logarithm:

$$\log K_{\text{syn}} = \log(D-D_0) - 4 \log [\text{HPBI}] - n \log [S]$$

$$+ 4 \log[H^+] + \log(1 + \sum \beta_i [\text{NO}_3]^{i}) \quad (9)$$

The organic phase adduct formation reaction is represented by

$$\text{Th(PBI)}_4(\text{org}) + n \text{S}_{\text{org}} \rightleftharpoons \text{Th(PBI)}_4 \cdot n \cdot \text{S} \quad (10)$$

$$\beta_n = \frac{K_{\text{syn,n}}}{K_{\text{PBI}}} \quad \text{where} \quad n = 1 \quad \text{for TBP}$$

$$n = 1 \text{ or } 2 \quad \text{for TOPO}$$

Fig. 10.3 indicates the plots of $\log(D-D_0)$ vs $\log[\text{HPBI}]$ at a fixed concentration of nitric acid (1 M) as well as neutral oxodonor. A slope value of $3.81 \pm 0.15$ indicates four HPBI moieties are attached to the ternary complexed species. The plots of $\log(D-D_0)$
vs. log[S] at fixed concentrations of HPBl and HNO₃ suggest that only one unit (slope = 0.97 ± 0.02) of the neutral donor is present in the ternary extracted complex of TBP (Fig. 10.4). In the case of TOPO apart from binary Th(PBI)₄ species, Th(PBI)₄·TOPO and Th(PBI)₄·2 TOPO, appeared to co-exist (slope = 1.30±0.10). A graphical method was therefore employed for computing the adduct formation constants [158] Table 10.4.

Table-10.4: Extraction constants of Th(IV) in binary and ternary systems.

<table>
<thead>
<tr>
<th>Extraction constant</th>
<th>Variable</th>
<th>Graphical method</th>
<th>Algebraic method</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>log K_{ex}</td>
<td>HPBl</td>
<td>7.95±0.18</td>
<td>8.22±0.04</td>
<td>8.26±0.04</td>
</tr>
<tr>
<td></td>
<td>H⁺</td>
<td>8.37±0.01</td>
<td>8.29±0.04</td>
<td></td>
</tr>
<tr>
<td>log K_{syn} (TBP)</td>
<td>HPBl</td>
<td>15.06±0.27</td>
<td>14.88±0.04</td>
<td>14.96±0.04</td>
</tr>
<tr>
<td></td>
<td>TBP</td>
<td>14.93±0.07</td>
<td>15.03±0.02</td>
<td></td>
</tr>
<tr>
<td>log K_{syn} (TOPO)</td>
<td>TOPO</td>
<td>16.04</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>log K_{syn} (2 TOPO)</td>
<td>TOPO</td>
<td>18.92</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

It is clear from the data summarized in Table 10.2 that the formation of the adduct increase with increasing basicity. The K_{syn} values clearly show that TOPO is a more effective synergist than TBP. This observation is in tune with earlier report for tri, tetra as well as hexavalent metal ions [156,158,159].
Fig. 10.3: Variation of $\log (D - D_o)$ vs $\log [\text{HPBI}]$. $[\text{TOPO}] = 2.5 \times 10^{-4}\text{ M}; [\text{TBP}] = 1.0 \times 10^{-3}\text{ M}$.

Fig. 10.4: Variation of $\log (D - D_o)$ vs $\log [S]$. $[\text{HPBI}] = 1.0 \times 10^{-3}\text{ M}, [\text{HNO}_3] = 1.0\text{ M}$.
It is interesting to note that the extracted species in the present work do not contain any nitrate ion as earlier reported by Irving [155] for the HTTA extraction system. This could be due to the better availability of the isoxazolonate anion for complex formation even at moderately high nitric acid concentrations eventually forming more organophilic ternary extractable species such as Th(PBI)₄S.

It was observed that inspite of significantly lower pKₐ value of HPBI as compared to HPMBP, extraction constant value of Pu⁴⁺ decrease marginally for the former (Fig. 10.5). This was attributed to the prominent role of steric factors in the case of HPBI (0-0 distance 2.9 A°) as compared to HPMBP (0-0 distance 2.7 A°) and HTTA (0-0 distance 2.5 A°). Fig. 10.5 also shows the extraction constant data of Th(IV) with the three β-diketones which follow a linear inverse relation with the pKₐ values of the ligands. This is similar to the trend reported earlier for UO₂(Ⅵ)-β-diketone system [159] Table 10.5.

<table>
<thead>
<tr>
<th>β-diketones</th>
<th>log K₀²⁺</th>
<th>log K₀²⁺</th>
<th>log K₀²⁺</th>
<th>log K₀²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPBI</td>
<td>1.41</td>
<td>6.53</td>
<td>9.11</td>
<td>5.12</td>
</tr>
<tr>
<td>HPMBP</td>
<td>0.48</td>
<td>4.76</td>
<td>6.93</td>
<td>4.28</td>
</tr>
<tr>
<td>HTTA</td>
<td>-2.44</td>
<td>2.66</td>
<td>4.61</td>
<td>5.10</td>
</tr>
</tbody>
</table>
Fig. 10.5: Dependence of log $k_{ex}$ on $pK_a$ of $\beta$-diketones. 
(HTTA, HPMBP, HPBI).
Inspite of the presence of four bulky PBI moieties around Th(IV) ion, steric factors do not influence the trend expected on the basis of electronic effects. This is in sharp contrast to the behaviour of similar extraction system involving Pu(IV), which can be explained on the basis of the larger size of Th(IV) (ionic radius = 1.05 Å) vis-a-vis Pu(IV) (0.96 Å) [162].

In the Pu(IV) synergistic systems involving TOPO as the oxodonor species of the type Pu(PBI)_3 .X.TOPO as well as Pu(PBI)_3 .X.2 TOPO coexist (where X = NO_3^-). It is interesting to note that in the present work with Th(IV), species of the type Th(PBI)_4 .TOPO and Th(PBI)_4 .2 TOPO were predominant indicating that there is no steric hindrance to the adduct formation. Adduct formation constant of Th(PBI)_4 with TOPO is larger by two orders of magnitude as compared to the corresponding value of Pu(PBI)_4 [156, 163].

10.4 **Analytical significance:**

Th-234, the daughter product of naturally occurring U-238 can be milked from the latter when the two nuclides are in secular equilibrium. It is desirable to develop efficient methods for the chemical separation of trace concentration of Th from kilogram quantities of U which enables the use of Th-234 as a radioactive tracer. The existing methods based on the preferential extraction or adsorption of U(VI) as \( \text{UO}_2\text{Cl}_4^{2-} \) using quaternary amines as ligand anion exchangers and Dowex 1X4 as anion exchange
resin material respectively. In view of the presence of large excess of U these methods have limitations in the recovery and purification of Th. Due to the large difference in the extraction constants of HPBI with Th(IV) \((\log K_{ex} = 8.3)\) and UO\(_2\)(VI) \((\log K_{ex} = 1.4)\), this reagent offers a promise in the recovery and purification of Th-234 from bulk U-238. Brief details of the analytical procedure are as follows:

30% Aliquot-336 in chloroform was saturated with uranium by contacting with 8 M HCl solution of UO\(_3\). The organic phase was stored for about three months to allow Th-234 \((t_\frac{1}{2} = 24.1\) days) activity to grow and attain secular equilibrium with U-238 \((t_\frac{1}{2} = 4.47 \times 10^9\) years). Th-234 thus produced was transferred to the aqueous phase by contacting the uranium loaded organic phase with 8 M HCl. Th(IV) at 10^{-12} M concentration level is associated with millimolar concentration of uranium at this stage. The aqueous medium was subsequently changed to 0.5 M HNO\(_3\). 0.01 M HPBI in xylene was used for the preferential extraction of Th(IV) followed by two cycles of scrubbing with 0.5 M HNO\(_3\). Separation factor (\(D_{Th}/D_{U}\)) of approximately 2000 was achieved at every step. Th from the uranium free organic phase was stripped by 8 M HNO\(_3\) and the aqueous phase was freed from any dissolved ligand by contacting it twice with xylene.

**Conclusion**

Formation of adducts of the stoichiometry Th(PBI)\(_4\)\(_{.5}\) and Th(PBI)\(_4\)\(_{.25}\) suggest the possibility of co-ordination number of 9 and 10 for Th\(^{4+}\) in these complexes. Adduct formation constant
values are distinctly larger by about 2 log units for the thorium(IV) ternary complexes as compared to the corresponding values for Pu(IV) complexes conform to the reduced role of steric factors in the case of Th$^{4+}$. Extraction constant values of Th-HPBI is larger by about 6 log units and of Th(IV)-HPBI-TBP by about 8 log units than the corresponding values with HTTA. Consequently thorium can be recovered from stronger acidic and complexing solutions. HPBI has been found to be a promising extractant for the separation of Th-234 from natural uranium.