Para-substituted 3-phenyl-4-aryl-5-isoxazolones as chelating agents for the synergistic extraction of thorium(IV) and uranium(VI) in the presence of various crown ethers
effects on the extraction behavior of thorium(IV) and uranium(VI) from nitric acid solutions.

![Structural formula of the compounds](image)

The synergistic extraction of thorium(IV) and uranium(VI) with 4-acyl-3-phenyl-5-isoxazolones in the presence of various neutral organophosphorus extractants [Mansingh et al. 1996; Thakur et al. 1996; Mohapatra et al. 1997] and amides [Banerjee et al. 2003; Bhattacharya et al. 2004] have been widely investigated. Recently from our laboratory, high selectivity has been reported between thorium (IV) and uranium(VI) with HPBI in the presence of B15C5 and has been attributed to the crown ether size compatibility with Th IV [Sahu et al. 2000]. The introduction of cation selectivity into synergistic solvent extraction is best accomplished by the use of crown ethers that form both stable in-cavity complexes with the target cation and have adequate functionalisation to impart organophilicity [Bond et al. 2000]. Hence in the present study, the synergistic extraction of thorium(IV) and uranium(VI) with HFBPI in the presence and absence of various crown ethers, benzo-15-crown-5 (B15C5), dicyclohexano-18-crown-6 (DC18C6) and dibenzo-18-crown-6 (DB18C6) has been investigated with a view to improve the selectivity between these actinides.
EXPERIMENTAL

Chemicals

3-Phenyl-5-isoxazolone and corresponding acid chlorides were obtained from Aldrich Chemical Company. All other chemicals used were the same as in Chapter 3.

Syntheses of various para-substituted 3-phenyl-4-aryl-5-isoxazolones

The para-substituted 3-phenyl-4-aryl-5-isoxazolones, HFBPI and HTPI were synthesized from 3-phenyl-5-isoxazolone and the corresponding acid chloride following the method described elsewhere [Korte and Storiko 1961] (Scheme 5.1).

\[
\text{Ca(OH)}_2 + \text{ClC-C-} \xrightarrow{\text{1,4-Dioxane, Reflux}} \text{N-} \xrightarrow{\text{Ca(OH)}_2} \text{O-} \xrightarrow{\text{1,4-Dioxane, Reflux}} \text{Ca(OH)}_2
\]

Scheme 5.1

3-phenyl-4-(4-fluorobenzoyl)-5-isoxazolone

The synthesized 3-phenyl-4-(4-fluorobenzoyl)-5-isoxazolone was identified by elemental analyses, IR and \(^1\)H NMR spectral data. HFBPI: m.p. 148°C. Elemental analyses: Calc. for C\(_{16}\)H\(_{10}\)NO\(_3\)F: C 67.84, H 3.53, N 4.95 %. Found: C 67.70, H 3.92, N 4.95 %. \(^1\)H NMR (CDCl\(_3\)) data \(\delta\) (ppm): 6.80-7.39 (m, 9H, phenyl); IR (KBr) data (v cm\(^{-1}\)): 3429, 1706 (C = O), 1619, 1480. In the \(^1\)H NMR spectrum of HFBPI (Fig. 5.1), no peak corresponding to the enolic –OH has been observed. However, the absence of a peak at \(\delta\) 3.8 ppm
corresponding to the methyne proton, at the fourth position of the isoxazolone ring, confirms the existence of HFBPI in the enolic form.

Figure 5.1. $^1$H NMR spectrum of HFBPI.

3-phenyl-4-(4-toluoyl)-5-isoxazolone

The synthesized 3-phenyl-4-(4-toluoyl)-5-isoxazolone was identified by elemental analyses, IR and $^1$H NMR spectral data. HTPI: m.p. 144°C; $^1$H NMR (CDCl$_3$) data $\delta$ (ppm): 6.92 – 7.34 (m, 9H, phenyl), 2.32 (s, 3H, CH$_3$ of the aromatic ring); IR (KBr) data (v cm$^{-1}$): 2600, 1706 (C=O), 1626, 1593; Elemental analyses: Calc. for C$_{17}$H$_{13}$N$_2$O$_3$: C 73.12, H 4.66, N 5.02%. Found: C 73.48, H 4.38, N 5.31%. In the $^1$H NMR spectrum of HTPI (Fig. 5.2), no peak corresponding to the enolic-OH has been observed. However, the absence of a peak at $\delta$ 3.8 ppm corresponding to the methyne proton, at the fourth position of the isoxazolone ring, confirms the existence of HTPI in the enolic form.
Figure 5.2. $^1$H NMR spectrum of HTPI.

Solvent extraction and analytical procedure

The solvent extraction and analytical procedures followed in this chapter are the same as described in Chapter 3. Preliminary experiments showed that the extraction equilibrium was attained within 30 min for thorium(IV) and 60 min for uranium(VI).

Preparation of metal complexes

The metal-3-phenyl-4-aryyl-5-isoxazolone complexes were prepared by the procedures as described in Chapter 3. The complexes were characterized by elemental analyses, IR and $^1$H NMR spectral data. The solutes studied were Th(FBPI)$_4$, Th(TPI)$_4$, Th(FBPI)$_4$-B15C5, UO$_2$(FBPI)$_2$, UO$_2$(TPI)$_2$, UO$_2$(FBPI)$_2$-B15C5.
RESULTS AND DISCUSSION

Extraction of thorium(IV) and uranium(VI) with HFBPI or HTPI

The extraction of thorium(IV) and uranium(VI) with HFBPI or HTPI (HX) alone in chloroform as a function of the extractant concentration from 1.0 mol/dm$^3$ sodium nitrate solutions at constant metal ($1 \times 10^{-4}$ mol/dm$^3$ for both thorium(IV) and uranium(VI)) and nitric acid (0.5 mol/dm$^3$) concentrations has been investigated and the results are depicted in Fig. 5.3. Plots (Fig. 5.3) of log $D_0$ vs. log [HX] have slopes of 4.0 ± 0.05 for thorium(IV) and 2.0 ± 0.1 for uranium(VI), indicating the extraction of complexes \(\text{Th(FBPI)}_4\), \(\text{Th(TPI)}_4\), \(\text{UO}_2\text{(FBPI)}_2\) and \(\text{UO}_2\text{(TPI)}_2\). These in conjunction with the slopes of -4.0 ± 0.05 and -2.0 ± 0.1 observed for thorium(IV) and uranium(VI), respectively, with hydrogen ion variation (Figs. 5.4 and 5.5) at constant HFBPI/HTPI (0.005 mol/dm$^3$ for thorium(IV) and 0.05 mol/dm$^3$ for uranium(VI)) concentration, confirm the extraction of simple metal-chelates.

Based on the above results, the extraction equilibria of thorium(IV) and uranium(VI) with chelating extractants HX (= HFBPI or HTPI) alone may be expressed as

\[
\text{Th}^{4+} + 4 \text{(HX)}_{\text{org}} \rightleftharpoons K_{\text{ex,0}} \text{ThX}_4 + 4 \text{H}^{+}_{\text{aq}} \tag{1}
\]

\[
\text{UO}_2^{2+} + 2 \text{(HX)}_{\text{org}} \rightleftharpoons K_{\text{ex,0}} \text{UO}_2\text{X}_2 + 2 \text{H}^{+}_{\text{aq}} \tag{2}
\]

where \(K_{\text{ex,0}}\) denotes the equilibrium constant. Since the partition coefficients of para-substituted 3-phenyl-4-aroil-5-isoaxolones were found to be very high (log \(K_D\) for HFBPI = 2.8; for HTPI = 2.78 [Odashima et al., 1985]), the concentration of isoaxolonate anion in the aqueous phase can be neglected.
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Figure 5.3. Effect of 3-phenyl-4-aroyl-5-isoxazolone (HX) concentration on the extraction of thorium(IV) and uranium(VI). Aqueous phase = 0.5 mol/dm³ + 0.5 mol/dm³ NaNO₃. Slope of the line (a) HFBPI = 4.0 ± 0.05 (b) HTPI = 4.0 ± 0.05 (c) HFBPI = 2.0 ± 0.1 (d) HTPI = 2.0 ± 0.1.

The distribution ratio, $D_\text{b}$, of thorium(IV) is given by

$$D_\text{b} = \frac{[\text{ThX}_{4}^{\text{org}}]}{[\text{Th}^{4+}]_{\text{aq}}\{1 + \beta_1[\text{NO}_3^-]_{\text{aq}} + \beta_2[\text{NO}_3^-]_{\text{aq}}^2\}}$$  \hspace{1cm} (3)$$

where $\beta_1$ is the complex formation constant of thorium(IV) with nitrate ions in the aqueous phase. The values of stability constants (log $\beta_1 = 0.1$; log $\beta_2 = 0.8$) were taken from the literature [Oliver and Davis 1972]. Then the distribution ratio, $D_\text{b}$, of thorium(IV) can be written from Eqs. (1) and (3) as
Figure 5.4. Effect of hydrogen ion concentration on the extraction of thorium(IV). Aqueous phase = 1.0 mol/dm$^3$ NaNO$_3$; [HFBI] = [HTPI] = 0.005 mol/dm$^3$. Slope of the line (a) HFBPI = -4.0 ± 0.05 (b) HTPI = -4.0 ± 0.05.

$$D_o = \frac{K_{ex,0}[HX]_{aq}^4}{[H^+]_{aq}^4\{1 + \beta_1[NO_3]_{aq} + \beta_2[NO_3]_{aq}^2\}}$$  \hspace{1cm} (4)

Similarly, the distribution ratio, $D_o$, for uranium(VI) can be written as

$$D_o = \frac{K_{ex,0}[HX]_{aq}^2}{[H^+]_{aq}^2\{1 + \beta_1[NO_3]_{aq}\}}$$  \hspace{1cm} (5)

The stability constant for uranium(VI) (log $\beta_1$ = -0.3) with nitrate ion was taken from the literature [Kotrly and Sucha 1985].

The formation of the above simple metal chelates were further confirmed by analyzing the equilibrium data (presented in the Figs. 5.3 - 5.5) using Eq. (4) for thorium(IV) and Eq. (5) for uranium(VI). The equilibrium constants for the above complexes were determined by nonlinear regression...
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Figure 5.5. Effect of hydrogen ion concentration on the extraction of uranium(VI). Aqueous phase = 0.5 mol/dm$^3$ HNO$_3$ + 0.5 mol/dm$^3$ NaNO$_3$; [HFBPI] = [HTPI] = 0.05 mol/dm$^3$. Slope of the line (a) HFBPI = -2.0 ± 0.1 (b) HTPI = -2.0 ± 0.1.

analysis as described in Chapter 3. The equilibrium constants thus calculated refer only to concentration quotients, calculated on the assumption that the activity coefficients of the species involved do not change significantly under the present experimental conditions. It is clear from Table 5.1 that the log equilibrium constant value of thorium(IV) with HFBPI is about 7-fold higher than that of uranium(VI). A similar behavior has been observed in the extraction of thorium(IV) and uranium(VI) with HPBI [Sahu et al. 2000] from nitric acid solutions. A linear correlation between log $K_{ex,0}$ values of various heterocyclic β-diketones for the extraction of thorium(IV) and uranium(VI) with their $pK_a$ values is shown in Fig. 5.6. It is clear from the figure that the log equilibrium constant value decreases as the $pK_a$ value increases.
Table 5.1. Log equilibrium constants (log $K_{ex,o}$) for the extraction of thorium(IV) and uranium(VI) with various heterocyclic $\beta$-diketones.

<table>
<thead>
<tr>
<th>Extractant</th>
<th>$pK_a$</th>
<th>Log $K_{ex,o}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Th(IV)</td>
</tr>
<tr>
<td>HFBPI</td>
<td>0.65$^a$</td>
<td>9.16 ± 0.02</td>
</tr>
<tr>
<td>HTPI</td>
<td>1.48$^a$</td>
<td>8.38 ± 0.03</td>
</tr>
<tr>
<td>HPBI</td>
<td>1.23$^b$</td>
<td>8.71 ± 0.03$^c$</td>
</tr>
<tr>
<td>HPMBP</td>
<td>3.92</td>
<td>6.72 ± 0.04$^d$</td>
</tr>
</tbody>
</table>


Figure 5.6. Plots of log $K_{ex,o}$ vs $pK_a$ for the extraction of thorium(IV) and uranium(VI) with various heterocyclic $\beta$-diketones.

The strong acidity of 4-aroyl-5-isoxazolones could be partly attributed to the heterocyclic $\pi$-electron conjugation system, which contains electronegative nitrogen and oxygen. The O---O distance between two donating oxygen atoms of the various derivatives of 4-aroyl-5-isoxazolones...
should be significant with respect to the stability of the intramolecular hydrogen bonding and the formation of metal complexes. Hence, the O---O distances of various para-substituted 4-aroyl-5-isoxazolones were determined by semi-empirical PM3/H molecular orbital calculations [Stewart 1989] taking into account the hydrogen bond. A ball-and-stick representation based on PM3/H optimized structures of HFBPI, HPBI and HTPI are given in Fig. 5.7. It is clear from the above results that the para-substitution in 3-phenyl-4-benzoyl-5-isoxazolones do not narrow the O---O distances (O---O distance of HPBI = 2.83 Å; HFBPI = 2.83 Å; HTPI = 2.83 Å) between the two donating oxygen atoms. The larger O---O distances observed in para-substituted 4-aroyl-5-isoxazolones would decrease the stability of the intramolecular hydrogen bonding, resulting in great enhancement of acidity. However, it is clear from the present study that the log $K_{ex,0}$ values for both thorium(IV) and uranium(VI) varies in accordance with the nature of the substituent, electron withdrawing (-F) or electron donating (-CH$_3$) group, on the benzoyl moiety of the HPBI system. It is also evident from the results that the extraction efficiency of these metal ions with various para-substituted derivatives of 3-phenyl-4-benzoyl-5-isoxazolones varies in accordance with their $pK_a$ values.

**Solid complexes of thorium(IV) and uranium(VI) with para-substituted 3-phenyl-4-aroyl-5-isoxazolones and their characterization**

Solid complexes of thorium(IV) and uranium(VI) with HFBPI/HTPI were characterized by elemental analyses, IR and $^1$H NMR techniques.
Figure 5.7. Ball-and-stick representation based on PM3/H optimized structures of HFBPI, HTPI and HPBI, respectively.
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Elemental analyses of binary complexes

The analytical data presented in Table 5.2 show that thorium(IV) and uranium(VI) reacted with HFBPI and HTPI, in the metal : ligand mole ratio of 1 : 4 and 1 : 2, respectively.

<table>
<thead>
<tr>
<th>Complex</th>
<th>%C Found</th>
<th>%H Found</th>
<th>%N Found</th>
<th>%M Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th(FBPI)₄.H₂O</td>
<td>56.62 (55.73)</td>
<td>2.77 (2.76)</td>
<td>4.08 (4.06)</td>
<td>16.93 (16.84)</td>
</tr>
<tr>
<td>UO₂(FBPI)₂.H₂O</td>
<td>46.22 (45.07)</td>
<td>2.52 (2.35)</td>
<td>3.61 (3.29)</td>
<td>28.26 (27.93)</td>
</tr>
<tr>
<td>Th(TPlkH₂O</td>
<td>60.55 (59.91)</td>
<td>3.71 (3.67)</td>
<td>4.15 (4.11)</td>
<td>16.97 (17.03)</td>
</tr>
<tr>
<td>UO₂(TPlH₂O</td>
<td>48.99 (48.34)</td>
<td>3.24 (3.08)</td>
<td>3.22 (3.32)</td>
<td>28.65 (28.20)</td>
</tr>
</tbody>
</table>

Figures in parentheses indicate calculated values.

IR spectra of binary complexes

Figs. 5.8 and 5.9 show the IR spectra of the complexes of thorium(IV) and uranium(VI) with HFBPI and HTPI, respectively along with free ligands. In the spectra of the complexes, the broad absorption in the region 3000-3500 cm⁻¹, indicate the presence of water of hydration, as observed in actinide metal complexes of 4-arylopyrazolonates [Meera and Reddy 2004]. The presence of inner and outer sphere of hydration in uranyl isoxazolonate has been well documented [Mohapatra et al. 1997; Banerjee et al. 2003].
Figure 5.8. IR spectra of HFBPI ligand, Th-HFBPI and U-HFBPI complexes.
Figure 5.9. IR spectra of HTPI ligand, Th-HTPI and U-HTPI complexes.
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The intense broad band centered around 2600 cm\(^{-1}\), which is assigned to the \(\nu\) (O-H) in the spectrum of the ligands, is absent in the spectra of the complexes, indicating the enolization of the O-H group and the involvement of oxygen of the hydroxyl group in chelation. The stretching frequency of the C=O group has been shifted from 1706 cm\(^{-1}\) in the free ligand to lower frequency (1640 in Th(FBPI)\(_4\), 1633 in Th(TPI)\(_4\) and UO\(_2\)(FBPI)\(_2\), 1620 cm\(^{-1}\) in UO\(_2\)(TPI)\(_2\)) in the complexes, which suggests that the carbonyl group is involved in complexation. The other strong absorption occurring around 937-944 cm\(^{-1}\) may be assigned to \(\nu\)(O=U=O) of UO\(_2^{2+}\) [Kannan et al. 2002].

\(^1\)H NMR spectra of binary complexes

The \(^1\)H NMR spectral data of the binary complexes (Table 5.3) shows all the expected resonances for 4-aroyl-5-isoxazolonates and the free ligands, the integration of the signals being in accordance with the formulae proposed. The downfield shift of the phenyl protons has been observed in both thorium(IV) and uranium(VI) complexes of HFBPI and HTPI. The signal of CH\(_3\) protons of methyl group in HTPI has also been shifted downfield upon coordination with metal ion in all the binary complexes. The downfield shifts observed were larger for thorium than in uranium complexes.

From the elemental analyses, FT-IR and \(^1\)H NMR spectral data, the proposed structures of thorium(IV) and uranium(VI) with HFBPI and HTPI is given in Fig. 5.10. The uranyl ion is surrounded by two molecules of HFBPI/HTPI and one water molecule to give a coordination number of seven and pentagonal bipyramidal geometry, as observed in uranium-HTTA and uranium-HPMBP/HPMAP complexes [Okafor et al. 1990; Kannan et al. 2001]. In the case of Th-HFBPI/HTPI complex, Th\(^{4+}\) is surrounded by four
HFBPI/HTPI molecules and one water molecule, to give a coordination number of 9.

Table 5.3. $^1$H NMR spectral data for free ligands and binary complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phenyl protons</th>
<th>Methyl protons</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFBPI</td>
<td>6.80–7.39 (m)</td>
<td>–</td>
</tr>
<tr>
<td>HTPI</td>
<td>6.92–7.34 (m)</td>
<td>2.32 (s)</td>
</tr>
<tr>
<td>Th-FBPI</td>
<td>7.01–7.46 (m)</td>
<td>–</td>
</tr>
<tr>
<td>U-FBPI</td>
<td>6.89–7.71 (m)</td>
<td>–</td>
</tr>
<tr>
<td>Th-TPI</td>
<td>6.75–7.91 (m)</td>
<td>2.68 (s)</td>
</tr>
<tr>
<td>U-TPI</td>
<td>6.98–7.70 (m)</td>
<td>2.52 (s)</td>
</tr>
</tbody>
</table>

It is clear from the results (Fig. 5.3) that the selectivity between thorium(IV) and uranium(VI) increases with increase in the concentration of HFBPI at constant nitric acid concentration (Separation Factor, S.F. = $5.4 \times 10^3$ at 0.02 mol/dm$^3$ HFBPI; S.F. = $2.2 \times 10^4$ at 0.04 mol/dm$^3$ HFBPI). Further, these S.F. values are found to be lower than that of HPMFBP (S.F. = $8.51 \times 10^3$ at 0.02 mol/dm$^3$ HPMFBP; S.F. = $3.42 \times 10^4$ at 0.04 mol/dm$^3$ HPMFBP) system [Meera and Reddy 2004]. These results suggest that the O–O distance is one of the most important factors that governs the selectivity. The separability of thorium(IV) and uranium(VI) with ligands of shorter O–O distance is found to be better (bite size of HPMFBP = 2.67 Å; bite size of HFBPI = 2.83 Å). In view of the better extraction efficiency and selectivity observed, HFBPI was chosen for further experimentation, especially to study the synergistic extraction in presence of crown ethers.
Figure 5.10. Proposed structures of thorium(IV) and uranium(VI) with HFBPI or HTPI.

Extraction of thorium(IV) and uranium(VI) with mixtures of HFBPI and crown ethers

The extraction of thorium(IV) and uranium(VI) from 0.5 mol/dm$^3$ nitric acid + 0.5 mol/dm$^3$ sodium nitrate solutions with mixtures of HFBPI (0.001-
0.008 mol/dm³ for thorium(IV) and 0.02-0.1 mol/dm³ for uranium(VI)) and DC18C6 (0.0004 - 0.002 mol/dm³ for thorium(IV) and 0.002 - 0.006 mol/dm³ for uranium(VI)), DB18C6 (0.0006 - 0.004 mol/dm³ for thorium(IV) and 0.002 - 0.007 mol/dm³ for uranium(VI)) or B15C5 (0.0004 - 0.002 mol/dm³ for thorium(IV) and 0.001 - 0.006 mol/dm³ for uranium(VI)) in chloroform has been studied. It was found that the extraction of these metal ions into chloroform with crown ether alone was negligible under these experimental conditions. However, with mixtures of HFBPI and crown ethers a considerable synergistic enhancement (Synergistic enhancement factor = $D/D_{HFBPI} + D_{CE}$, where $D$ = distribution ratio with HFBPI + CE; $D_{HFBPI}$= distribution ratio with HFBPI alone and $D_{CE}$=distribution ratio with CE alone) in the extraction of these metal ions has been observed (Table 5.4).

Table 5.4. Synergistic enhancement factors of thorium(IV) and uranium(VI) with HFBPI in presence of crown ethers.

<table>
<thead>
<tr>
<th>Extraction system</th>
<th>Synergistic enhancement factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Th(IV)</td>
</tr>
<tr>
<td>HFBPI + DC18C6</td>
<td>3</td>
</tr>
<tr>
<td>HFBPI + DB18C6</td>
<td>2</td>
</tr>
<tr>
<td>HFBPI + B15C5</td>
<td>9</td>
</tr>
</tbody>
</table>

Th(IV): 0.005 mol/dm³ HFBPI + 0.002 mol/dm³ CE; U(VI): 0.1 mol/dm³ HFBPI + 0.006 mol/dm³ CE.

It is clear from the plots (Figs. 5.11 and 5.12) of log $(D - D_0)$ vs log [HFBPI] that at constant CE (0.001 mol/dm³ for thorium(IV) and 0.005 mol/dm³ for uranium(VI) and nitric acid concentrations (0.5 mol/dm³), only four HFBPI moieties in the case of thorium(IV) and two HFBPI moieties in
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Figure 5.11. Effect of HFBPI concentration on the extraction of thorium(IV) at constant CE (0.001 mol/dm³) concentration. Aqueous phase = 0.5 mol/dm³ HNO₃ + 0.5 mol/dm³ NaNO₂. Slope of the line (a) B15C5 = 4.0 ± 0.05 (b) DC18C6 = 4.0 ± 0.05 (c) DB18C6 = 4.0 ± 0.1.

the case of uranium(VI) are involved in the synergistic species extracted into the organic phase. The plots (Figs. 5.13 and 5.14) of log (D - D₀) vs log [Cl⁻] at constant HFBPI concentration (0.005 mol/dm³ for thorium(IV) and 0.1 mol/dm³ for uranium(VI)) gave slopes of unity for both metal ions indicating the participation of only one CE molecule in the synergistic extracted species. These in conjunction with the slopes of -4.0 ± 0.05 and -2.0 ± 0.05 observed for the extraction of thorium(IV) and uranium(VI) (Figs. 5.15 and 5.16), respectively, with H⁺ variation experiments at constant HFBPI + CE, indicate
the nature of the extracted complexes as Th(FBPI)$_4$·CE and UO$_2$(FBPI)·CE. Similar synergistic complexes, Th(PBI)$_4$·CE and UO$_2$(PBI)$_2$·CE have been observed with HPBI in presence of various crown ethers [Sahu et al. 2000].

![Figure 5.12](image)

**Figure 5.12.** Effect of HFBPI concentration on the extraction of uranium(VI) at constant CE (0.005 mol/dm$^3$) concentration. Aqueous phase = 0.5 mol/dm$^3$ HNO$_3$ + 0.5 mol/dm$^3$ NaN$\_3$. Slope of the line (a) DC18C6 = 2.0 ± 0.1 (b) B15C5 = 2.0 ± 0.05 (c) DB18C6 = 2.0 ± 0.05.

From the preceding studies, the synergistic extraction equilibrium of thorium(IV) with HFBPI (HX) in the presence of crown ether, CE, may be represented as

$$\text{Th}^{4+}_{\text{aq}} + 4\text{HX}_{\text{org}} + n\text{CE}_{\text{org}} \rightleftharpoons K \rightarrow \text{ThX}_{4n}\text{CE}_{n\text{org}} + 4\text{H}^+_{\text{aq}} \quad (6)$$

The overall extraction constant, $K$, is given as
where \( n = 0 \) or 1. The distribution ratio, \( D \), of the synergistic extraction system is given by Eq. (8)

\[
D = \frac{[\text{ThX}_4 \text{CE}]_{\text{org}} + [\text{ThX}_4 \text{CE}]}{[\text{Th}^{4+}]_{\text{aq}} \{1 + \beta_1 [\text{NO}_3]_{\text{aq}} + \beta_2 [\text{NO}_3]_{\text{aq}}^2\}}
\]  

(8)

**Figure 5.13.** Effect of CE concentration on the extraction of thorium(IV) at constant HFBPI (0.005 mol/dm³) concentration. Aqueous phase = 0.5 mol/dm³ HNO₃ + 0.5 mol/dm³ NaNO₃. Slope of the line (a) B15C5 = 1.0 ± 0.1 (b) DC18C6 = 1.0 ± 0.05 (c) DB18C6 = 1.0 ± 0.05.
Figure 5.14. Effect of CE concentration on the extraction of uranium(VI) at constant HFBPI (0.1 mol/dm$^3$) concentration. Aqueous phase = 0.5 mol/dm$^3$ HNO$_3 + 0.5$ mol/dm$^3$ NaNO$_3$. Slope of the line (a) DC18C6 = 1.0 ± 0.1 (b) B15C5 = 1.0 ± 0.05 (c) DB18C6 = 1.0 ± 0.1.

From Eqs. (3), (7) and (8)

$$K = \frac{(D - D_0)\left[H^+\right]^{1+\beta_1\left[NO_3^-\right]_{aq} + \beta_2\left[NO_3^-\right]^2_{aq}}}{[HX]_{org}[CE]_{org}}$$  \hspace{1cm} (9)

Taking logarithms for Eq. (9),

$$\log K = \log (D - D_0) - 4 \log [HX]_{org} - \log [CE]_{org} + 4 \log [H^+]_{aq}$$

$$+ \log \{1+\beta_1[NO_3^-]_{aq} + \beta_2[NO_3^-]^2_{aq}\}$$  \hspace{1cm} (10)

The organic phase adduct formation reaction is represented as

$$\text{ThX}_4^{n\text{CE}_{org}} \rightleftharpoons K_{CE} \text{ThX}_4.n\text{CE}_{org}$$  \hspace{1cm} (11)

where $K_{CE}$ is the organic phase adduct formation constant and is given as
From Eqs. (1), (6) (11) and (12)

\[
K_{\text{CE}} = \frac{K}{K_{\text{ex,0}}}
\]  

(13)

Figure 5.15. Effect of hydrogen ion concentration on the extraction of thorium(IV) at constant HFBPI (0.005 mol/dm\(^3\)) + CE (0.001 mol/dm\(^3\)) concentration. Slope of the line (a) B15C5 = -4.0 \pm 0.05 \text{ (b) DC18C6 = -4.0 \pm 0.05 (c) DB18C6 = -4.0 \pm 0.05.}

For a synergistic extraction system employing CE, the extraction equilibrium of uranium(VI) may be represented as

\[
\text{UO}_2^{2+} + 2(HX)_{\text{org}} + n \text{CE}_{\text{org}} \rightleftharpoons \text{K} \rightarrow \text{UO}_2X_{2n}\text{CE}_{\text{org}} + 2H^+_{\text{aq}}
\]  

(14)
where \( n = 0 \) or 1. Then the distribution ratio, \( D \), of the synergistic extraction system for uranium(VI) is given by

\[
D = \frac{[\text{UO}_2\text{X}_2]_{\text{org}} + [\text{UO}_2\text{X}_2,\text{CE}]_{\text{org}}}{[\text{UO}_2^{2+}]_{\text{aq}}(1 + \beta_1[\text{NO}_3^-]_{\text{aq}})}
\]  

(15)

From Eqs. (5), (14) and (15)

\[
K = \frac{(D - D_0)[\text{H}^+]_{\text{aq}}(1 + \beta_1[\text{NO}_3^-]_{\text{aq}})}{[\text{HX}]_{\text{org}}[\text{CE}]_{\text{org}}}
\]  

(16)

![Graph](image)

**Figure 5.16.** Effect of hydrogen ion concentration on the extraction of uranium(VI) at constant HFBPI (0.1 mol/dm\(^3\)) + CE (0.005 mol/dm\(^3\)) concentration. Slope of the line (a) DC18C6 = -2.0 \pm 0.05 (b) B15C5 = -2.0 \pm 0.05 (c) DB18C6 = -2.0 \pm 0.05.

The organic phase adduct formation reaction is represented as

\[
\text{UO}_2\text{X}_2,\text{org} + n\text{CE}_{\text{org}} \xrightleftharpoons{K_{CE}} \text{UO}_2\text{X}_2,n\text{CE}_{\text{org}}
\]  

(17)
where \( K_{CE} \), the organic phase adduct formation constant is given by

\[
K_{CE} = \frac{K}{K_{ex,5}} \quad (18)
\]

Since the partition coefficients of CEs used (\( \log K_{(D,DC18C6)} = 3.52 \) [Mohapatra et al. 1991], \( \log K_{(D,DB18C6)} = 3.9 \) [Hasegawa et al. 1984], and \( \log K_{(D,B15C5)} = 2.5 \) [Hasegawa et al. 1984]) are known to be quite large, no correction is necessary for the partitioning of these crown ethers in the aqueous phase. It has been reported that the interaction between the chelating agent and a neutral oxo-donor in chloroform are, in general, weaker when the diluent itself has strong interaction with the oxo-donor [Sekine et al.1983]. Hence it is assumed that there is negligible interaction between HFBPI and CEs in chloroform. The above extracted complexes were further confirmed by analyzing the equilibrium data using Eq. (9) for thorium(IV) and Eq. (16) for uranium(VI). The synergistic equilibrium constants of the above extracted complexes for these metal ions were deduced by nonlinear regression analysis and are given in Table 5.5.

**Table 5.5.** Two phase synergistic equilibrium constants (\( K \)) and organic phase adduct formation constants (\( K_{CE} \)) of thorium(IV) and uranium(VI) with HFBPI-CE-Chloroform systems.

<table>
<thead>
<tr>
<th>CE</th>
<th>Th(IV)</th>
<th>U(VI)</th>
<th>Th(IV)</th>
<th>U(VI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC18C6</td>
<td>12.23 ± 0.02</td>
<td>4.97 ± 0.02</td>
<td>3.07 ± 0.02</td>
<td>3.11 ± 0.02</td>
</tr>
<tr>
<td>DB18C6</td>
<td>11.71 ± 0.03</td>
<td>3.99 ± 0.02</td>
<td>2.56 ± 0.03</td>
<td>2.13 ± 0.01</td>
</tr>
<tr>
<td>B15C5</td>
<td>12.77 ± 0.02</td>
<td>4.64 ± 0.01</td>
<td>3.6 ± 0.02</td>
<td>2.78 ± 0.02</td>
</tr>
</tbody>
</table>

The adduct formation constants, \( K_{CE} \), for the organic phase synergistic reaction of Th-HFBPI-chelate or U-HFBPI-chelate with various crown ethers were calculated and are given in Table 5.5. The sharp decrease in the
Complexation for both thorium(IV) and uranium(VI) from DC18C6 to DB18C6 mostly reflect the increase in steric effects and decrease in basicity of crown ethers. A similar trend has been observed in the extraction of thorium(IV) and uranium(VI) with HPBI [Sahu et al. 2000] and HTTA [Mathur and Choppin 1993] in the presence of these crown ethers. The adduct formation constant \( \log K_{CE} = 3.60 \) of \( \text{Th}(\text{FBPI})_4\text{B15C5} \) is higher than that of \( \text{Th}(\text{PBI})_4\text{B15C5} \) \( \log K_{CE} = 3.41 \) [Sahu et al. 2000]). It is well known that stable adduct formation reaction is usually brought out by strong acidic extractants \( \text{pK}_a \) of HFBPI = 0.65; HPBI= 1.23) as observed in the present system. The maximum in \( \log K_{CE} \) for \( \text{Th}(\text{FBPI})_4\text{B15C5} \) is likely to be associated with a good fit of \( \text{Th}^{4+} \) (ionic diameter = 0.20 nm [Yonezawa and Choppin 1989]) in the cavity of B15C5 (cavity size = 0.17 - 0.22 nm [Mathur and Khopkar 1988]). On the other hand, in the case of uranium(VI) (ionic diameter = 0.15 nm for U in \( \text{UO}_2^{2+} \) [Yonezawa and Choppin 1989]) adduct formation constant values increases regularly to DC18C6 (cavity size = 0.26 - 0.32 nm [Mathur and Khopkar 1988]). It can be concluded that the relationship between the cavity size and the ionic diameter is not the determining factor in the complexation of \( \text{UO}_2^{2+} \). The unusual behavior observed in the present investigations may be attributed to a variety of geometric (cavity size and steric repulsion between extractants), enthalpic (donor basicity) and entropic (cation dehydration) effects involved in the extraction of f-elements with crown ethers in the presence of HFBPI. A better understanding of the origin of the selectivity displaced in the extraction of thorium(IV) will require more detailed investigations of the solution structure of the complexes.
Solid complexes of thorium(IV) and uranium(VI) with mixtures of HFBPI and CE and their characterization

**Elemental analyses of ternary complexes**

The analytical data presented in Table 5.6 show that thorium(IV) and uranium(VI) reacted with HFBPI and crown ether in the metal : ligand : crown ether mole ratio of 1 : 4 : 1 and 1 : 2 : 1, respectively.

**Table 5.6. Elemental analyses of ternary complexes.**

<table>
<thead>
<tr>
<th>Complex</th>
<th>% C Found</th>
<th>% H Found</th>
<th>% N Found</th>
<th>% M Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th(FBPI)₄·B15C₅·H₂O</td>
<td>57.65</td>
<td>3.38</td>
<td>3.77</td>
<td>14.14</td>
</tr>
<tr>
<td></td>
<td>(56.87)</td>
<td>(3.52)</td>
<td>(3.40)</td>
<td>(14.10)</td>
</tr>
<tr>
<td>UO₂(FBPI)₂·B15C₅·H₂O</td>
<td>50.45</td>
<td>3.07</td>
<td>2.94</td>
<td>21.82</td>
</tr>
<tr>
<td></td>
<td>(49.29)</td>
<td>(3.57)</td>
<td>(2.50)</td>
<td>(21.25)</td>
</tr>
</tbody>
</table>

Figures in parentheses indicate calculated values.

**IR Spectra of ternary complexes**

The IR spectra of the ternary complexes of the metal ions (Fig. 5.17) show a broad absorption in the region 3000 - 3500 cm⁻¹, indicating the presence of water of hydration [Marchetti 2001]. The intense broad band centered around 2600 cm⁻¹, which is assigned to the ν (O-H) of HFBPI, is absent in the spectra of the complexes, indicating the enolization of the O-H...
Figure 5.17. IR spectra of B15C5 ligand, Th-HFBPI-B15C5 and U-HFBPI-B15C5 complexes.
group and the involvement of oxygen of the hydroxyl group in chelation. The stretching frequency of the C=O group of HFBPI has been shifted from 1706 to 1633 cm\(^{-1}\) in both Th-FBPI-B15C5 and U-FBPI-B15C5 complexes, which suggests that the carbonyl group is involved in chelation. The other strong absorption occurring around 937 - 944 cm\(^{-1}\) may be assigned to \(\nu(O=U=O)\) of UO\(_2^{2+}\) [Sahu et al. 2000]. In the complexes of Th-FBPI-B15C5 and U-FBPI-B15C5 bands at 1129 - 1241 cm\(^{-1}\) are assigned to \(\nu (C-O)\) of polyether, and became noticeably weaker as compared to free B15C5, which suggests the involvement of oxygen of the crown ether in the adduct formation.

\(^1\text{H NMR spectra of ternary complexes}\)

Table 5.7 shows the \(^1\text{H NMR}\) chemical shifts of free HFBPI, B15C5 and its thorium and uranium complexes, the integration of the signals being in accordance with the formulae proposed. The downfield shift of the phenyl protons has been observed in both the ternary complexes. For B15C5 alone, the methylenic protons appears in the region 3.76-4.15 ppm, while the ring hydrogens are in the 6.8-6.9 ppm range. However, in the complex of Th(FBPI)\(_4\)-B15C5 a singlet appears at 4.69 ppm with downfield shift, indicating the uniform interaction of all ethereal oxygens of B15C5 with the Th\(^{4+}\) ion within the NMR time scale. On the other hand, in the case of UO\(_2\)(FBPI)\(_2\)-B15C5 two peaks were observed at 4.68 and 4.12 ppm with downfield shifts, indicating the nonuniform interaction of ethereal oxygens of B15C5 with UO\(_2^{2+}\). Similar behavior has been observed in the ternary complex of uranium with mixtures of dibenzoylmethane and B15C5 [Thakur et al. 1998].
Table 5.7. $^1$H NMR spectral data for the free ligands and ternary complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phenyl protons (ppm)</th>
<th>CH$_2$ protons of CE (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFBPI</td>
<td>6.80–7.39 (m)</td>
<td></td>
</tr>
<tr>
<td>B15C5</td>
<td>6.89 (d)</td>
<td>3.76 (s), 3.90 – 3.93 (t), 4.13 – 4.15 (t)</td>
</tr>
<tr>
<td>Th-FBPI-B15C5</td>
<td>6.52–7.36 (m)</td>
<td>4.69 (s)</td>
</tr>
<tr>
<td>U-FBPI-B15C5</td>
<td>6.86–7.80 (m)</td>
<td>4.07 – 4.14 (q), 4.68 (s)</td>
</tr>
</tbody>
</table>

From the elemental analyses and FT-IR spectra of the Th(FBPI)$_4$H$_2$O·B15C5 and UO$_2$(FBPI)$_2$H$_2$O·B15C5 complexes, it is clear that crown ethers are not able to replace water molecules in the binary complexes of Th(FBPI)$_4$H$_2$O and UO$_2$(FBPI)$_2$H$_2$O. Similar hydrated complexes have also been noticed earlier in the extraction of Th(TTA)$_4$H$_2$O·18C6 [Mathur and Choppin 1993] and [UO$_2$(TTA)$_2$H$_2$O]$_2$(B15C5) [Kannan et al. 2001]. Since the maximum coordination number for these metal ions is 6 to 10, this hydration strongly suggests that the oxygens of the crown ethers are not all equally bound to the metal ion. Further, crown ethers may form a secondary coordination sphere with UO$_2$(FBPI)$_2$H$_2$O and hydrogen bonded to the water molecule, as reported elsewhere in the molecular structure of [UO$_2$(TTA)$_2$H$_2$O]$_2$·B15C5 with the aid of X-ray single crystal data [Kannan et al. 2001]. There is evidence that the metal ion may interact with only a few of the potential donor oxygens and steric effects are probably significant in establishing this number [Mathur and Choppin 1993]. The weakness of the metal-crown ether interactions is reflected in residual hydration of the extracted complexes. What is clear about the extraction of these metal ions by mixtures of crown ethers
and HFBPI is that crown ether basicity, steric effects, cation dehydration and the number of ether oxygens bound to the cation are the combined factors which seemingly determine the pattern of metal-chelate and crown ether interactions.

Table 5.8 gives the separation factors (S.F.) between thorium(IV) and uranium(VI), defined as the ratio of respective distribution ratios, with HFBPI and HFBPI + CE systems at 0.5 mol/dm$^3$ nitric acid + 0.5 mol/dm$^3$ sodium nitrate solutions.

Table 5.8. Separation factors between thorium(IV) and uranium(VI) with HFBPI (0.02 mol/dm$^3$) and HFBPI (0.02 mol/dm$^3$) + CE (0.005 mol/dm$^3$) systems.

<table>
<thead>
<tr>
<th>Extraction system</th>
<th>Separation factor (S.F.) $D_{Th}/D_{U}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFBPI</td>
<td>$5.4 \times 10^5$</td>
</tr>
<tr>
<td>HFBPI + DC18C6</td>
<td>$5.9 \times 10^5$</td>
</tr>
<tr>
<td>HFBPI + DB18C6</td>
<td>$2.3 \times 10^4$</td>
</tr>
<tr>
<td>HFBPI + B15C5</td>
<td>$3.9 \times 10^4$</td>
</tr>
</tbody>
</table>

It is interesting to note that the addition of B15C5 significantly improves the S.F. values between thorium(IV) and uranium(VI) as compared with HFBPI alone. This can be explained on the basis of the 'size-fitting effect' of thorium(IV) with B15C5. The addition of DB18C6 to the HFBPI system also improves the selectivity between thorium(IV) and uranium(VI) and this can be interpreted in terms of steric factors of DB18C6. On the other hand, the addition of DC18C6 moderately enhances the S.F. value between thorium(IV) and uranium(VI) as compared to HFBPI alone. Further the selectivity observed between thorium(IV) and uranium(VI) has been found to be significantly higher than that of TBP system. Thus, these mixed-ligand systems
may find potential applications in the reprocessing of spent thorium based nuclear fuels and also for the recovery of thorium from mineral resources.