# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.1</td>
<td>Various steps of a typical nuclear fuel cycle</td>
<td>3</td>
</tr>
<tr>
<td>Figure 1.2</td>
<td>Alkali digestion process flow-sheet of Monazite/Xenotime</td>
<td>12</td>
</tr>
<tr>
<td>Figure 1.3</td>
<td>Acid digestion process flow-sheet of Monazite/Xenotime</td>
<td>13</td>
</tr>
<tr>
<td>Figure 1.4</td>
<td>Redox potential of actinide ions in 1M HClO₄ (Volts)</td>
<td>19</td>
</tr>
<tr>
<td>Figure 1.5</td>
<td>Co-current extraction in three stages</td>
<td>27</td>
</tr>
<tr>
<td>Figure 1.6</td>
<td>Counter-current extraction scheme</td>
<td>28</td>
</tr>
<tr>
<td>Figure 1.7</td>
<td>Pictorial view of supported liquid membrane</td>
<td>35</td>
</tr>
<tr>
<td>Figure 1.8</td>
<td>Co-transport steps in SLM</td>
<td>36</td>
</tr>
<tr>
<td>Figure 1.9</td>
<td>Counter-transport steps in SLM</td>
<td>37</td>
</tr>
<tr>
<td>Figure 2.1</td>
<td>Potentiometric titration of DNPPA with standard 0.1 M NaOH using Phenolphthalein as indicator; EP: End Point</td>
<td>46</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>A typical membrane transport cell used in the present study</td>
<td>52</td>
</tr>
<tr>
<td>Figure 3.1</td>
<td>Variation of $D_U$ with aqueous phase acidity; [U(VI)]: 0.1 M; Diluent: n-dodecane;  T: 298 K</td>
<td>62</td>
</tr>
<tr>
<td>Figure 3.2</td>
<td>Variation of $D_U$ with hydrogen ion concentration; [PC88A]: 5x10⁻³ M; [U(VI)]: 1x10⁻³ M; [NO₃⁻]: 3 M; Diluent: n-dodecane;  T: 298 K</td>
<td>62</td>
</tr>
<tr>
<td>Figure 3.3</td>
<td>Variation of $D_U$ with PC88A concentration; Diluent: n-dodecane; [U(VI)]: 0.1 M;  T: 298 K</td>
<td>63</td>
</tr>
</tbody>
</table>
Figure 3.4: Variation of $D_U$ with nitrate ion concentration; [U(VI)]: 0.1 M; [PC88A]: 0.0.25 M; Diluent: n-dodecane; [$H^+$]: 0.3 M; T: 298 K

Figure 3.5: Variation of $D_U$ with temperature; [U(VI)]: 0.1 M; [HNO$_3$]: 4 M; [PC88A]: 0.5 F; Diluent: n-dodecane

Figure 3.6: Variation of $D_U$ with aqueous phase acidity; [DNPPA]: 0.01 M; Diluent: n-paraffin; T: 298 K

Figure 3.7: Variation of $D_U$ with hydrogen ion concentration; [U(VI)]: 1×10$^{-3}$ M; Diluents: n-paraffin; [NO$_3^-$]: 3 M; T: 298 K

Figure 3.8: Variation of $D_U$ with DNPPA concentration; [HNO$_3$]: 3 M; Diluent: n-paraffin; T: 298 K

Figure 3.9: Comparison of variation of $D_U$ with nitric acid concentration using various organophosphorous acidic extractants; [U(VI)]: 0.1 M; Diluent: n-paraffin; T: 298 K

Figure 4.1: Variation of $D_U$ with H$_2$SO$_4$ concentration; Diluent: n-dodecane; T: 298 K

Figure 4.2: Effect of [H$^+$] on distribution ratio of uranium; [PC88A]: 0.05 M; Diluent: n-dodecane; T: 298 K

Figure 4.3: Dependence of distribution ratio on extractant concentrations for the extraction of U(VI); [U(VI)]: 0.02 M; [H$^+$]: 3 M; Diluent: n-dodecane; T: 298 K

Figure 4.4: Non linear least square regression plot for the extraction of various concentrations of U(VI) with 0.5 M PC88A; Diluent: n-dodecane; T: 298 K.
Figure 4.5: Dependence of distribution ratio on acidity at various concentrations of U(VI); [PC88A] : 0.5 M; Diluent: n-dodecane, T: 298 K

Figure 4.6: Plot of $D_{exp}$ vs $D_{cal}$ using mathematical model; Refer Equation 4.11

Figure 4.7: Variation of % extraction (% E) of U(VI) with PC88A concentration at constant neutral donor (TOPO) concentration; [U(VI)]: 0.015 M; [TOPO] : 0.015 M; [H$^+$]: 3 M

Figure 4.8: Variation of % extraction (% E) of U(VI) with TOPO concentration at constant PC88A concentration; [U(VI)]: 0.015 M; [PC88A] : 0.1 M; [H$^+$]: 3 M

Figure 4.9: Plot of % $E_{exp}$ vs % $E_{cal}$ using mathematical model

Figure 5.1: Variation of $D_U$ with HNO$_3$ concentration for 1.1M TEHP and TBP, Diluents: n-paraffin; T: 298 K

Figure 5.2: Variation of $D_{Th}$ with HNO$_3$ concentration for 1.1M TEHP and TBP; Diluents: n-paraffin; T: 298 K.

Figure 5.3: Variation of log $D$ vs log [TEHP]; [HNO$_3$] : 4 M; [U(VI)] : 2×10$^{-3}$ M; [Th(IV)] : 2×10$^{-3}$ M; Diluents: n-paraffin; T: 298 K

Figure 5.4: McCabe-Thiele diagram of extraction of U(VI) from 2 M HNO$_3$ medium using 0.2 M TEHP, Diluent: n-paraffin; T: 298 K

Figure 5.5: McCabe-Thiele diagram of stripping of U(VI) from 0.2 M TEHP; Strippant: water; Diluent: n-paraffin; T: 298 K
Figure 5.6: Process flow-sheet for separation of U(VI), Th(IV), REEs during processing of Monazite mineral, TEHP: 0.2 M, Diluent: n-paraffin; T: 298 K.

Figure 6.1: Uranium transport behavior of various organophosphorous carrier in the membrane phase; [U(VI)]_{feed}: 2x10^{-3} M at 1.12 M HNO_3; Carrier concentration: 1.1 M in n-paraffin

Figure 6.2: Comparison of uranium transport across PTFE supported membrane impregnated with different carriers and with different feed solutions; Carrier(s): 1.1 M TBP/TBEP/TEHP in n-paraffin; Feed solution(s): 2x10^{-3} M U(VI) at 1.1 - 3.3 M HNO_3; Strippant: Distilled Water

Figure 6.3: Effect of acidity on uranium transport using 1.1M TBEP in n-paraffin as a carrier; [U(VI)]_{feed}: 2x10^{-3} M; Strippant: Distilled Water

Figure 6.4: Transport steps of uranium in SLM in presence of neutral extracatnt

Figure 6.5: Variation of flux (J) with U(VI) concentration in the feed solution; Carrier: 1.1 M TEHP/ n-paraffin; Feed acidity: 2 M; Receiver phase: Distilled Water

Figure 6.6: Effect of U(VI) concentration in the feed solution on its permeation; Feed acidity: 2 M HNO_3; Carrier: 1.1 M TEHP in n-paraffin; Receiver phase: Distilled Water
Figure 6.7: Effect of membrane pore size on U(VI) transport across SLM employing 1.1 M TEHP/n-paraffin; Feed: 2x10^{-3} M U(VI) at 2 M HNO_3; Receiver phase: Distilled Water

Figure 6.8: Effect of membrane thickness on U(VI) transport across SLM employing 1.1M TEHP/n-paraffin; Feed: 2x10^{-3} M U(VI) at 2 M HNO_3; Receiver phase: Distilled Water

Figure 6.9: Uranium transport across SLM impregnated with various acidic extractants as carrier; [U(VI)]_{feed}: 2x10^{-3} M at 2 M HNO_3; Carrier: 0.1 M in n-paraffin; Receiver phase: 2 M H_2SO_4

Figure 6.10: Effect of receiver phase on U(VI) transport; [U(VI)]_{feed}: 2x10^{-3} M at 2 M HNO_3; Carrier: 0.1 M Cyanex 272 in n-paraffin

Figure 6.11: Effect of various neutral donors in the carrier solution in presence of 0.1 M Cyanex 272 on uranium transport; Feed: 2x10^{-3} M U(VI) at 2 M HNO_3; Diluent: n-paraffin; Receiver phase: 2 M H_2SO_4

Figure 6.12: Uranium transport as a function of H_2SO_4 concentration in the receiver phase; [U(VI)]_{feed}: 2x10^{-3} M at 2 M HNO_3; Carrier: 0.1 M Cyanex 272 + 0.05 M Cyanex 923 in n-paraffin

Figure 6.13: Uranium transport as a function of feed acidity; Carrier: 0.1 M Cyanex 272 + 0.05M Cyanex 923 in n-paraffin; [U(VI)]_{feed}: 2x10^{-3} M; Receiver phase: 2 M H_2SO_4

Figure 6.14: Counter-current U(VI) transport steps in SLM using acidic extractants (H_2A_2)
Figure 6.15: Effect of U(VI) concentration in the feed solution on its permeation; Carrier: 0.1 M Cyanex 272 + 0.05 M Cyanex 923 in n-paraffin; Feed acidity: 2 M HNO₃; Receiver phase: 2 M H₂SO₄

Figure 6.16: Variation of flux ($J$) with U concentration in the feed solution; Carrier: 0.1 M Cyanex 272 + 0.05 M Cyanex 923 / n-paraffin; Receiver phase: 2 M H₂SO₄

Figure 6.17: Variation of U(VI) transport with membrane thickness; Feed: $2 \times 10^{-3}$ M U(VI) at 2 M HNO₃; Carrier: 0.1 M Cyanex 272 + 0.05 M Cyanex 923 in n-paraffin; Receiver phase: 2 M H₂SO₄

Figure 6.18: Variation of U(VI) permeability with membrane thickness; [U(VI)]$_{feed}$: $2 \times 10^{-3}$ M; Receiver phase: 2 M H₂SO₄; Carrier: 0.1 M Cyanex 272 + 0.05 M Cyanex 923 in n-paraffin

Figure 6.19: Effect of pore size on U(VI) permeation; Feed: $2 \times 10^{-3}$ M U(VI) at 2 M HNO₃; Carrier: 0.1 M Cyanex 272 + 0.05 M Cyanex 923 in n-paraffin; Receiver phase: 2 M H₂SO₄

Figure 6.20: Plot of $1/P$ vs $1/K$ at different DNPPA concentration; Feed acid: 2 M HNO₃; U(VI): $2 \times 10^{-3}$ M Receiver phase: 6 M H₂SO₄, [U(VI)]$_{feed}$: $2 \times 10^{-3}$ M

Figure 6.21: Variation of U(VI) transport with membrane thickness; Feed: $2 \times 10^{-3}$ M U(VI) at 2 M HNO₃; Carrier: 0.1 M DNPPA in n-paraffin; Receiver phase: 6 M H₂SO₄

Figure 6.22: Variation of U(VI) permeability with membrane thickness; [U(VI)]$_{feed}$: $2 \times 10^{-3}$ M; Receiver phase: 6 M H₂SO₄; Carrier: 0.1 M DNPPA in n-paraffin
Figure 6.23: Effect of different neutral donors on U(VI) transport across SLM containing 0.1M DNPPA/n-paraffin in the membrane phase; Feed: 2x10^{-3} M U(VI) in 2 M HNO₃; Receiver phase: 2 M H₂SO₄

Figure 6.24: Effect of varying concentrations of Cyanex 923 on U(VI) transport across SLM; [DNPPA]: 0.1 M DNPPA; Diluent: n-paraffin; Feed: 2x10^{-3} M U(VI) in 2 M HNO₃; Receiver phase: 2 M H₂SO₄

Figure 7.1: Effect of diluents on the aggregation behavior of 0.05 M DNPPA pre-equilibrated with different nitric acid solutions; [DNPPA]: 0.05M; Temperature: 25 ºC

Figure 7.2: Absorbance spectra of DNPPA solutions dissolved in n-dodecane and pre-equilibrated with different nitric acid solutions: 5x10^{-3} M DNPPA; 5x10^{-4} M DNPPA

Figure 7.3: Variation of Dₓ with aqueous phase acidity; [U(VI)]: 1×10^{-3} M; Extractant: 1×10^{-2} M DNPPA; Diluent: n-dodecane; temperature: 25 ºC

Figure 7.4: Effect of DNPPA concentration on its aggregation behavior pre-equilibrated with 1 & 3 M HNO₃; Diluent: n-dodecane; Temperature: 25 ºC

Figure 7.5: Absorbance spectra of DNPPA solutions dissolved in n-dodecane and pre-equilibrated with 3 M HNO₃

Figure 7.6: Effect of Eu(III)/U(VI) on the aggregation behavior of 0.05 M DNPPA pre-equilibrated with different nitric acid solutions; Diluent: n-dodecane; temperature: 25 ºC
Figure 7.7: Effect of neutral donors on the aggregation behavior of 0.05 M DNPPA in n-dodecane pre-equilibrated with different nitric acid solutions; temperature: 25 °C

Figure 7.8: Absorbance spectra of $5 \times 10^{-4}$ M DNPPA + $5 \times 10^{-4}$ M Cyanex 923 solutions in n-dodecane pre-equilibrated with different nitric acid solutions

Figure 7.9 (a): Absorbance spectra of $5 \times 10^{-4}$ M DNPPA + $5 \times 10^{-4}$ M TBP solutions in n-dodecane pre-equilibrated with 0.1 - 0.5 M HNO₃

Figure 7.9(b): Absorbance spectra of $5 \times 10^{-4}$ M DNPPA + $5 \times 10^{-4}$ M TBP solutions in n-dodecane pre-equilibrated with 2 - 8 M HNO₃

Figure 8.1: Absorption spectra of U-Br-PADAP complexes in 0.1M PC88A+TOPO/Cyclohexane medium

Figure 8.2: Calibration plot of determination of U(VI) in sulphate medium using Br-PADAP in 0.1M PC88A + 0.05M TOPO/Cyclohexane organic medium

Figure 8.3: Effect of ethanol content in absorbance of U(VI)-Br-PADAP complexes in 0.1M PC88A+ 0.05M TOPO/cyclohexane medium