CHAPTER III

SYNERGISTIC EXTRACTION OF URANIUM WITH MIXTURES OF ORGANOPHOSPHOROUS ACIDIC AND NEUTRAL EXTRACTANTS
3.1. Introduction

Solvent extraction has played a key role in the separation of actinides both for industrial scale as well as for analytical applications. New challenges in nuclear industry relate to the recovery of uranium from its lean resources including effluent wastes of uranium plants. During the purification of diuranate by tri \( n \)-butyl phosphate (TBP) route, uranyl nitrate raffinate (UNR) is generated as waste containing 0.3-1 g/L U [112]. In view of the presence of the large concentrations of uranium in uranyl nitrate raffinate waste, it is imperative to optimize the conditions of its recovery. Extraction, separation and purification of U(VI) from nitric acid medium are generally carried out by organophosphorous extractants. The most commonly used organophosphorous extractants are TBP [113,114], tri \( n \)-Octyl phosphine oxide (TOPO) [3], di (2 ethyl hexyl) phosphoric acid (D2EHPA) [4]. 2-ethyl hexyl phosphonic acid 2-ethyl hexyl monoester (PC88A) is an acidic organophosphorous extractant (HA), which is widely used in extractive metallurgy of rare earths and base metals [115-117]. Several synergistic extractions studies of metal ions are reported with neutral oxodonors from different acid media [118,119]. Major advantages of the synergistic extraction include low ligand inventory and possibility of extraction from high concentration of acids or complexing agents. Singh et al. studied the synergistic extraction of U(VI) from hydrochloric acid medium using PC88A and its mixture with neutral oxodonors TBP, TOPO, and Cyanex 923 [120]. Mishra and Chakravortty reported the synergistic extraction of U(VI) from phosphoric acid medium using a binary mixture of Aliquat 336 (tricaprylmethyl ammonium chloride) and PC88A in xylene [121]. Godbole et al. observed synergism in U(VI) extraction by a mixture of PC88A and TOPO from sulphuric acid medium [122]. Several studies have been reported on the evaluation of phenyl phosphoric acids either alone or in combination with various synergistic agents for the extraction of uranium from
phosphate media [123-127]. Dignylphenyl phosphoric acid (DNPPA) finds special place as a powerful extractant for uranium recovery from phosphoric acid solutions [128]. These studies suggested that synergistic mixture DNPPA+ TBP can be used for recovery of uranium from wet phosphoric acid (WPA). Some feasibility studies were also carried out on uranium extraction from merchant grade phosphoric acid (55-60 % P₂O₅, 0.2-0.3 g/L U₃O₈) [129]. However, no sufficient data are available on extraction of uranium from nitrate media using PC88A and DNPPA as an extractant. This is relevant for the recovery of uranium from different waste solutions generated during its extraction and purification.

3.2. The present work

In the present study, uranium extraction from nitrate medium was investigated using PC88A/DNPPA (acidic extractants, HA) either alone or its mixture with neutral donors such as TBP, TOPO, Cyanex 923 (a mixture of four trialkyl phosphine oxides viz. R₃PO, R₂R’PO, RR’₂PO and R’₃PO where R: n-octyl and R’: n-hexyl chain), di-n-Octyl sulphoxide (DOSO), and methyl isobutyl ketone (MIBK) in n-dodecane/n-paraffin as extractants. The effects of different experimental parameters such as aqueous phase acidity, temperature, diluents and nature of strippants on the extraction/stripping behavior of U(VI) were investigated. Synergistic coefficient were calculated and correlated with the basicity of neutral oxodonor ligands. Further, the conditions for the recovery of uranium from the uranyl nitrate waste solutions were through liquid-liquid extraction route optimized using extractants PC88A and its mixtures with TBP, TOPO and DOSO. Extraction efficiencies of different organophosphoric acids such as D2EHPA, PC88A, and dioctyl phenyl phosphoric acid (DOPPA) for uranium from nitric acid medium have been evaluated vis-à-vis DNPPA.
3.3. Results and Discussion
3.3.1. Extraction of U(VI) from nitric acid medium with PC88A and neutral donors

3.3.1.1. Effect of nitric acid concentration

The extraction of U(VI) (0.1 M) from nitric acid medium (0.1 to 10 M HNO₃) was carried out with 0.25 and 0.5 F (F = formality) PC88A in n-dodecane. Figure 3.1 shows decrease in \( D_U \) values with increased nitric acid concentration. This was attributed to the acidic nature of PC88A, which extracts uranium by cation exchange process up to 3 M HNO₃ concentration liberating H⁺ ion in the aqueous solution. Figure 3.2 shows the plot of log \( D_U \) vs log [H⁺] with a slope of 1.02(±0.05), which means for each mole of complex formation there is a liberation of one mole of H⁺ ion. However, the extraction mechanism (Equation 3.5) of uranium apparently change at HNO₃ concentration >3M where the solvation process rather than cation exchange.

There was a drastic decrease in \( D_U \) value beyond 8M which was attributed to the competition of nitric acid extraction with U(VI) extraction by the solvent. Similar observations have been reported during the extraction of uranium using other acidic extractants such as D2EHPA and bis (2,4,4-trimethylpentyl) phosphonic acid (Cyanex 272) different aqueous media [118,129].

Ligand variation experiments were done to determine the stoichiometry of the extracted species. Figures 3.3 & 3.4 represent the variation of log \( D_U \) with log \([H_2A_2]\) (\(H_2A_2\) = dimeric form of PC88A) and log \([NO_3^-]\) and their corresponding slopes are ~ 2.0 and 1.04 ± 0.01, respectively. This suggests that each mole of uranium in the organic phase is associated with two moles of PC88A dimer and one mole of nitrate ion. So, the extracted species in the organic phase has the composition of \(\text{UO}_2(\text{NO}_3)(\text{HA}_2)\cdot\text{H}_2\text{A}_2\). This observation is in sharp contrast to that of uranium extraction using PC88A from HCl medium. The reported extracted species in the case of latter is \(\text{UO}_2(\text{HA}_2)_2\) showing no involvement of chloride anion [121]. Chetty et al. on the other hand, demonstrated
Figure 3.1. Variation of $D_U$ with aqueous phase acidity; [U(VI)]: 0.1 M; Diluent: $n$-dodecane; T: 298 K

Figure 3.2. Variation of $D_U$ with hydrogen ion concentration; [PC88A]: $5 \times 10^{-3}$ M; [U(VI)]: $1 \times 10^{-3}$ M; [NO$_3$]: 3 M; Diluent: $n$-dodecane T: 298 K
the involvement of nitrate ion in the extracted species of Pu(IV) using PC88A as the extractant [86]. The extraction mechanism of uranium from HNO$_3$ medium using PC88A/n-paraffin can be summarized as follows:

At low nitric acid concentration ($0.1 \text{ M} < [\text{HNO}_3] \leq 3 \text{ M}$):

$$UO_2^{2+} + NO_3^- + 2H_2A_2 \leftrightarrow UO_2(NO_3)(HA_2).H_2A_2$$

$$K_{ex} = \frac{([UO_2(NO_3)(HA_2)H_2A_2]_{org}[H^+]_{aq})}{([UO_2^{2+}]_{aq}[NO_3^-]_{aq}[H_2A_2]_{org}^2)}$$ (3.1)

$$K_{ex} = \frac{(D_U[H^+]_{aq})}{([NO_3^-]_{aq}[H_2A_2]_{org}^2)}$$ (3.2)

$$\log D_U = \log K_{ex} + \log[NO_3^-] + 2 \log[H_2A_2] - \log[H^+]$$ (3.3)

At high nitric acid concentration ($[\text{HNO}_3] \geq 3 \text{ M}$):

$$UO_2^{2+} + 2NO_3^- + 2H_2A_2 \leftrightarrow UO_2(NO_3)_22H_2A_2$$ (3.5)

![Figure 3.3. Variation of $D_U$ with PC88A concentration; Diluent: $n$-dodecane; [U(VI)]: 0.1 M; T: 298 K](image-url)
Similarly, nitrate coordination has been reported for the extraction of U(VI) from HNO₃ medium using Cyanex 272 as extractant [129].

3.3.1.2. Effect of temperature

Extraction of uranium by 0.5 F PC88A in dodecane was carried out at different temperature and the data were plotted in Figure 3.5. It is observed that log $D_U$ vs $1/T$ (K$^{-1}$) is a straight line with the slope and intercept values as 399.74(±40.14), and 0.71(±0.13), respectively. The enthalpy change (ΔH) for the above extraction process was calculated from the slope as $–7.65(±0.77)$ kJ mol$^{-1}$ suggesting the exothermic nature of the extraction process [18]. This result indicates that high temperature may favor the stripping of uranium from organic medium.
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

3.3.1.3. Effect of diluents

Nature of the diluents influences the extraction and solubilization of the extracted species containing metal ions in the organic phase. It was therefore, desirable to investigate the influence of different diluents on the extraction of uranium from nitric acid medium using 0.5 F PC88A as extractant at 298 K. Extraction efficiency increased in the order: xylene < carbon tetrachloride (CCl$_4$) < $n$-dodecane < MIBK (Table 3.1). There is marginal variation of $D_U$ values for Xylene, CCl$_4$ and dodecane as diluents, but $D_U$ value for MIBK is distinctly larger suggesting higher solubility of extracted species.
Table 3.1. Effect of various diluents on extraction of uranium; Extractant: 0.5 F PC88A;
Aqueous phase: 0.1 M U(VI) at 4 M HNO$_3$; Organic-to-aqueous phase ratio (O/A): 1; T: 298 K

<table>
<thead>
<tr>
<th>Diluent</th>
<th>$D_U$</th>
<th>%E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylene</td>
<td>72.2</td>
<td>98.6</td>
</tr>
<tr>
<td>CCl4</td>
<td>72.5</td>
<td>98.6</td>
</tr>
<tr>
<td>$n$-dodecane</td>
<td>113.0</td>
<td>99.1</td>
</tr>
<tr>
<td>MIBK</td>
<td>255.0</td>
<td>99.9</td>
</tr>
</tbody>
</table>

3.3.1.4. Synergistic extraction

Tables 3.2-3.5 list the distribution data of uranium at different acidities (0.05 – 6 M HNO$_3$) using 0.03 F PC88A either alone as a mixture of 0.03 F PC88A and 0.03 M of oxodonors such as TBP/TOPO/DOSO/MIBK in $n$-dodecane as extractants. It is evident that $D_U$ increases with aqueous phase acidity for TBP and reaches a maximum at 5 M HNO$_3$ whereas for PC88A, the $D_U$ values decrease up to 3 M HNO$_3$ and then increase slowly. For PC88A–TBP mixture, there is an overall enhancement in $D_U$ values, which decrease with increase in aqueous phase acidity. This enhancement in extraction with binary mixture may be explained as due to the formation of synergistic adduct species. The synergistic extraction is due to the more organophilic nature of the extracted species formed by the enhanced dehydration of uranium by neutral extractants. At low acidity, the synergistic coefficient (S.C.) for uranium extraction varies with the basicity of neutral oxodonors, i.e. TOPO > TBP > DOSO > MIBK [130]. The S.C. values increase with aqueous phase acidity up to ~ 2-3 M HNO$_3$ for all the neutral donors (except TOPO), and thereafter decrease marginally. The different behavior appears to be due to larger interaction of TOPO with HNO$_3$ resulting reduced free TOPO concentration available for adduct formation.
Table 3.2. Variation of $D_U$ with nitric acid concentration; [U(VI)]: $2\times10^{-3}$ M; Extractant(s):
3×10$^{-2}$ M TBP, 3×10$^{-2}$ F PC88A and their mixture in n-dodecane; T: 298 K

<table>
<thead>
<tr>
<th>[HNO$_3$], M</th>
<th>$D_1$</th>
<th>$D_2$</th>
<th>$D_{mix}$</th>
<th>$\Delta D$</th>
<th>S.C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.02</td>
<td>15.2</td>
<td>34.4</td>
<td>19.2</td>
<td>0.36</td>
</tr>
<tr>
<td>1</td>
<td>0.04</td>
<td>5.64</td>
<td>24.9</td>
<td>19.2</td>
<td>0.64</td>
</tr>
<tr>
<td>2</td>
<td>0.14</td>
<td>2.13</td>
<td>20.5</td>
<td>18.3</td>
<td>0.96</td>
</tr>
<tr>
<td>3</td>
<td>0.21</td>
<td>1.76</td>
<td>16.8</td>
<td>14.8</td>
<td>0.93</td>
</tr>
<tr>
<td>4</td>
<td>0.32</td>
<td>1.85</td>
<td>13.7</td>
<td>11.5</td>
<td>0.80</td>
</tr>
<tr>
<td>5</td>
<td>0.58</td>
<td>1.89</td>
<td>12.7</td>
<td>10.2</td>
<td>0.71</td>
</tr>
<tr>
<td>6</td>
<td>0.45</td>
<td>2.32</td>
<td>11.8</td>
<td>9.0</td>
<td>0.63</td>
</tr>
</tbody>
</table>

$D_1$: 3\times10^{-2}$ M TBP, $D_2$: 3\times10^{-2}$ F PC88A, $D_{mix}$: 3\times10^{-2}$ M TBP + 3\times10^{-2}$ F PC88A

Table 3.3. Variation of $D_U$ with nitric acid concentration; [U(VI)]: $2\times10^{-3}$ M; Extractant(s):
3×10$^{-2}$ M TOPO, 3×10$^{-2}$ F PC88A and their mixture in n-dodecane; T: 298 K

<table>
<thead>
<tr>
<th>[HNO$_3$], M</th>
<th>$D_1$</th>
<th>$D_2$</th>
<th>$D_{mix}$</th>
<th>$\Delta D$</th>
<th>S.C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>73.8</td>
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<td>907.8</td>
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<tr>
<td>1</td>
<td>72.3</td>
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<td>524.3</td>
<td>446.4</td>
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<tr>
<td>2</td>
<td>71.9</td>
<td>2.13</td>
<td>480.6</td>
<td>406.6</td>
<td>0.81</td>
</tr>
<tr>
<td>3</td>
<td>45.2</td>
<td>1.76</td>
<td>299.4</td>
<td>252.4</td>
<td>0.80</td>
</tr>
<tr>
<td>4</td>
<td>31.6</td>
<td>1.85</td>
<td>194.5</td>
<td>161.0</td>
<td>0.76</td>
</tr>
<tr>
<td>5</td>
<td>25.9</td>
<td>1.89</td>
<td>168.3</td>
<td>140.5</td>
<td>0.78</td>
</tr>
<tr>
<td>6</td>
<td>22.7</td>
<td>2.32</td>
<td>145.0</td>
<td>119.9</td>
<td>0.76</td>
</tr>
</tbody>
</table>

$D_1$: 3\times10^{-2}$ M TOPO, $D_2$: 3\times10^{-2}$ F PC88A, $D_{mix}$: 3\times10^{-2}$ M TOPO + 3\times10^{-2}$ F PC88A;
Table 3.4. Variation of $D_U$ with nitric acid concentration; [U(VI)]: $2\times10^{-3}$ M; Extractant(s): $3\times10^{-2}$ M DOSO, $3\times10^{-2}$ F PC88A and their mixture in $n$-dodecane; T: 298 K.

<table>
<thead>
<tr>
<th>$[\text{HNO}_3]$, M</th>
<th>$D_1$</th>
<th>$D_2$</th>
<th>$D_{\text{mix}}$</th>
<th>$\Delta D$</th>
<th>S.C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.06</td>
<td>15.2</td>
<td>30.3</td>
<td>15.0</td>
<td>0.30</td>
</tr>
<tr>
<td>1</td>
<td>0.07</td>
<td>5.64</td>
<td>28.1</td>
<td>22.4</td>
<td>0.69</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>2.13</td>
<td>25.5</td>
<td>23.3</td>
<td>1.06</td>
</tr>
<tr>
<td>3</td>
<td>0.12</td>
<td>1.76</td>
<td>17.9</td>
<td>16.0</td>
<td>0.98</td>
</tr>
<tr>
<td>4</td>
<td>0.14</td>
<td>1.85</td>
<td>14.2</td>
<td>12.2</td>
<td>0.58</td>
</tr>
<tr>
<td>5</td>
<td>0.22</td>
<td>1.89</td>
<td>13.1</td>
<td>11.0</td>
<td>0.79</td>
</tr>
<tr>
<td>6</td>
<td>0.17</td>
<td>2.32</td>
<td>11.9</td>
<td>9.41</td>
<td>0.68</td>
</tr>
</tbody>
</table>

$D_1$: $3\times10^{-2}$ M DOSO, $D_2$: $3\times10^{-2}$ F PC88A, $D_{\text{mix}}$: $3\times10^{-2}$ M DOSO $+ 3\times10^{-2}$ F PC88A

Table 3.5. Variation of $D_U$ with nitric acid concentration; [U(VI)]: $2\times10^{-3}$ M; Extractant(s): $3\times10^{-2}$ M MIBK, $3\times10^{-2}$ F PC88A and their mixture in $n$-dodecane; T: 298 K.

<table>
<thead>
<tr>
<th>$[\text{HNO}_3]$, M</th>
<th>$D_1$</th>
<th>$D_2$</th>
<th>$D_{\text{mix}}$</th>
<th>$\Delta D$</th>
<th>S.C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.01</td>
<td>15.2</td>
<td>16.3</td>
<td>1.11</td>
<td>0.03</td>
</tr>
<tr>
<td>1</td>
<td>0.03</td>
<td>5.64</td>
<td>6.53</td>
<td>0.86</td>
<td>0.06</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>2.13</td>
<td>3.26</td>
<td>1.08</td>
<td>0.17</td>
</tr>
<tr>
<td>3</td>
<td>0.08</td>
<td>1.76</td>
<td>2.83</td>
<td>1.00</td>
<td>0.19</td>
</tr>
<tr>
<td>4</td>
<td>0.15</td>
<td>1.85</td>
<td>2.78</td>
<td>0.78</td>
<td>0.14</td>
</tr>
<tr>
<td>5</td>
<td>0.20</td>
<td>1.89</td>
<td>2.70</td>
<td>0.61</td>
<td>0.11</td>
</tr>
<tr>
<td>6</td>
<td>0.25</td>
<td>2.32</td>
<td>2.62</td>
<td>0.05</td>
<td>0.01</td>
</tr>
</tbody>
</table>

$D_1$: $3\times10^{-2}$ M MIBK, $D_2$: $3\times10^{-2}$ F PC88A, $D_{\text{mix}}$: $3\times10^{-2}$ M MIBK $+ 3\times10^{-2}$ F PC88A
3.3.1.5. Recovery of uranium from raffinate waste

3.3.1.5.1. Evaluation of different extractants

An attempt was made to optimize the conditions for the recovery of uranium from the raffinate solution (generated during uranium purification by TBP solvent extraction) through solvent extraction route using different extractants such as PC88A and oxodonors (TBP, TOPO, PC88A, DOSO) either alone or as their mixtures. Table 3.6 shows the value of %E of uranium from a typical uranium raffinate waste containing 0.4 g/L U in 1.12 M HNO₃ medium using different extractants.

Table 3.6. Extraction of U(VI) from 0.4g/L uranyl nitrate raffinate at 1.12 M HNO₃ by various extractants; Diluent: n-dodecane; T: 298 K

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>Extractant</th>
<th>% E</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.03 M TBP</td>
<td>10.5</td>
</tr>
<tr>
<td>2</td>
<td>1.1 M TBP</td>
<td>~ 90.0</td>
</tr>
<tr>
<td>3</td>
<td>3×10⁻² M DOSO</td>
<td>10.2</td>
</tr>
<tr>
<td>4</td>
<td>3×10⁻² F PC88A</td>
<td>87.4</td>
</tr>
<tr>
<td>5</td>
<td>3×10⁻² M TOPO</td>
<td>99.3</td>
</tr>
<tr>
<td>6</td>
<td>3×10⁻² F PC88A + 3×10⁻² M TBP</td>
<td>95.9</td>
</tr>
<tr>
<td>7</td>
<td>3×10⁻² F PC88A + 3×10⁻² M DOSO</td>
<td>96.9</td>
</tr>
<tr>
<td>8</td>
<td>3×10⁻² F PC88A + 3×10⁻² M TOPO</td>
<td>99.7</td>
</tr>
</tbody>
</table>

It is evident that any combination of PC88A with neutral donors gives high extraction of uranium (>95 %) due to synergistic effect and the order of synergism TOPO > DOSO > TBP, follows their basicities. Whereas quantitative extraction (>99 %) of uranium was achieved using 0.03 M TOPO/n-dodecane solution; only ~10 % uranium recovery was observed using 0.03 M TBP/n-dodecane solution as extractant. The highest extraction in case of TOPO is obviously due
to of its very high basicity \(K_B = 8.6\). However, the use of 1.1 M TBP or \(3 \times 10^{-2}\) F PC88A solutions in \(n\)-dodecane as extractants showed \(\sim 90\%\) uranium recovery from the waste solutions. These extractants were further evaluated by performing stripping studies. Table 3.7 lists the stripping (%) data of uranium from various loaded organic phases employing 5 % \((\text{NH}_4)_2\text{CO}_3\), 8 M HCl and 8 M HNO\(_3\), as the strippants. 8 M HCl and 8 M HNO\(_3\) are not effective strippants of uranium. Though \(3 \times 10^{-2}\) M TOPO either alone or its synergistic mixture with \(3 \times 10^{-2}\) F PC88A in \(n\)-dodecane showed quantitative recovery of uranium, its stripping from the organic phase was very poor. By contrast, other extract combinations of PC88A with TBP and DOSO displayed relatively easy stripping of uranium. In view of efficient extraction and stripping considerations, it is suggested that 30% TBP/\(n\)-dodecane or \(3 \times 10^{-2}\) F PC88A + \(3 \times 10^{-2}\) M TBP mixture in \(n\)-dodecane may be used for the recovery of uranium from raffinate solution. It is evident that only \((\text{NH}_4)_2\text{CO}_3\) can effectively strip uranium from the loaded organic phase.

Table 3.7. Stripping of uranium from loaded organic phases using various strippants; Diluent: \(n\)-dodecane; T: 298 K

<table>
<thead>
<tr>
<th>Organic Phase</th>
<th>Stripping (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5% ((\text{NH}_4)_2\text{CO}_3)</td>
</tr>
<tr>
<td>1.1 M TBP#</td>
<td>&gt; 95</td>
</tr>
<tr>
<td>(3 \times 10^{-2}) F PC88A</td>
<td>90.8</td>
</tr>
<tr>
<td>0.03 M TOPO</td>
<td>29.3</td>
</tr>
<tr>
<td>(3 \times 10^{-2}) F PC88A + (3 \times 10^{-2}) M TBP</td>
<td>98.0</td>
</tr>
<tr>
<td>(3 \times 10^{-2}) F PC88A +(3 \times 10^{-2}) M DOSO</td>
<td>97.5</td>
</tr>
<tr>
<td>(3 \times 10^{-2}) F PC88A + (3 \times 10^{-2}) M TOPO</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>

\(^\#\text{Water: \sim 45 \% stripping in one stage}\)
3.3.1.5.2. Uranium recovery from actual waste samples

Based on these studies, the recovery of uranium was attempted from different batches of uranyl nitrate raffinate waste samples of varying concentrations of uranium and nitric acid using 1.1 M TBP/n-dodecane as extractant and \((\text{NH}_4)_2\text{CO}_3\) as the strippant. It is evident from Table 3.8 that three extraction stages are sufficient for quantitative recovery (~99.9%) of uranium from uranyl nitrate raffinate waste. The extracted uranium could easily be stripped by 5% \((\text{NH}_4)_2\text{CO}_3\) solution.

Table 3.8. Uranium recovery from different batches of uranyl nitrate raffinate (UNR) waste;

Extractant: 1.1 M TBP/n-dodecane; O/A: 1; T: 298 K

<table>
<thead>
<tr>
<th>Batch No.</th>
<th>[HNO(_3)]</th>
<th>[U(VI)]; g/L</th>
<th>(D_U)</th>
<th>%(E^#)</th>
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</table>

#: one stage

3.3.2. Extraction of U(VI) from nitric acid medium with DNPPA and neutral donors

Synergistic extraction of metal ions has been noted in several extraction systems [115,119,121,129,130]. The present study deals with the synergistic extraction of U(VI) by organophosphorous compounds such as DNPPA in combination with TBP, TEHP, Cyanex 923 in \(n\)-paraffin medium.
3.3.2.1. *Effect of nitric acid and extractant concentration*

Figure 3.6 shows the variation of distribution ratio values of U(VI) with aqueous phase acidity (1-8 M HNO$_3$) and uranium concentration (1×10$^{-3}$ -1×10$^{-2}$ M) employing using 1×10$^{-2}$ M DNPPA solution in $n$-paraffin as extractant. The $D_U$ values decreased gradually with increased nitric acid and uranium concentrations in the aqueous phase. This observation was attributed to acidic nature of DNPPA and that of uranium loading in the organic phase. The decrease in uranium extraction with aqueous phase acidity is typical of acidic extractants suggesting the involvement of cation exchange mechanism. Similar observations have been reported during the extraction of uranium using other acidic extractants such as D2EHPA, DOPPA, PC88A, and Cyanex 272 (bis(2,4,4-trimethylpentyl)phosphinic acid) in different aqueous media [116, 82, 83, 84,129].

![Figure 3.6](image_url)
extraction mechanism and stoichiometry of the extracted species in organic phase were determined using slope techniques. **Figure 3.7** shows the variation of log $D_U$ with log $[H^+]$ at a fixed nitrate ion concentration (3 M) with a slope of ~2. This indicates that for each mole of complex formation, there is liberation of at least two moles of $H^+$ ions in the aqueous phase.

![Figure 3.7](image)

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

**Figure 3.8** represents the variation of log $D_U$ with log $[H_2A_2]$ at fixed nitric acid concentration (3 M) with a slope ~2. This suggests that two moles of DNPPA dimer are associated with each mole of uranium extracted in the organic phase. However, nitrate ions are not a part of the moiety extracted in the organic phase. Based on these observations, the stoichiometry of the extracted species in the organic phase was proposed as $UO_2(HA_2)_2$ where HA and $H_2A_2$ are the monomeric and dimeric forms of DNPPA, respectively.
Figure 3.8. Variation of $D_U$ with DNPPA concentration; [HNO$_3$]: 3 M; Diluent: $n$-paraffin; T: 298 K

The extraction mechanism of uranium in HNO$_3$ medium using DNPPA can be shown as follows:

$$UO_2^{2+} + 2H_2A_2 \leftrightarrow UO_2(HA_2)_2 + 2H^+$$  \hspace{1cm} (3.6)

$$K_{ex} = \frac{([UO_2(HA_2)_2]_{org} [H^+]_{aq}^2)}{([UO_2^{2+}]_{aq} [H_2A_2]^2_{org})}$$  \hspace{1cm} (3.7)

$$K_{ex} = \frac{(D_U[H^+]_{aq}^2)}{[H_2A_2]_{org}^2}$$  \hspace{1cm} (3.8)

$$\log D_U = \log K_{ex} + 2 \log[H_2A_2] - 2\log[H^+]$$  \hspace{1cm} (3.9)

where ‘aq’ and ‘org’ represent the aqueous and organic phases, respectively and $K_{ex}$ is the conditional extraction constant. It is interesting to note that nitrate ion is not involved in the extracted species of U(VI) with DNPPA. However, with increased nitric acid concentration in the aqueous phase, nitrate ion gets involved in the extracted species as $UO_2(NO_3)(HA_2)\cdot H_2A_2$ [131].
### 3.3.2.2 Comparison with other acidic organophosphorous extractants

**Figure 3.9** shows the extraction of U(VI) from nitric acid medium using various acidic organophosphorous extractants like DNPPA, D2EHPA, PC88A and Cyanex 272 (0.02 M) in *n*-paraffin under identical conditions. It was observed that for DNPPA, $D_U$ decreased with increased in HNO$_3$ concentration (up to 8 M) conforming cation exchange mechanism of U(VI) extraction.

![Graph showing comparison of variation of $D_U$ with nitric acid concentration using various organophosphorous acidic extractants](image)

**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

Similarly, for D2EHPA, PC88A and Cyanex 272, $D_U$ decreased with increased in HNO$_3$ concentration up to 3M and then increased up to 5 M (6 M for D2EHPA) beyond 5 M $D_U$ decreased. Extraction of U(VI) using D2EHPA, PC88A and Cyanex 272 at low HNO$_3$ concentration occurred via cation exchange mechanism (up to 3M) and above 3 M via salvation mechanism [116,82,83,84,129]. The order of U(VI) extraction using various organophosphorous extractants up to 3M is: Cyanex 272 > DNPPA > PC88A > D2EHPA and above 4M: Cyanex.
272 > PC88A > D2EHPA > DNPPA. The U(VI) extraction profile from HNO₃ can be explained on the basis of pKₐ values of the extractants. The anomalous behavior of DNPPA at low HNO₃ concentration may be due to presence of phenyl substituents in the extractant.

3.3.2.3. Synergistic extraction

Addition of neutral donors to DNPPA like TBP, TEHP, Cyanex 923 increase the distribution ratio of U(VI) significantly as compared to pure extractants. This phenomenon is called synergism in hydrometallurgy. Tables 3.9, 3.10 and 3.11 represent the distribution ratio, $D_U$ and synergistic coefficient (S.C.) values for $2 \times 10^{-2}$ M DNPPA in combination with $2 \times 10^{-2}$ M neutral donors (dissolved in $n$-paraffin) at 0.5-8 M HNO₃. As expected, the $D_U$ values for TBP/TEHP increased with acid concentration and maximum was attained at 4-5 M HNO₃ and those with DNPPA decreased sharply with increased nitric acid concentration in the aqueous phase. However, the $D_U$ values were higher in the case of Cyanex 923 at lower acivities. Interestingly, there was a synergistic enhancement in $D_U$ values for binary mixtures of DNPPA – TBP/TEHP/Cyanex 923 mixtures at lower acivities, which decreased at higher nitric acid concentrations. This enhancement in extraction with extractant mixtures was attributed to the formation of hydrophobic adducts. The synergistic coefficient (S.C.) calculation showed that the synergistic effect by the neutral donors followed the order: Cyanex 923 $>>$ TBP $\geq$ TEHP. The higher synergism in case of Cyanex 923 was due its higher basicity ($K_H = 8.5$) [82] and lower enhancement in the case of TEHP was attributed to the steric hindrance exerted by branched 2-ethylhexyl group. DNPPA being acidic in nature extracts U(VI) from nitric acid medium by cation exchange mechanism and $D_U$ value decrease with increase in aqueous phase acidity. Similar observations were made during the extraction of uranium using acidic extractants like DEHPA, PC88A, and Cyanex 272 and their mixtures with neutral oxodonors [116, 82, 129].
<table>
<thead>
<tr>
<th>[HNO₃], M</th>
<th>$D₁$</th>
<th>$D₂$</th>
<th>$D_{mix}$</th>
<th>$ΔD$</th>
<th>S.C.</th>
</tr>
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<td>2.18</td>
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$D₁$: 2×10⁻² M TBP, $D₂$: 2×10⁻² M DNPPA, $D_{mix}$: 2×10⁻² M TBP + 2×10⁻² M DNPPA

<table>
<thead>
<tr>
<th>[HNO₃], M</th>
<th>$D₁$</th>
<th>$D₂$</th>
<th>$D_{mix}$</th>
<th>$ΔD$</th>
<th>S.C.</th>
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$D₁$: 2×10⁻² M TEHP, $D₂$: 2×10⁻² M DNPPA, $D_{mix}$: 2×10⁻² M TEHP + 2×10⁻² M DNPPA
Table 3.11. Variation of $D_U$ with nitric acid concentration; [U]: $2\times10^{-3}$ M; Extractant(s): $2\times10^{-2}$ M Cyanex 923, $2\times10^{-2}$ M DNPPA and their mixture in $n$-paraffin; T: 298 K

<table>
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<th>$\Delta D$</th>
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<td>0.68</td>
<td>91.66</td>
<td>87.27</td>
<td>1.32</td>
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</table>

$D_1$: $2\times10^{-2}$ M Cyanex 923, $D_2$: $2\times10^{-2}$ M DNPPA, $D_{mix}$: $2\times10^{-2}$ M Cyanex 923 + $2\times10^{-2}$ M DNPPA

3.4. Conclusions

PC88A in combination with neutral extractants such as TBP, TOPO, and DOSO shows synergistic enhancement in uranium extraction from nitric acid medium ($0.5$-$6$ M HNO$_3$). The extracted species of uranium using PC88A as extractant were identified as UO$_2$(NO$_3$)(HA$_2$)$\cdot$H$_2$A$_2$ (low acidity: $< 3$ M HNO$_3$) and UO$_2$(NO$_3$)$_2$$\cdot$2(H$_2$A$_2$) (high acidity: $> 3$ M HNO$_3$). Use of MIBK as diluent also showed significant enhancement in uranium due to synergistic extraction. Temperature variation studies using PC88A as extractant showed exothermic nature of extraction process and stripping was more favored at elevated temperatures. Batch extraction studies were carried out to optimize the conditions for the recovery of uranium from raffinate generated during the purification of uranium using different extractants. 1.1M
TBP was the more efficient extractant and 5% (NH₄)₂CO₃ was the most effective uranium stripping agent.

Similarly, extraction of U(VI) from nitric acid medium using DNPPA showed that with increase in acid concentration there was a decrease in $D_U$, indicating cation exchange mechanism of the U(VI) extraction. Slope ratio analysis indicate the formation of UO₂(HA₂)₂ type of complex in the organic phase. Presence of neutral donors like TBP, TEHP and Cyanex 923 along with DNPPA in the organic phase increase $D_U$ due to synergism and calculation of synergistic coefficient showed the order of synergism: Cyanex 923 $>>$ TBP $\geq$ TEHP.