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Thermodynamic Studies to Support Actinide/Lanthanide Separations:

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# APPENDIX E

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<td>Thermodynamics and Kinetics – LBNL FT-15LB030403</td>
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SUMMARY

This milestone report summarizes the data obtained in FY15 on the complexation of HEDTA with Np(V) and U(VI) in a temperature range from 25 to 70°C. The results show the effect of temperature on the chemical speciation of Np(V) and U(VI) in the modified TALSPEAK Process, and help to evaluate the effectiveness of the process when the operation envelope (e.g., temperature) varies. Eventually, the results from this study will help to achieve a better control of the separation process based on the HEDTA/HEH[EHP] combination.
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ACRONYMS

HDEHP  
bis-2-ethyl(hexyl) phosphoric acid

HEDTA  
N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid

HEH[EHP]  
2-ethyl (hexyl) phosphonic acid mono-2-ethylhexyl ester

NE FCRD  
Nuclear Energy Fuel Cycle Research and Development

TALSPEAK  
Trivalent Actinium Lanthanide Separations by Phosphorus-reagent Extraction from Aqueous Komplexes
1. INTRODUCTION

Though the TALSPEAK process was proven to work for the separation of trivalent lanthanides and actinides, detailed fundamental chemistry studies under the NE FCRD Separations and Waste Form Campaign have indicated undesirable complex interactions between various components in aqueous and organic phases of TALSPEAK. A number of modifications of TALSPEAK have been proposed and studied, with the objectives of simplifying the process. One modification involves using 2-ethyl (hexyl) phosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) as the extractant in the organic phase to replace bis-2-ethyl(hexyl) phosphoric acid (HDEHP), while using a weaker aqueous complexant (N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid, HEDTA) to replace DTPA in the conventional TALSPEAK. Preliminary studies have demonstrated that the combination of HEDTA with HEH[EHP] results in an almost flat pH dependence between 2.5 and 4.5, in contrast with conventional TALSPEAK. In addition, the HEDTA/HEH[EHP] combination has shown more rapid kinetics in phase transfer for the heavier lanthanides without using high concentrations of a lactate buffer as in the conventional TALSPEAK.

This milestone report summarizes the data obtained in FY15 on the complexation of HEDTA with Np(V) and U(VI). The results show the effect of temperature on the chemical speciation of Np(V) and U(VI) in the modified TALSPEAK Process, and help to evaluate the effectiveness of the process when the operation envelope (e.g., temperature) varies. Eventually, the results from this study will help to achieve a better control of the separation process based on the HEDTA/HEH[EHP] combination.

2. RESULTS

2.1 Complexation of Np(V) with HEDTA

2.1.1 Stability constants

Spectrophotometric titration data are shown in Figure 1. Three isosbestic points at λ = 984.1 nm, 989.8 nm, and 993.4 nm are observed, indicating the formation of three NpO$_2^+$/HEDTA complexes. The best fit of the spectra was achieved by assuming successive formation of three NpO$_2^+$/HEDTA complexes, NpO$_2$HL$^-$, NpO$_2$L$_2^-$, and NpO$_2$H$_3$L$^-$ as shown by eq. 1, 2, and 3.

\[
\begin{align*}
\text{NpO}_2^+ + H^+ + L^3^- & = \text{NpO}_2\text{HL}^- \quad (1) \\
\text{NpO}_2^+ + L^3^- & = \text{NpO}_2L_2^- \quad (2) \\
\text{NpO}_2^+ + L^3^- + H_2O & = \text{NpO}_2H_3L^3^- + H^+ \quad (3)
\end{align*}
\]

It was found that it is necessary to include a species, noted as NpO$_2$H$_3$L$^-$, to fit the data in the higher pH region. This species could be a ternary hydrolyzed species, NpO$_2$(OH)L$^-$, or a species with the hydroxyl group in HEDTA deprotonated. The equilibrium constants (log$\beta$) for eq. 1, 2, and 3 were calculated to be $13.45 \pm 0.02$, $7.06 \pm 0.03$, and $-(4.74 \pm 0.03)$ for NpO$_2$HL$^-$, NpO$_2$L$^2^-$, and NpO$_2$H$_3$L$^-$, respectively (Table 1).
Thermodynamic Studies to Support Actinide/Lanthanide Separations

Figure 1. Spectrophotometric titration of NpO$_2^+$/HEDTA complexation. $I = 1.0$ M NaClO$_4$. (A) Initial solution in cuvette: 2.100 mL; $n_{H} = 0.6201$ μmol, $n_{\text{Np}} = 0.5366$ μmol; Titrant: 1.512 mM HEDTA / 0.3949 mM H$^+$. (B) Initial solution in cuvette: 2.125 mL; $n_{H} = 4.366$ μmol, $n_{\text{Np}} = 0.5359$ μmol; $n_{L} = 1.249$ μmol. Titrant: 0.01 M NaOH. (C) Initial solution in cuvette: 2.150 mL; $n_{H} = 8.113$ μmol, $n_{\text{Np}} = 0.5357$ μmol; $n_{L} = 2.498$ μmol. Titrant: 0.015 M NaOH. (D) Initial solution in cuvette: 2.100 mL; $n_{H} = 0.6180$ μmol; $n_{\text{Np}} = 0.5344$ μmol. Titrant: 4.902 mM HEDTA / 4.454 mM H$^+$.

Table 1. Thermodynamic parameters for the complexation of NpO$_2^+$/HEDTA, $I = 1.00$ M NaClO$_4$, $t = 25^\circ$C.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Log$\beta$</th>
<th>$\Delta H$ $\text{kJ}$·mol$^{-1}$</th>
<th>$\Delta S$ $\text{J}$·mol$^{-1}$·K$^{-1}$</th>
</tr>
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<tr>
<td>L$^3^-$ + NpO$_2^+$ + H$^+$ = NpO$_2$HL$^-$</td>
<td>13.46 ± 0.02</td>
<td>7.0 ± 2.0</td>
<td>234 ± 8.0</td>
</tr>
<tr>
<td>L$^3^-$ + NpO$_2^+$ = NpO$_2$L$^2^-$</td>
<td>7.06 ± 0.03</td>
<td>-(19.0 ± 2.0)</td>
<td>199 ± 8.0</td>
</tr>
<tr>
<td>L$^3^-$ + NpO$_2^+$ + H$_2$O = NpO$_2$H$_4$L$^3^-$ + H$^+$</td>
<td>-(4.74 ± 0.03)</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

2.1.2 Enthalpy of complexation

Figure 2 shows the thermograms of the complexation titrations (upper) and the associated speciation diagrams (lower) for the NpO$_2^+$/HEDTA systems. By using the stability constants determined by spectrophotometry, the enthalpies of complexation for the NpO$_2^+$/HEDTA complexes were calculated, and are listed in Table 1.
2.1.3 Speciation of Np(V)

The speciation diagrams for 1.0 mM NpO$_2^+$ in the absence and presence of 1.0 mM HEDTA were calculated using Hyss 2009 based on the available formation constants at 25 °C. In the presence of HEDTA, NpO$_2$HL$^-$ is the major species in acidic regions, while NpO$_2$L$^2-$ is the dominant species in pH region from 7 to 11. The hydrolysis of 1.0 mM Np(V) is effectively prevented by the presence of HEDTA in an equal concentration.
Figure 3. Speciation diagram of 1.0 mM Np(V), (a) in the absence of HEDTA; (b) in the presence of 1.0 mM HEDTA.

### 2.2 Complexation of U(VI) with HEDTA at 25 – 70°C

#### 2.2.1 Stability constants

Potentiometric titrations were performed to determine the stability constants of U(VI)/HEDTA complexes at different temperatures (Figure 4). The HypQuad program was used to calculate the equilibrium constants for reactions 4 – 6 (Table 2).

\[
UO_2^{2+} + H^+ + L^3- \rightarrow UO_2HL(aq) \quad (4)
\]

\[
UO_2^{2+} + L^3- \rightarrow UO_2L^- \quad (5)
\]

\[
UO_2^{2+} + L^3- + H_2O \rightarrow UO_2H_3L^2- + H^+ \quad (6)
\]
Figure 4. Representative potentiometric titrations for U(VI)/HEDTA complexation. (left) 25°C, In cup: 14.44 mL, 0.0221 mmol U(VI), 0.0507 mmol HEDTA, 0.1771 mmol H; titrant: 0.1003 mM NaOH; (right) 70°C, In cup: 14.31 mL, 0.0221 mmol U(VI), 0.0255 mmol L, 0.1016 mmol H, titrant: 0.1003 mM NaOH.

Table 2. Thermodynamic parameters for the complexation of UO$_2^{2+}$/HEDTA, $I$ = 1.00 M NaClO$_4$.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$t$, °C</th>
<th>log$\beta_M$</th>
<th>$\Delta H$, kJ·mol$^{-1}$</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Van’t Hoff</td>
</tr>
<tr>
<td>$L^3- + UO_2^{2+} + H^+ = UO_2HL(aq)$</td>
<td>25</td>
<td>15.13 ± 0.01</td>
<td>-3.58</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>15.08 ± 0.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>15.08 ± 0.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>15.04 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>$L^3- + UO_2^{2+} = UO_2L^-$</td>
<td>25</td>
<td>9.89 ± 0.02</td>
<td>15.6</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>10.07 ± 0.02</td>
<td></td>
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<td></td>
<td>55</td>
<td>10.11 ± 0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>10.27 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>$L^3- + UO_2^{2+} + H_2O = UO_2H_4L^2- + H^+$</td>
<td>25</td>
<td>3.35 ± 0.03</td>
<td>36.9</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>3.69 ± 0.03</td>
<td></td>
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<td></td>
<td>55</td>
<td>3.93 ± 0.03</td>
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</tr>
<tr>
<td></td>
<td>70</td>
<td>4.20 ± 0.03</td>
<td></td>
</tr>
</tbody>
</table>

### 2.2.2 Enthalpy of complexation

The enthalpy of complexation between U(VI) and HEDTA was determined by microcalorimetry (Figure 5). The HypDH program was used to calculate the enthalpy of complexation. The enthalpies of complexation obtained by calorimetry are in excellent agreement with those calculated by van’t Hoff equation (Table 2).
2.2.3 NMR experiments

$^1$H/$^{13}$C NMR experiments have been conducted to help understand the coordination modes of U(VI) with HEDTA. Data processing is in progress.

3. CONCLUSION

The stability constants and enthalpies of the complexation of HEDTA with Np(V) and U(VI) help to predict the change of the speciation of Np(V) and U(VI), as well as their extraction behavior in the modified TALSPEAK system at different operating temperatures.

4. PUBLICATIONS


5. ACKNOWLEDGMENTS

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