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Thermodynamic Studies to Support Actinide/Lanthanide Separations

Fuel Cycle Research & Development

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U.S. Department of Energy
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Development
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Lawrence Berkeley National Laboratory
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APPENDIX E

FCT DOCUMENT COVER SHEET ¹

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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 Actinide 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.

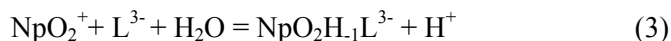
This milestone report summarizes the data obtained in FY15 on the complexation of HEDTA with Np(V) and U(VI). The results show the effect of temperature on the chemical speciation of Np(V) and U(VI) in the modified TALSPEAK Process, and help to evaluate the effectiveness of the process when the operation 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 $\lambda = 984.1$ nm, 989.8 nm, and 993.4 nm are observed, indicating the formation of three $\text{NpO}_2^+/\text{HEDTA}$ complexes. The best fit of the spectra was achieved by assuming successive formation of three $\text{NpO}_2^+/\text{HEDTA}$ complexes, NpO_2HL^- , $\text{NpO}_2\text{L}^{2-}$, and $\text{NpO}_2\text{H}_1\text{L}^{3-}$ as shown by eq. 1, 2, and 3.



It was found that it is necessary to include a species, noted as $\text{NpO}_2\text{H}_1\text{L}^{3-}$, to fit the data in the higher pH region. This species could be a ternary hydrolyzed species, $\text{NpO}_2(\text{OH})\text{L}^{3-}$, 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 ± 0.02 , 7.06 ± 0.03 , and $-(4.74 \pm 0.03)$ for NpO_2HL^- , $\text{NpO}_2\text{L}^{2-}$, and $\text{NpO}_2\text{H}_1\text{L}^{3-}$, respectively (Table 1).

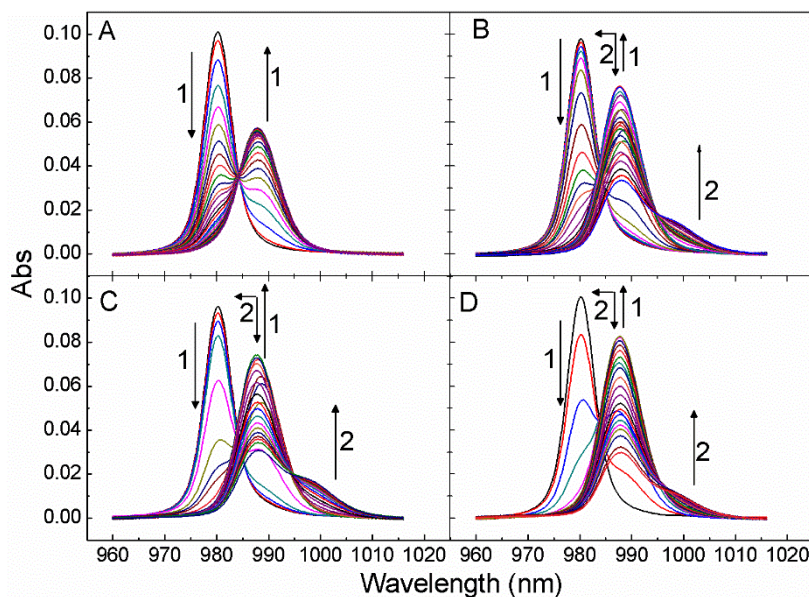


Figure 1. Spectrophotometric titration of $\text{NpO}_2^+/\text{HEDTA}$ complexation. $I = 1.0 \text{ M NaClO}_4$. (A) Initial solution in cuvette: 2.100 mL; $n_{\text{H}} = 0.6201 \mu\text{mol}$, $n_{\text{Np}} = 0.5366 \mu\text{mol}$; Titrant: 1.512 mM HEDTA / 0.3949 mM H^+ . (B) Initial solution in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

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

Reaction	$\text{Log}\beta$	ΔH $\text{kJ}\cdot\text{mol}^{-1}$	ΔS $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$\text{L}^{3+} + \text{NpO}_2^+ + \text{H}^+ = \text{NpO}_2\text{HL}^-$	13.46 ± 0.02	7.0 ± 2.0	234 ± 8.0
$\text{L}^{3+} + \text{NpO}_2^+ = \text{NpO}_2\text{L}^{2-}$	7.06 ± 0.03	$-(19.0 \pm 2.0)$	199 ± 8.0
$\text{L}^{3+} + \text{NpO}_2^+ + \text{H}_2\text{O} = \text{NpO}_2\text{H}_1\text{L}^{3+} + \text{H}^+$	$-(4.74 \pm 0.03)$	/	/

2.1.2 Enthalpy of complexation

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

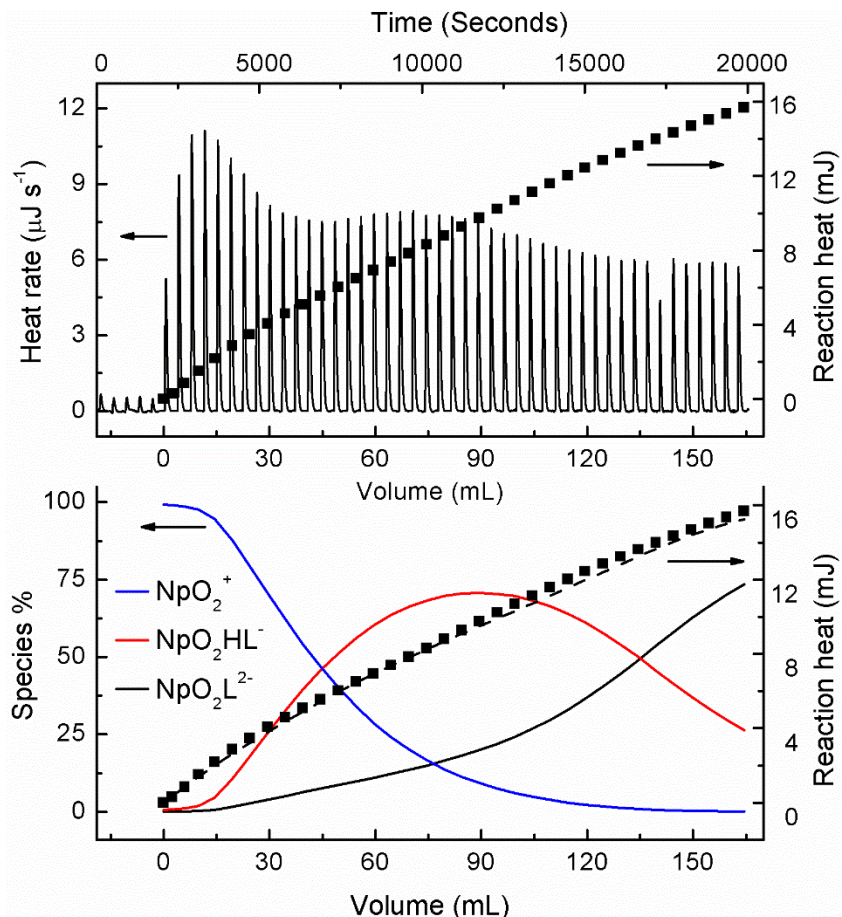


Figure 2. Calorimetric titration of $\text{NpO}_2^+/\text{HEDTA}$ complexation ($t = 25\text{ }^\circ\text{C}$, $I = 1.0\text{ M NaClO}_4$). Upper figure: thermogram (left y axis) and total reaction heat (right y axis); lower figure: total reaction heat (right y axis; ■: experimental data; dashed line, fit) and speciation of Np(V) (left y axis; solid lines) versus the volume of the titrant.

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 $25\text{ }^\circ\text{C}$. In the presence of HEDTA, NpO_2HL^- is the major species in acidic regions, while $\text{NpO}_2\text{L}^{2-}$ 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.

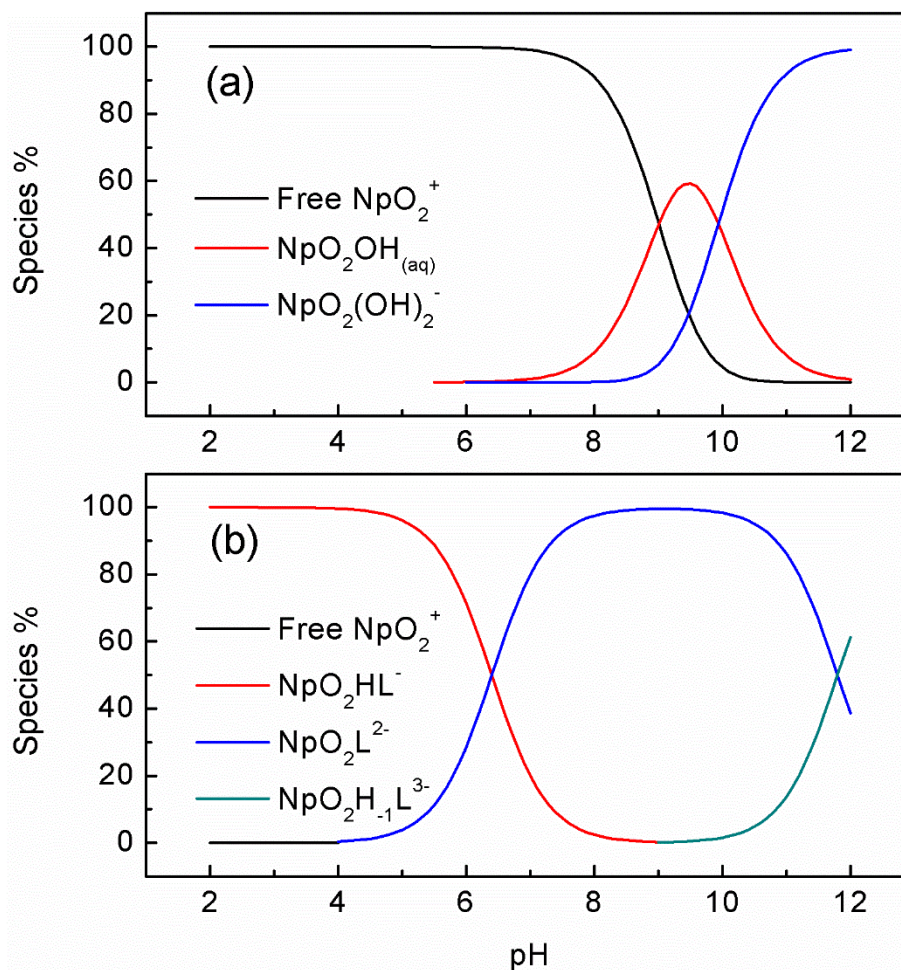
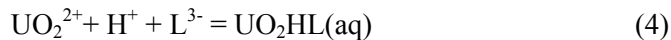


Figure 3. Speciation diagram of 1.0 mM Np(V), (a) in the absence of HEDTA; (b) in the presence of 1.0 mM HEDTA.

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).



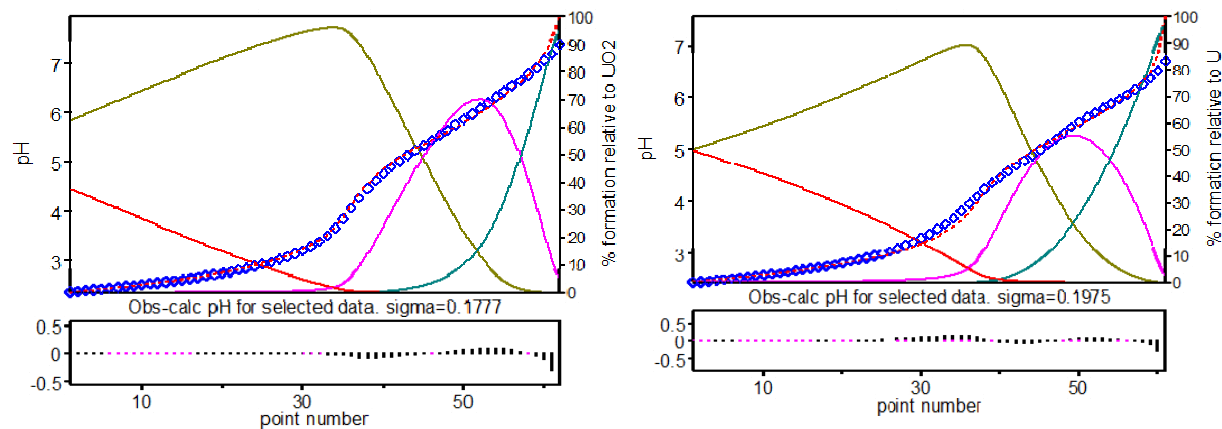


Figure 4. Representative potentiometric titrations for U(VI)/HEDTA complexation. (left) 25°C, In cup: 14.44 mL, 0.0221 mmol U(VI), 0.0507 mmol HEDTA, 0.1771 mmol H; titrant: 0.1003 mM NaOH; (right) 70°C, In cup: 14.31 mL, 0.0221 mmol U(VI), 0.0255 mmol L, 0.1016 mmol H, titrant: 0.1003 mM NaOH.

Table 2. Thermodynamic parameters for the complexation of UO_2^{2+} /HEDTA, $I = 1.00 \text{ M NaClO}_4$.

Reaction	$t, ^\circ\text{C}$	$\log\beta_M$	$\Delta H, \text{kJ}\cdot\text{mol}^{-1}$	
			Van't Hoff	Calorimetry
$\text{L}^{3-} + \text{UO}_2^{2+} + \text{H}^+ = \text{UO}_2\text{HL}(\text{aq})$	25	15.13 ± 0.01	-3.58	-5
	40	15.08 ± 0.01		
	55	15.08 ± 0.01		
	70	15.04 ± 0.01		
$\text{L}^{3-} + \text{UO}_2^{2+} = \text{UO}_2\text{L}^-$	25	9.89 ± 0.02	15.6	17
	40	10.07 ± 0.02		
	55	10.11 ± 0.02		
	70	10.27 ± 0.03		
$\text{L}^{3-} + \text{UO}_2^{2+} + \text{H}_2\text{O} = \text{UO}_2\text{H}_2\text{L}^{2-} + \text{H}^+$	25	3.35 ± 0.03	36.9	39
	40	3.69 ± 0.03		
	55	3.93 ± 0.03		
	70	4.20 ± 0.03		

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).

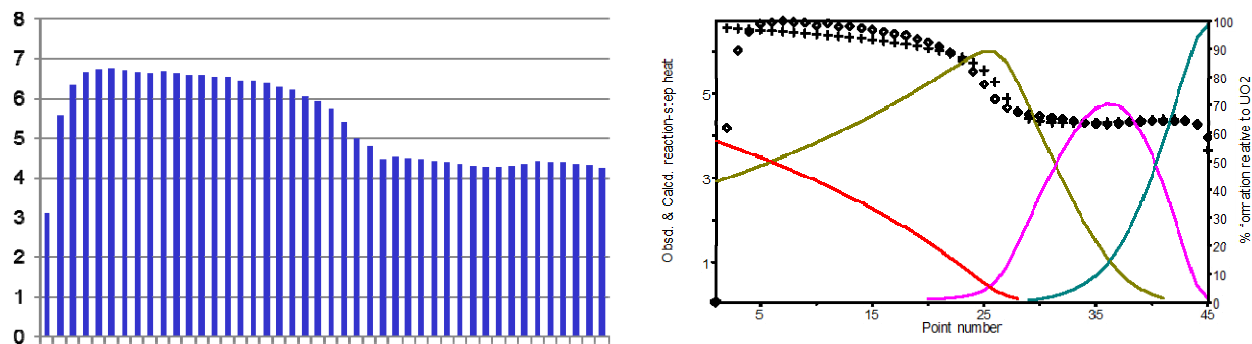


Figure 5. Calorimetric titration of U(VI)/HEDTA complexation at 25 °C. $I = 1.0$ M NaClO₄. Left figure: Calorimetric diagram (x – time, y – heat rate, μ J/s). Right figure: corresponding speciation diagram and stepwise heat.

2.2.3 NMR experiments

¹H/¹³C 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

Xingliang Li, Zhicheng Zhang, Leigh R. Martin, Shunzhong Luo, Linfeng Rao, Effect of Temperature on the Protonation of *N*-(2-hydroxyethyl)ethylenediamine-*N,N',N'*-triacetic Acid in Aqueous Solutions: Potentiometric and Calorimetric Studies, *J. Chem. Thermodynamics*, 85 (2015), 35–41.

G. Tian, Z. Zhang, L. R. Martin, L. Rao, Complexation of Curium(III) with DTPA at 10-70°C: Comparison with Eu(III)/DTPA in Thermodynamics, Luminescence, and Coordination Modes, *Inorg. Chem.*, 54 (2015), 1232-1239.

5. ACKNOWLEDGMENTS

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