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Thermodynamic Studies to Support Actinide/Lanthanide Separations

Fuel Cycle Research & Development

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Lawrence Berkeley National Laboratory
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APPENDIX E

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SUMMARY

This milestone report summarizes the data obtained in FY14 on the protonation and complexation of HEDTA with lanthanides in a temperature range from 25 to 70°C. The results show the effect of temperature on the chemical speciation of lanthanides 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.

CONTENTS

SUMMARY v

FIGURES

Figure 1. Potentiometric titrations of the protonation of HEDTA at 25°C and 70°C 1
 Figure 2. Protonation constants of HEDTA at different temperatures 2
 Figure 3. Calorimetric titrations of the protonation of HEDTA 3
 Figure 4. Speciation of HEDTA as a function of acidity ($-\log[H^+]$) at different temperatures 4
 Figure 5. Potentiometric titrations of HEDTA/Nd(III) complexation at 25°C and 70°C 5
 Figure 6. Representative spectrophotometric titration of Nd(III) HEDTA complexation at 25 °C 5
 Figure 7. Calorimetric titration of Nd(III)/HEDTA complexation at 25 °C 6
 Figure 8. Fluorescence emission spectra of Eu(III)/HEDTA systems at 25 °C. 6
 Figure 9. Luminescence decay of the Eu(III)/HEDTA systems at 25 °C. 7

TABLES

Table 1. Thermodynamic parameters for the protonation of HEDTA 2
 Table 2. Thermodynamic parameters for Nd(III)/HEDTA complexes at different temperatures 5
 Table 3. Luminescence lifetime and the hydration number of Eu(III)/HEDTA systems at 25 °C 7

ACRONYMS

DTPA	diethylenetriaminepentaacetate
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 FCRI	Nuclear Energy Fuel Cycle Research Initiative
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 FCRI 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 [1-3].

This milestone report summarizes the data obtained in FY14 on the protonation and complexation of HEDTA with lanthanides in a temperature range from 25 to 70°C. The results show the effect of temperature on the chemical speciation of lanthanides 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 Protonation of HEDTA at 25 – 70°C

2.1.1 Protonation constants

Representative potentiometric titrations at 25°C and 70°C and the fitting curve obtained by using the Hyperquad program [4] are shown in Figure 1. The speciation of the ligands in the course of the titrations is also shown in the figures. From multiple titrations at each temperature, the protonation constants of HEDTA at different temperatures were calculated. The calculated protonation constants from this work, together with the protonation constants in the literature [5-7], are shown in Figure 2 and Table 1.

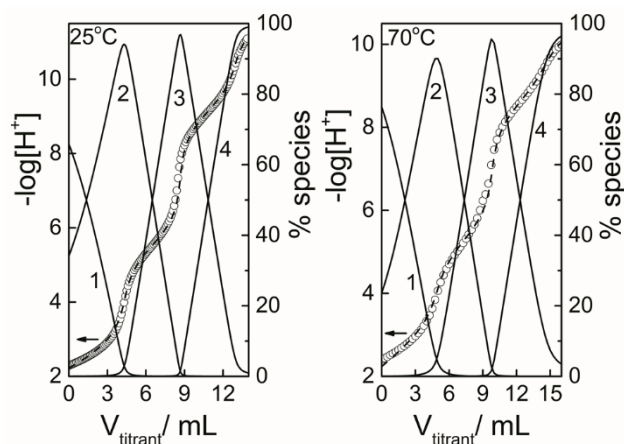


Figure 1. Potentiometric titrations of the protonation of HEDTA at 25°C (left) and 70°C (right). $I=1.0$ mol/L NaClO₄. Cup solution: $V_o(25^\circ\text{C}) = 24.97$ mL, $C_L(25^\circ\text{C})=17.32$ mmol/L, $V_o(70^\circ\text{C}) = 20.15$ mL, $C_L(70^\circ\text{C})=24.31$ mmol/L. Titrant: 99.83 mmol/L NaOH. Symbols: o – experimental data ($-\log[\text{H}^+]$), dashed line – fit ($-\log[\text{H}^+]$), solid lines – percentage of HEDTA species relative to the total HEDTA concentration (L^{3-} , HL^{2-} , H_2L^- , and H_3L , where H_3L stands for the neutral HEDTA).

Table 1 Thermodynamic parameters for the protonation of HEDTA. $I = 1.0$ M NaClO₄ and $\log\beta_{H,M}$ represents the protonation constants in molarity.

Reaction	$t, ^\circ\text{C}$	$\log\beta_{H,M}$	$\Delta H,$ $\text{kJ}\cdot\text{mol}^{-1}$
$\text{H}^+ + \text{L}^{3-} = \text{HL}^{2-}$	0	10.33 [5]	-26.04 ^a ;
	10	10.09 [5]	-27.8(2) ^b
	25	9.14 ± 0.01, 9.89 [5], 9.20 [6], 8.65 [7]	
	35	9.70 [5]	
	40	8.94 ± 0.01	
	45	9.63 [5]	
	55	8.69 ± 0.01	
	60	9.34 [5]	
	70	8.56 ± 0.01	
	$2\text{H}^+ + \text{L}^{3-} = \text{H}_2\text{L}^-$	0	15.97 [5]
10		15.67 [5]	-49.3(2) ^b
25		14.66 ± 0.01, 15.29 [5], 14.72 [6], 13.76 [7]	
35		15.04 [5]	
40		14.34 ± 0.01	
45		14.91 [5]	
60		14.52 [5]	
55		13.97 ± 0.02	
70		13.81 ± 0.02	
$3\text{H}^+ + \text{L}^{3-} = \text{H}_3\text{L}$		0	18.61 [5]
	10	18.26 [5]	-46.5(3) ^b
	25	17.20 ± 0.01, 17.85 [5], 18.52 [6], 16.06 [7]	
	35	17.54 [5]	
	40	16.95 ± 0.02	
	45	17.39 [5]	
	55	16.62 ± 0.02	
	60	16.93 [5]	
	70	16.54 ± 0.03	

^aAverage enthalpies calculated from Van't Hoff plots; ^bdirectly measured enthalpies by calorimetry at 25°C.

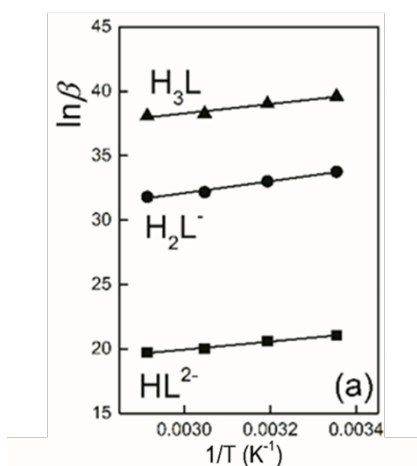


Figure 2. Protonation constants of HEDTA at different temperatures. $I = 1.0$ mol/L NaClO₄.

The results have demonstrated that the first two protonation constants decrease and the third one slightly increases with the increase of temperature (Table 1 and Figure 2), implying that HEDTA becomes a stronger acid at higher temperatures. This observation could have impact on the speciation of An(III)/Ln(III) in the TALSPEAK system, because the hydrogen ions would compete less strongly with An(III)/Ln(III) ions for the complexation of the anionic HEDTA species at higher temperatures. The Van't Hoff plot of $\ln\beta_H$ vs. $1/T$ (Figure 2) indicates that all three overall protonation reactions are exothermic (with positive slopes). However, stepwise, the first two steps of protonation are exothermic and the last step is endothermic (the slope of the top line for H_3L is less positive than the other two lines for H_2L^- and HL^{2-}). In order to confirm the thermodynamic parameters for the protonation reactions of HEDTA, calorimetric titrations were performed.

2.1.2 Enthalpy of protonation

Data of the calorimetric titrations for the protonation of HEDTA are shown in Figure 3. The observed reaction heat ("partial" or stepwise Q) is a function of a number of parameters, including the concentrations of reactants (C_H , C_L), the protonation constants ($\log\beta_H$) and the enthalpy of protonation of the ligand (ΔH). Using the stoichiometric concentrations of the reactants and the protonation constants measured by potentiometry measured in this work, the enthalpies for the protonation reaction of HEDTA at 25°C are calculated from the calorimetric titration data, and are presented in Table 1.

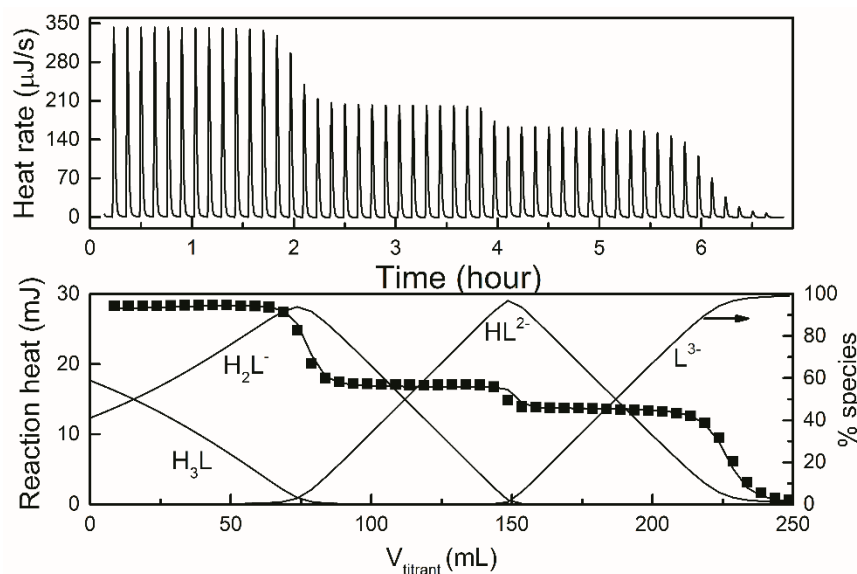


Figure 3. Calorimetric titrations of the protonation of HEDTA, $I = 1 \text{ mol/L NaClO}_4$, $t = 25^\circ\text{C}$. (Top) a representative thermogram. (Bottom) A plot of Q_{partial} vs. the volume of titrant, Symbols of the bottom: ■ - experimental Q , lines – fit. Initial cup solutions: HEDTA, C_H^0/C_L^0 (mmol/L) = 29.88/9.96; titrant: 99.83mmol/L NaOH, 5.0 μL /addition.

The stepwise enthalpy for the first protonation step (HL^{2-}) measured by microcalorimetry is $-27.83 \text{ kJ}\cdot\text{mol}^{-1}$, in good agreement with those from the linear fits of the Van't Hoff plots (-26.04 and $-27.32 \text{ kJ}\cdot\text{mol}^{-1}$). The first two protonation reactions for the HEDTA are exothermic, but the enthalpies become increasingly endothermic in successive protonation step(s). Similar to those in the system of EDTA [8], the first two protonation steps probably occur on the nitrogen atoms [9].

2.1.3 Effect of Temperature on the Speciation of HEDTA

With the protonation constants measured at different temperatures, it is possible to evaluate the change of speciation of HEDTA in the $-\log[H^+]$ region of 2 to 12, an acidity region covering the operating envelop of the TALSPEAK process. Figure 4 compares the speciation of the ligand (in the absence of metal ions) at 25°C and 70°C. Small but definite differences for all species between the two temperatures can be observed. For example, at higher temperature, there is less H_2L^- species and more H_3L and L^{3-} species. In brief, the protonation of HEDTA generally becomes weaker at higher temperatures. Such changes in the speciation would certainly affect the speciation of An(III) and Ln(III) in the modified TALSPEAK system. The significance of the effect will be evaluated in conjunction with the stability constants of the An(III)/Ln(III) complexes with HEDTA at different temperatures.

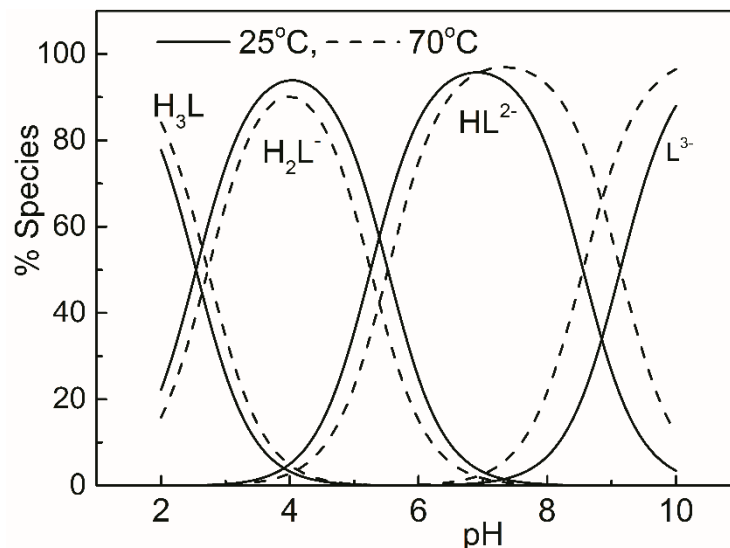


Figure 4. Speciation of HEDTA as a function of acidity ($-\log[H^+]$) at different temperatures. $I = 1$ mol/L $NaClO_4$, Cup solution: $V_o(25^\circ C) = 24.97$ mL, $C_L(25^\circ C) = 17.32$ mmol/L, $V_o(70^\circ C) = 20.15$ mL, $C_L(70^\circ C) = 24.31$ mmol/L, Titrant: 99.83 mmol/L NaOH. lines – percentage of HEDTA species relative to the total HEDTA concentration (L^{3-} , HL^{2-} , H_2L^- , and H_3L , where H_3L stands for the neutral HEDTA).

2.2 Complexation of Ln(III) with HEDTA at 25 – 70°C

2.2.1 Stability constants

Potentiometric (Figure 5) and spectrophotometric (Figure 6) titrations were performed to determine the stability constants of Nd(III)/HEDTA complexes at different temperatures. The HypQuad and HypSpec programs were used to calculate the stability constants (Table 2). It was found that it is necessary to include a species, noted as $NdH_{-1}L^-$, to fit the data in the higher pH region. This species could be a ternary hydrolyzed species, $Nd(OH)L^-$, or a species with the hydroxyl group in HEDTA deprotonated. Thermodynamic data alone do not allow the differentiation between these two species.

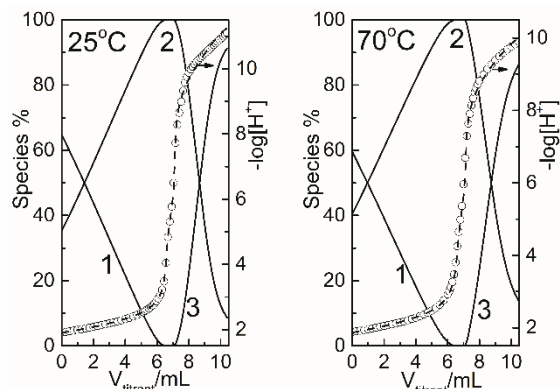


Figure 5 Potentiometric titrations of HEDTA/Nd(III) complexation at 25°C (left) and 70°C (right), $I=1.0$ mol/L NaClO₄. Titrant: 99.83 mmol/L NaOH. Cup solution: $V_o(25^\circ\text{C}) = 20.35$ mL, $C_L(25^\circ\text{C}) = 12.18$ mmol/L, $C_{\text{Nd}}(25^\circ\text{C}) = 9.60$ mmol/L, $C_H(25^\circ\text{C}) = 37.48$ mmol/L, $V_o(70^\circ\text{C}) = 20.67$ mL, $C_L(70^\circ\text{C}) = 12.04$ mmol/L, $C_{\text{Nd}}(70^\circ\text{C}) = 9.47$ mmol/L, $C_H(70^\circ\text{C}) = 37.03$ mmol/L, Symbols: \circ – experimental data ($-\log[\text{H}^+]$), dashed line – fit ($-\log[\text{H}^+]$); solid lines – percentage of Nd(III) species relative to total Nd³⁺ concentration (1- Nd³⁺, 2- NdL, 3- NdH₁L⁻).

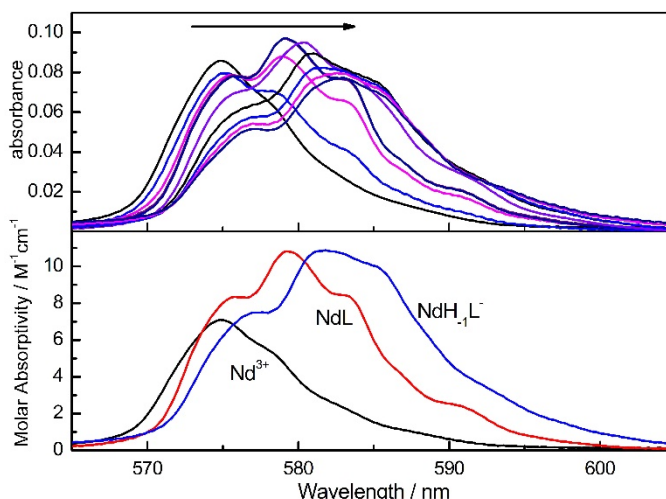


Figure 6. Representative spectrophotometric titration of Nd(III) HEDTA complexation at 25 °C, $I = 1.0$ mol/L NaClO₄. Upper figure: Absorption spectra. Lower figure: calculated molar absorptivity of Nd³⁺ and Nd(III)/HEDTA complexes. Initial solution in the cuvette: 2.15 mL, 25.83mmol Nd(ClO₄)₃ / 43.05mmol HClO₄. Titrant: 50.23mmol HEDTA / 60.83mmol NaOH.

Table 2 Thermodynamic parameters for the Nd(III)/HEDTA complexes at different temperatures. $I = 1$ M NaClO₄. $\log\beta_M$ represents the complex formation constants in molarity.

Reaction	$t, ^\circ\text{C}$	$\log\beta_M$	$\Delta H, \text{kJ}\cdot\text{mol}^{-1}$
$\text{Nd}^{3+} + \text{L}^{3-} = \text{NdL}$	25	13.29 ± 0.02	-13.49^{a} ;
	40	13.10 ± 0.03	$-28 \pm 1^{\text{b}}$
	55	13.58 ± 0.02	
	70	12.96 ± 0.03	
$\text{Nd}^{3+} + \text{L}^{3-} + \text{H}_2\text{O} = \text{NdH}_{1,1}\text{L}^- + \text{H}^+$	25	3.11 ± 0.03	29.89^{a} ;
	40	3.25 ± 0.03	$14 \pm 2^{\text{b}}$
	55	3.42 ± 0.03	
	70	3.82 ± 0.04	

^aAverage enthalpies calculated from Van't Hoff plots in this work, ^bdirectly measured enthalpies at 25°C by microcalorimetry in this work.

2.2.2 Enthalpy of complexation

The enthalpy of complexation between Nd(III) and HEDTA was determined by microcalorimetry (Figure 7). The HypDH program was used to calculate the enthalpy of complexation (Table 2).

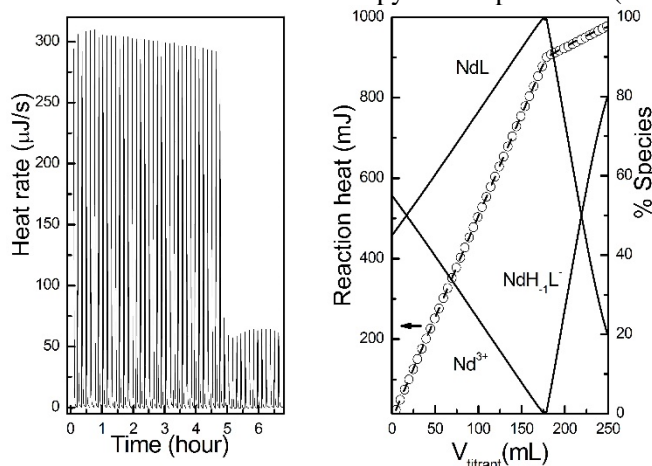


Figure 7. Calorimetric titration of Nd(III)/HEDTA complexation at 25 °C. $I = 1.0$ M NaClO₄. Initial solution: 750 μL, 7.332 μmol Nd(ClO₄)₃/7.506 μmol HEDTA/18.01 μmol HClO₄. Titrant: 0.1 mmol NaOH. Left figure: Calorimetric diagram. Right figure: corresponding speciation diagram and cumulative heat.

2.2.3 Fluorescence measurements

The fluorescence of the Eu(III)/HEDTA system was measured to help understand the coordination modes of Ln(III) with HEDTA. Figures 8 and 9 show the variation of the emission spectra and the lifetime as the basicity of the solutions was increased. From the lifetime, the hydration number of Eu(III) was calculated using the correlation in the literature, and shown in Table 3.

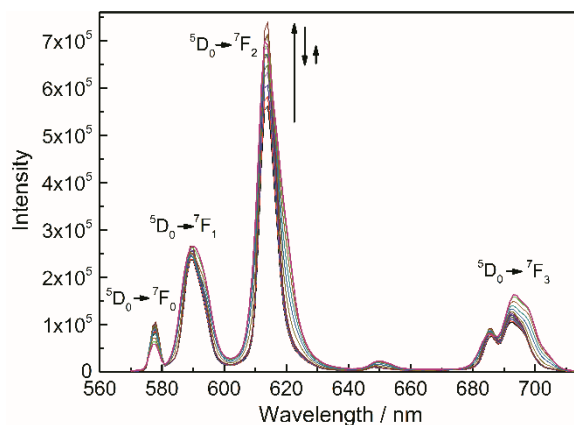


Figure 8. Fluorescence emission spectra of Eu(III)/HEDTA systems at 25 °C. $I = 1$ mol/L NaClO₄. Wavelength of excitation. 395nm, Initial solution: 5.04mL, 36.26mmol Eu(ClO₄)₃ / 37.30mmol HEDTA / 80.00 mmol HClO₄. Titrant: 0.1mmol NaOH.

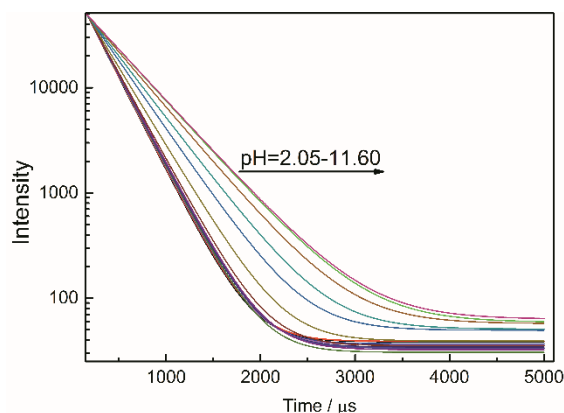


Figure 9. Luminescence decay of the Eu(III)/HEDTA systems at 25 °C. $I = 1$ mol/L NaClO_4 . Wavelength of excitation: 395nm. Wavelength of emission: 615nm. Initial solution: 5.04mL, 36.26mmol $\text{Eu}(\text{ClO}_4)_3$ / 37.30 mmol HEDTA / 80.00 mmol HClO_4 . Titrant: 0.1mmol NaOH.

Table 3. Luminescence lifetime and the average hydration number of of Eu(III) / HEDTA systems at 25 °C.

-log[H ⁺]	τ_{exp} , μs	$n_{\text{H}_2\text{O}, exp}$	% Eu species		
			Eu^{3+}	EuL	EuH_1L^-
2.06	245.4	3.58	32.88	67.12	/
2.12	247.1	3.55	28.18	71.82	/
2.19	249.4	3.51	23.51	76.49	/
2.26	250.0	3.50	18.89	81.11	/
2.36	252.2	3.46	14.36	85.64	/
2.48	254.1	3.43	9.97	90.03	/
2.66	256.3	3.40	5.78	94.22	/
2.98	258.0	3.37	1.96	98.04	/
9.30	264.5	3.27	/	99.40	0.60
10.71	292.2	2.89	/	86.79	13.21
11.03	335.1	2.43	/	75.73	24.27
11.22	370.7	2.13	/	66.55	33.45
11.37	412.2	1.85	/	58.99	41.01
11.47	441.1	1.68	/	52.77	47.23
11.56	445.8	1.66	/	47.63	52.37

3. SUMMARY

The overall protonation constants of HEDTA decrease by 0.58 – 0.85 orders of magnitude as the temperature is increased from 25 to 70°C. On the other hand, the stability of the 1:1 Nd(III)/HEDTA complex, NdL, becomes weaker as the temperature is increased. Integration of the data on the protonation and complexation will help to predict the change of the speciation of the actinides and lanthanides, as well as their extraction behavior in the modified TALSPEAK system at different operating temperatures.

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