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Experimental Thermodynamic Studies for Efficient Extraction of Uranium from Seawater

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 three major tasks, including (1) thermodynamic studies of the interaction between Ca(II)/Mg(II) and the triscarbonato uranyl species, with the objective of evaluating the speciation of U(VI) in seawater; (2) Thermodynamic studies of the interactions between Ca(II)/Mg(II) and glutarimidedioxime; and (3) Preliminary investigation of the binding strength of vanadium with glutarimidedioxime and evaluation of the competition between U(VI) and V(V) for binding amidoxime ligands.

The data on the interactions of Ca(II)/Mg(II) with the triscarbonato uranyl species have particular importance, because they show that the dominant U(VI) species under seawater conditions is the neutral complex, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ (~ 60%), instead of the anionic $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^{4-}$ species suggested by the previous literature. The results have important implications in the design of effective sorbents to extract uranium from seawater.

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1. INTRODUCTION

To improve the extraction efficiency and reduce the extraction cost, fundamental understanding of the coordination chemistry of the extraction process is necessary. Therefore, thermodynamic studies need to be conducted to determine the stability constants of the complexes of uranium and other major metal ions in seawater with amidoxime-type ligands, by a combination of techniques including potentiometry and spectrophotometry.

In FY14, three major tasks were taken, including (1) thermodynamic studies of the interaction between Ca(II)/Mg(II) and the triscarbonato uranyl species, with the objective of evaluating the speciation of U(VI) in seawater; (2) Thermodynamic studies of the interactions between Ca(II)/Mg(II) and glutarimidedioxime; and (3) Preliminary determination of the binding strength of vanadium with glutarimidedioxime and evaluation of the competition between U(VI) and V(V) for binding amidoxime-type ligands. This report presents the data obtained for these tasks in FY14.

2. RESULTS

2.1 Interaction between Ca(II)/Mg(II) and $\text{UO}_2(\text{CO}_3)_3^{4-}$

2.1.1 Stability constants

Figure 1 shows an example of potentiometric titrations carried out to study the formation of the successive complexes of Ca^{2+} with $\text{UO}_2(\text{CO}_3)_3^{4-}$. The data were processed with the minimization software *Hyperquad* [1]. The best fit was obtained with a model consistent with the formation of two successive complexes, described by equations (1) and (2) (see Table 1). As shown in Figure 1, the agreement between the experimental and calculated values is excellent.

Figure 1. A representative Ca^{2+} ion selective electrode potentiometric titration. $[\text{UO}_2^{2+}]_{\text{initial}} = 0.469 \text{ mM}$; $[\text{CO}_3^{2-}]_{\text{initial}} = 1.85 \text{ mM}$; $[\text{Ca}^{2+}]_{\text{titrant}} = 10.05 \text{ mM}$; $\text{pH} = 10.3\text{--}10.0$. Symbols: (left y-axis, E in mV) $\square$ observed E ; solid line - calculated E ; (right y-axis, percentage of U(VI) species) -- $\text{UO}_2(\text{CO}_3)_3^{4-}$, - - $\text{CaUO}_2(\text{CO}_3)_3^{2-}$, ... $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$.

Figure 2 shows a representative spectrophotometric titration for the complexation of Mg^{2+} with the triscarbonato uranyl species. As MgCl_2 was added into the solution of $\text{UO}_2(\text{CO}_3)_3^{4-}$, subtle changes in the spectra were observed in the wavelength region of 220 – 400 nm (Figure 2, upper left diagram). The data were processed with the minimization software *HypSpec* [1]. Factor analysis of the data indicated that there were two absorbing species, $\text{UO}_2(\text{CO}_3)_3^{4-}$ and an $\text{Mg}^{2+}/\text{UO}_2(\text{CO}_3)_3^{4-}$ complex. The best fit was obtained with the model consistent with the formation of the 1:1 complex, described by equation (3).

Figure 2. Spectrophotometric titration of $\text{Mg}^{2+}/\text{UO}_2(\text{CO}_3)_3^{4-}$. $[\text{UO}_2^{2+}]_{\text{initial}} = 0.040 \text{ mM}$; $[\text{CO}_3^{2-}]_{\text{initial}} = 0.200 \text{ mM}$; $[\text{Mg}^{2+}]_{\text{titrant}} = 10.22 \text{ mM}$ (final $n(\text{Mg})/n(\text{UO}_2^{2+}) = 70.8$); pH = 9.75–9.68. Upper left: un-normalized spectra (the number of spectra was reduced for clarity). Upper right: Calculated molar absorptivities of $\text{UO}_2(\text{CO}_3)_3^{4-}$ and $\text{MgUO}_2(\text{CO}_3)_3^{2-}$. Lower left: Experimental and calculated spectra at $n(\text{Mg})/n(\text{UO}_2^{2+}) = 45.5$ (some experimental points omitted for clarity). Lower right: experimental and calculated absorbance at 255 nm as a function of $n(\text{Mg})/n(\text{UO}_2^{2+})$ and the percentage distribution relative to total uranyl on the right axis of the diagram.

Table 1 Equilibrium constants of Ca/Mg complexation with $\text{UO}_2(\text{CO}_3)_3^{4-}$.

Reaction	$\log \beta \pm \sigma$		
	$I = 0 \text{ M}$	$I = 0.1 \text{ M}$ NaCl	$I = 0.5 \text{ M}$ NaCl
$\text{Ca}^{2+} + \text{UO}_2(\text{CO}_3)_3^{4-} = \text{CaUO}_2(\text{CO}_3)_3^{2-}$	5.15 ± 0.06	3.42 ± 0.06	2.43 ± 0.10
$2\text{Ca}^{2+} + \text{UO}_2(\text{CO}_3)_3^{4-} = \text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$	9.00 ± 0.06	6.42 ± 0.06	4.96 ± 0.10
$\text{Mg}^{2+} + \text{UO}_2(\text{CO}_3)_3^{4-} = \text{MgUO}_2(\text{CO}_3)_3^{2-}$	4.41 ± 0.06	2.69 ± 0.06	1.77 ± 0.10

2.1.2 Enthalpy of Ca(II) complexation with $\text{UO}_2(\text{CO}_3)_3^{4-}$

Figure 3 shows the thermogram of a representative calorimetric titration (heat rate vs time, left diagram), and the experimental/fitted heat as a function of the titrant volume (right diagram). As the thermogram shows, small positive heat was observed as Ca(II) was added into the solution containing $\text{UO}_2(\text{CO}_3)_3^{4-}$, indicating that the formation of the calcium complexes is slightly exothermic. The reaction heat, in conjunction with the stability constants of $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ obtained by potentiometry, was fitted with the minimization software *HypDeltaH* [1] to calculate the enthalpies of complexation for the two complexes. As shown in Figure 3 (right diagram), the fitting of the data is reasonably good considering the very small amounts of reaction heat developed during the titrations (50 - 200 $\mu\text{J}/\text{addition}$). The calculated enthalpies of complexation for reactions (1) and (2) are $-(8 \pm 6) \text{ kJ} \cdot \text{mol}^{-1}$, and $-(8 \pm 7) \text{ kJ} \cdot \text{mol}^{-1}$, respectively.

Figure 3. Microcalorimetric titrations on the complexation of Ca^{2+} with $\text{UO}_2(\text{CO}_3)_3^{4-}$ (0.1 M NaCl, 25.0°C). $[\text{UO}_2^{2+}]_{\text{initial}} = 0.20 \text{ mM}$; $[\text{CO}_3^{2-}]_{\text{initial}} = 0.80 \text{ mM}$; $[\text{Ca}^{2+}]_{\text{titrant}} = 10.05 \text{ mM}$; pH=10.3–10.0. Left: thermogram (Power, μW vs time, min). Each peak corresponds to an addition of titrant. Right: cumulative experimental and calculated heats (mJ) on the left axis, percentage distribution of the complexes with respect to total uranyl on the right axis. Symbols: -- $\text{UO}_2(\text{CO}_3)_3^{4-}$; --- $\text{CaUO}_2(\text{CO}_3)_3^{2-}$; ... $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$; $\square$ experimental cumulative heat (mJ); + Calculated cumulative heat (mJ).

2.1.3 Speciation of U(VI) under seawater conditions

Though the complexation between Ca/Mg and $\text{UO}_2(\text{CO}_3)_3^{4-}$ is fairly weak, the speciation of U(VI) in seawater could be affected due to the high concentrations of Ca and Mg relative to U(VI) in seawater ($[\text{Ca(II)}] = 0.01 \text{ M}$, $[\text{Mg(II)}] = 0.053 \text{ M}$, and $[\text{U(VI)}] = 1.4 \times 10^{-8} \text{ M}$). Consequently, neglecting the formation of Ca/Mg complexes with $\text{UO}_2(\text{CO}_3)_3^{4-}$ could probably lead to erroneous speciation of U(VI) under seawater conditions. As shown in the lower diagram of Figure 4, when pH is above 6, the aqueous chemistry of U(VI) in the presence of Ca(II) (0.01 M) and Mg(II) (0.053 M) is dominated by the formation of the $\text{M}_n\text{UO}_2(\text{CO}_3)_3^{2(2-n)-}$ ($\text{M} = \text{Ca}$ or Mg , and $n = 1$ or 2) complexes. In particular, at the seawater pH (8.2), $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ accounts for 58% of the total uranium in solution, $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ and $\text{MgUO}_2(\text{CO}_3)_3^{2-}$ 18% each, and $\text{UO}_2(\text{CO}_3)_3^{4-}$ only 6%. In contrast, more than 97% of U(VI) would exist as $\text{UO}_2(\text{CO}_3)_3^{4-}$ if the formation of Ca/Mg complexes with $\text{UO}_2(\text{CO}_3)_3^{4-}$ was neglected, as shown in the upper speciation diagram of Figure 4.

Understanding the speciation of U(VI) under seawater conditions is of great significance in the development of strategies for the extraction of uranium from seawater. Since the dominant species of U(VI) is the neutral complex, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$, instead of the highly negatively charged $\text{UO}_2(\text{CO}_3)_3^{4-}$ as previously believed, the sorbents must be able to interact with $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ effectively to achieve efficient collection [2].

Figure 4. U(VI) speciation under seawater conditions in the absence (upper figure) and presence of 0.01 M Ca(II) and 0.053 M Mg(II) (lower figure). $C_{\text{U}} = 1.4 \times 10^{-8} \text{ M}$, $C_{\text{carbonate}} = 0.0023 \text{ M}$. 1 – UO_2^{2+} , 2 – $\text{UO}_2(\text{CO}_3)(\text{aq})$, 3 – $\text{UO}_2(\text{CO}_3)_2^{2-}$, 4 – $\text{UO}_2(\text{CO}_3)_3^{4-}$, 5 – $\text{CaUO}_2(\text{CO}_3)_3^{2-}$, 6 – $\text{MgUO}_2(\text{CO}_3)_3^{2-}$, 7 – $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$.

2.2 Complexation of Ca(II)/Mg(II) with glutarimidedioxime

2.2.1 Stability constants

Potentiometric titrations (Figure 5) were performed to determine the stability constants of Ca(II) and Mg(II)/complexes with glutarimidedioxime. The HypQuad program was used to calculate the stability constants (Table 2). It was found that the complexation of Ca(II) and Mg(II) with glutarimidedioxime is significantly weaker than those of U(VI).

Figure 5. Potentiometric titrations for calcium and magnesium with glutarimidedioxime (denoted as H_2AmidA in the figure). Top: $V_o = 15.5$ mL, $[Ca]_{TOT} = 7.95$ mM, $[H_2AmidA]_{TOT} = 19.9$ mM, $[NaOH]$: 0.086 M. Titrant: 0.0994 M HCl. Bottom: $V_o = 21.1$ mL, $[Mg]_{TOT} = 1.87$ mM, $[H_2AmidA]_T = 4.69$ mM. Titrant: 0.0102 M NaOH.

Table 2 Stability constants of calcium, magnesium, and uranium complexes with glutarimidedioxime (denoted as H_2L in the table)

Reaction [*]	Log β
$Ca^{2+} + L^{2-} \rightarrow Ca(L)$	2.44 ± 0.02
$UO_2^{2+} + L^{2-} \rightarrow UO_2(L)$	17.8 ± 1.1
$Ca^{2+} + H^+ + L^{2-} \rightarrow Ca(HL)^+$	14.56 ± 0.02
$Mg^{2+} + H^+ + L^{2-} \rightarrow Mg(HL)^+$	14.40 ± 0.04
$UO_2^{2+} + H^+ + L^{2-} \rightarrow UO_2(HL)^+$	22.7 ± 1.3
$Ca^{2+} + H^+ + 2L^{2-} \rightarrow Ca(HA)(L)^-$	17.27 ± 0.06
$Mg^{2+} + H^+ + 2L^{2-} \rightarrow Mg(HA)(L)^-$	18.56 ± 0.15
$UO_2^{2+} + H^+ + 2L^{2-} \rightarrow UO_2(HA)(L)^-$	36.8 ± 2.1

2.2.2 Enthalpy of complexation

The enthalpy of complexation between Ca(II) and glutarimidedioxime was determined by microcalorimetry (Figure 6). The HypDH program was used to calculate the enthalpy of complexation (Table 3).

Figure 6. Calorimetric titration of glutarimidedioxime (denoted as H_2AmidA in the figure) with calcium. Top: Thermogram showing reaction heat flow rate as a function of time for a typical calorimetric titration. Bottom: Fit of the data with overlapping speciation. Titration conditions are as follows: cup: $V_o = 0.750 \text{ mL}$, $[\text{H}_2\text{AmidA}]_{\text{TOT}} = 0.0101 \text{ M}$, $[\text{H}^+]_{\text{TOT}} = -0.020 \text{ M}$. Titrant: 0.05 M CaCl_2 ($I=0.5 \text{ M}$).

Table 3 Summary of reaction enthalpies and entropies for calcium-glutarimidedioxime (as H_2L in the table) complexes

Reaction	ΔH (kJ mol^{-1})	ΔS ($\text{J mol}^{-1} \text{ K}^{-1}$)
$\text{H}^+ + \text{L}^{2-} \rightarrow \text{HL}^-$	-36.1 ± 0.5	110 ± 2
$2\text{H}^+ + \text{L}^{2-} \rightarrow \text{H}_2\text{L}$	-69.7 ± 0.9	202 ± 3
$3\text{H}^+ + \text{L}^{2-} \rightarrow \text{H}_3\text{L}^+$	-77 ± 6	218 ± 14
$\text{Ca}^{2+} + \text{L}^{2-} \rightarrow \text{Ca(L)}$	10.5 ± 4	82 ± 13
$\text{Ca}^{2+} + \text{H}^+ + \text{L}^{2-} \rightarrow \text{Ca(HL)}^+$	-30.3 ± 4	117 ± 13
$\text{Ca}^{2+} + \text{H}^+ + 2\text{L}^{2-} \rightarrow \text{Ca(HL)(L)}^-$	-29.9 ± 0.7	230 ± 3

2.3 Interactions between vanadium(V) and glutarimidedioxime

Potentiometric titrations were performed to evaluate the binding interactions of V(V) with glutarimidedioxime (Figure 7). The tentative stability constants of V(V)/glutarimidedioxime complexes are listed in Table 4, in comparison with those of U(VI).

Figure 7. Representative titration of vanadium with glutarimidedioxime (denoted as H₂AmidA). Cup solution: [V]_{TOT} = 5.24 mM, [H₂AmidA]_{TOT} = 10.3 mM, 0.015 M NaOH, 19.9 mL. Titrant: 0.100M HCl.

The stability constants for the vanadium complexes with glutarimidedioxime are at least 8 orders of magnitude stronger than the analogous uranyl complexes as indicated in Table 4. Furthermore, as indicated by the potentiometric data, vanadium forms complexes with glutarimidedioxime over a large range of pH values, which may complicate efforts to remove vanadium from the polymeric fibers that are being developed to sequester uranium.

Table 4 Comparison of the stability constants of V(V) and U(VI) complexes with glutarimidedioxime (denoted as H₂L in the table)

Overall Reaction	Log β _{MLH}
VO ₂ ⁺ + L ²⁻ → VO ₂ (L) ⁻	(~26-27)
UO ₂ ²⁺ + L ²⁻ → UO ₂ (L)	17.8 ± 1.1
VO ₂ ⁺ + H ⁺ + L ²⁻ → VO ₂ (HL)	31.56 ± 0.06
UO ₂ ²⁺ + H ⁺ + L ²⁻ → UO ₂ (HL) ⁺	22.7 ± 1.3
VO ₂ ⁺ + 2H ⁺ + 2L ²⁻ → VO ₂ (HL) ₂ ⁻	54.96 ± 0.04
UO ₂ ²⁺ + 2H ⁺ + 2L ²⁻ → UO ₂ (HL) ₂	43.0 ± 1.1
VO ₂ ⁺ + H ⁺ + 2L ²⁻ → VO ₂ (HL)(L) ²⁻	48.52 ± 0.06
UO ₂ ²⁺ + H ⁺ + 2L ²⁻ → UO ₂ (HL)(L) ⁻	36.8 ± 2.1
VO ₂ ⁺ + 2L ²⁻ → VO ₂ (L) ₂ ³⁻	38.24 ± 0.07
UO ₂ ²⁺ + 2L ²⁻ → UO ₂ (L) ₂ ²⁻	36.0 ± 1.1

3. SUMMARY

Though Ca(II) and Mg(II) form weak complexes with triscarbonato uranyl anion, about 60% of U(VI) exists as the neutral $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ species under seawater conditions, due to the high concentrations of Ca(II) and Mg(II) in seawater.

The complexes of Ca(II) and Mg(II) with glutarimidedioxime are a number of orders of magnitude lower than those of U(VI) with glutarimidedioxime. They are not expected to have strong competition with U(VI) for the sorption sites of the amidoxime-based sorbents. However, due to their high concentrations in seawater, sorption of Ca(II) and Mg(II) is expected to occur.

Preliminary studies suggest the vanadium(V) interacts with glutarimidedioxime much more strongly than U(VI). Further studies are to be conducted to confirm the binding strength, and gain fundamental understanding of the high binding strength of V(V) by glutarimidedioxime.

4. REFERENCES

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