
Developing a Fundamental Basis for the Characterization, Separation, and Disposal of Plutonium and Other Actinides in High Level Radioactive Waste: The Effect of Temperature and Electrolyte Concentrations on Actinide Speciation

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Research Objectives

This research involves establishing a foundation for describing the speciation of Pu and the other actinides in the extremely non-ideal systems found in HLW. We are developing a thermodynamic database of Pu and actinide complexing in alkaline systems, and at elevated temperatures and electrolyte concentrations. Initially, we are using chemical analogs for Pu; later we will conduct experiments using Pu itself. We are investigating complexation by OH⁻, acetate, oxalate, and ethylenediaminetetraacetate (EDTA⁴⁻). In addition, we are complementing our thermodynamic measurements with spectroscopic studies to validate assumptions made concerning speciation and stoichiometry.

Research Progress and Implications

This project began early in the 1999 fiscal year, and we have completed less than one year of the three year project. Our research progress and spending is on schedule. Initial work has been focused on the trivalent actinide systems, as models for Pu³⁺ and Am³⁺. Prof. Wood's group at University of Idaho has been studying the solubility of the Nd(OH)₃ system as a function of temperature from 30-290°C. Their data are shown in Figure 1 (below).

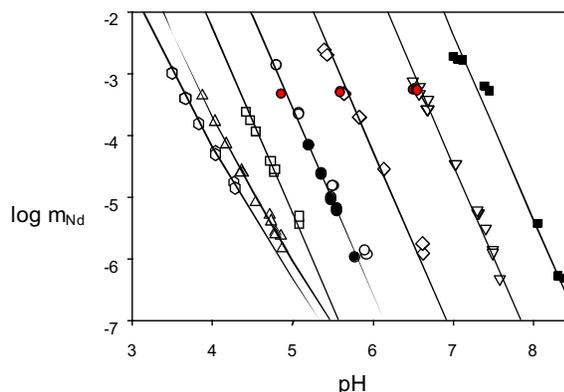


Figure 1: Plot of results of Nd(OH)₃ solubility experiments in 0.03 molal Na-triflate media as a function of pH at various temperatures. The temperatures of the data are, from right to left, 30°C, 50°C, 100°C, 150°C, 200°C, 250°C and 290°C. The symbols are the raw experimental data and the lines are best fits. The red symbols are replicate runs.

The dominant solubility controlling reaction in this system appears to be:



Modeling of the reactions in the temperature range of 30-200° C indicates hydrolysis behavior is as expected. However, when $T = 250 - 290^\circ \text{C}$, the data suggests that NdOH^{2+} is an important species, which is not predicted based on previous studies. From this work, the stability quotient for the formation of the 1:1 hydrolysis species has been estimated, which now makes it possible to determine stability constants for complexation with acetate, oxalate, EDTA⁴⁻, and other inorganic ligands under more alkaline conditions.

At Lawrence Berkeley National Laboratory (LBNL), the research group of Dr. Linfeng Rao has been studying the complexation of the trivalent *f*-elements with simple carboxylate ligands. Dr. Rao has measured the formation constants between Nd^{3+} (an analog for trivalent actinides) and acetate using potentiometry. Dr. Rao's results are shown below in Figure 2, and summarized in Table 1 (next page). Dr. Rao's results are consistent with unpublished work by Profs. Wood and Clark. As expected, these data show that complexation increases with increasing temperature. The formation constants of the 1:1, 1:2, and 1:3 complexes increase, but interestingly the 1:3 complex appears to increase more dramatically than the other two. *Such a marked increase in the formation constant of the 1:3 complex was not anticipated.*

To corroborate the results of Dr. Rao, research in Prof. Clark's group to date had focused on spectroscopic studies of the trivalent – acetate system. Lanthanide luminescence spectroscopy is being used to study speciation of Eu^{3+} in acetate as temperature is increased from 10 - 70° C. *The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of the Eu^{3+} emission spectrum increases markedly with temperature.* This indicates an overall increase in complexation, as shown by Prof. Wood and Dr. Rao. In addition, we are using high resolution of the $^3\text{D}_0 \rightarrow ^7\text{F}_0$ transition to directly observe changes in the distribution of Eu^{3+} between the 1:1, 1:2, and 1:3 acetate species as a function of temperature. Spectral deconvolution of this transition at 25° C is shown in Figure 3. The effect of temperature on this transition is shown in Figure 4. Consistent with the results of Dr. Rao, *we see significant increases in the contributions of the 1:2 and 1:3 complexes, which were not expected.*

Our results demonstrate the importance of understanding the influence of temperature on the speciation of the actinides. *Our results show that a simple van't Hoff extrapolations of data representing ambient conditions has limitations especially for the treatment of the higher order complexes, and*

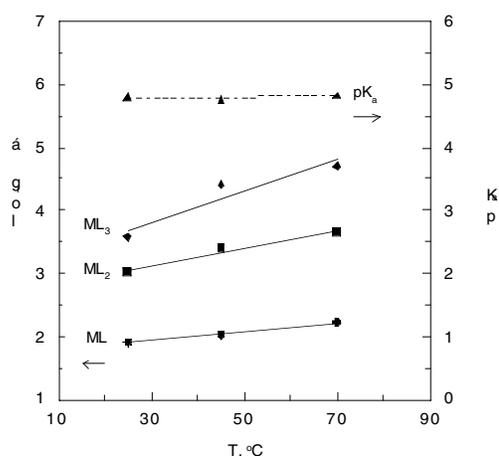


Figure 2: The constants of acetate protonation and complexation with Nd(III) at variable temperatures (Ionic strength = 2.0 M). The data at 25°C are from the literature (Smith and Martell, "Critical Stability Constants, Vol.6") for comparison.

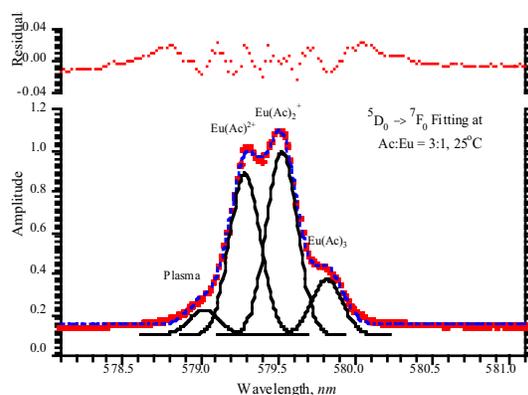


Figure 3: Spectral deconvolution of the ${}^5D_0 \rightarrow {}^7F_0$ transition of the Eu^{3+} emission spectrum. The 1:1, 1:2, and 1:3 species can be directly elucidated.

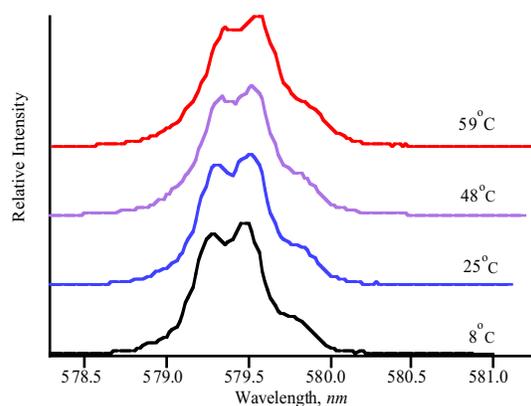


Figure 4: High resolution spectra of the ${}^5D_0 \rightarrow {}^7F_0$ transition of the Eu^{3+} emission spectrum as a function of temperature. Overall complexation increases markedly in this temperature range, and the prominence of the 1:2 and particularly the 1:3 peaks increase significantly.

Table 1 Thermodynamic parameters of acetate protonation and complexation with Nd(III) at different temperatures (Ionic strength = 2.0 M)

T, °C	$\log K^a$	$\log \beta_1^b$	$\log \beta_2^b$	$\log \beta_3^b$
25 ^c	4.80 ± 0.01	1.92 ± 0.04	3.02 ± 0.05	3.58 ± 0.08
45	4.76 ± 0.01	2.05 ± 0.03	3.40 ± 0.05	4.36 ± 0.12
70	4.82 ± 0.01	2.24 ± 0.01	3.65 ± 0.03	4.71 ± 0.10

^a $K = [\text{HL}]/([\text{H}^+][\text{L}^-])$, where L stands for acetate. The error limits from the data obtained in this work represent 3σ .

^b $\beta_i = [\text{ML}_i]/([\text{M}][\text{L}]^i)$, where $i = 1, 2$ and 3 , M and L stand for Nd and acetate. The error limits for the data obtained in this work represent 1σ .

^c data at 25°C are from the literature (Smith and Martell, "Critical Stability Constants, Vol.6") for comparison.

that more experimental measurements are needed to extend existing thermodynamic models to consider elevated temperature systems. To date, we have made significant progress on the trivalent *f*-element system. Future work will focus on extending this work to include other actinides and Pu.

Planned Activities

For the next fiscal year, we plan to extend our complexation studies of the trivalent actinides into more alkaline pH regions. This is now possible based on the hydrolysis results of Prof. Wood. Prof. Wood's group will continue to study temperature regions in excess of 100° C. Prof. Clark's group will continue to pursue spectroscopic studies using other ligands (oxalate, EDTA⁴⁻, nitrate, chloride, etc.). Dr. Rao is installing a calorimeter, which his group will use to directly measure enthalpies and entropies of reaction as a function of temperature.

We will also begin to study actinides in other oxidation states. Prof. Clark's research group is setting up potentiometric studies of the uranyl cation, and solvent extraction studies of the neptunyl cation. Prof. Wood's group is beginning to study the solubility of Th⁴⁺ in highly alkaline solutions; this work will aid in the planning of studies with Pu in various oxidation states.

Information Access

An extended summary was also submitted with this Progress Report.

"The aqueous geochemistry of the rare earth elements. IX. A potentiometric study of Nd³⁺ complexation with acetate in 0.1 molal NaCl solutions from 25-225° C, *Geochim. Cosmochim. Acta*, in press.

"A spectroscopic investigation of temperature effects on solution complexation in the Eu³⁺-acetate system," M. Yeh, T. Riedener, K. Bray, and S. B. Clark, *J. Alloys Compounds*, submitted.

"Temperature dependence of chloride complexation for the trivalent *f*-elements", M. Yeh, A. Maddison, S. B. Clark, *J. Radioanalyt. Nucl. Chem.*, submitted.