

Environmental Management Sciences Program

Annual Report

EMSP Project Number 65352

Project Title

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 actinides and lanthanides in the highly alkaline, concentrated electrolyte systems found in HLW. We are developing an experimentally-derived thermodynamic description of Pu and actinide complexation in these systems. Initially, we are using chemical analogs for Pu; later we will conduct experiments using Pu itself. The primary matrix of interest is the Na-NO₃-OH-H₂O system. We are investigating complexation by OH⁻, acetate, oxalate, and multidentate organic ligands. 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 are nearing completion of our second year of this three year project. Our research progress and spending is on schedule. During our first year, work was focused on the trivalent actinide systems. This year, we completed additional work on the trivalent lanthanides and actinides, but the main focus of the research has been on the hexavalent f-elements.

For the trivalent lanthanides and actinides, the stability constants determined to date are listed in Table 1 (below). In general, increasing temperature results in increases in measured stability constants, and these differences are much larger than expected based on available numerical models. The exception is complexation by OH⁻. Although numerical models also suggested that these stability constants should increase with temperature, experimental measurements generated in this work suggest otherwise [give ref. to Scott's paper].

Table 1: Stability constants for the formation of 1:1 complexes with the trivalent lanthanides and actinides with a variety of ligands.

Stability constants for the reaction:

$$\text{M}^{3+}_{(\text{aq})} + \text{L}^{-}_{(\text{aq})} \leftrightarrow \text{ML}^{2+}_{(\text{aq})}$$

M	L	Method	Medium	log β ₁				
				10 °C	25 °C	50 °C	59 °C	75 °C
Am ³⁺	Chloride	se ¹	1 M NaClO ₄		0.11	0.38		
Eu ³⁺		se ¹	1 M NaClO ₄		-0.05	0.21		0.45

M	L	Method	Medium	log β ₁				
				10 °C	25 °C	40 °C	59 °C	75 °C
Eu ³⁺	Nitrate	se ²	1 M NaClO ₄	0.38	0.41	0.43	0.62	1.26
		lumn ²	0.1 M NaClO ₄		0.79			
Eu ³⁺	Acetate	se ²	1 M NaClO ₄	2.03	2.14	2.24	2.31	2.44
		lumn ²	0.1 M NaClO ₄		2.17			
Eu ³⁺	Oxalate	se ²	1 M NaClO ₄		3.40	3.45		

Notation: lumn indicates luminescence study, se indicates solvent extraction. ¹ indicates pH 2.1; ² indicates pH 5.5

For the hexavalent actinides, research has been completed to date using the uranyl cation (UO_2^{2+}) as an analog for hexavalent PuO_2^{2+} . As with the work on the trivalent systems, we have used a combination of indirect and direct methods to obtain stability constants. Potentiometric titrations and calorimetry have been used to estimate stability constants and enthalpies and entropies of complexation for the 1:1, 1:2, and 1:3 uranyl:acetate complexes, as reported in Table 2. Stepwise, the thermodynamic parameters of the third complex significantly differ from the first two complexes in two respects: 1) the third step is exothermic while the first two steps are endothermic; 2) the entropy of the third step is much smaller than the first two steps. Such difference could be well explained with the structural information obtained by EXAFS. As shown in Figure 1A, the third acetate coordinates to uranyl in a monodentate fashion. This means that the third step of complexation does not cause as much dehydration and disorder as the first two steps. Figure 1B shows that, at higher pH, the hydroxyl group could compete with acetate for uranyl coordination. Again, these data indicate that, for the hexavalent actinide systems, the effect of temperature on coordination could be underestimated from ambient temperature thermodynamic data

Table 2: Thermodynamic data for the complexation of the uranyl cation with acetate as a function of temperature (The data at 25°C marked with * are from the literature).

	t °C	$\lg\beta_{j,m}$	$-\Delta G_{j,m}$ kJ·mol ⁻¹	$\Delta H_{j,m}$ kJ·mol ⁻¹	$\Delta S_{j,m}$ J·K ⁻¹ ·mol ⁻¹
[UO ₂ Ac] ⁺	25	2.60±0.07	14.84	8.9±0.8	79.6
		2.47±0.02 ^[*]		11.3±0.8	84.5
	70	3.15±0.05	20.70	12.7±0.8	97.3
[UO ₂ Ac ₂]	25	4.44±0.15	25.35	23±3	162
		4.48±0.04 ^[*]		19±2	149
	70	5.34±0.06	35.06	33±2	198
[UO ₂ Ac ₃] ⁻	25	6.94±0.05	39.62	16.6±0.7	188.5
		6.52±0.09 ^[*]		16±2	179
	70	7.82±0.05	51.38	24.0±0.5	219.6

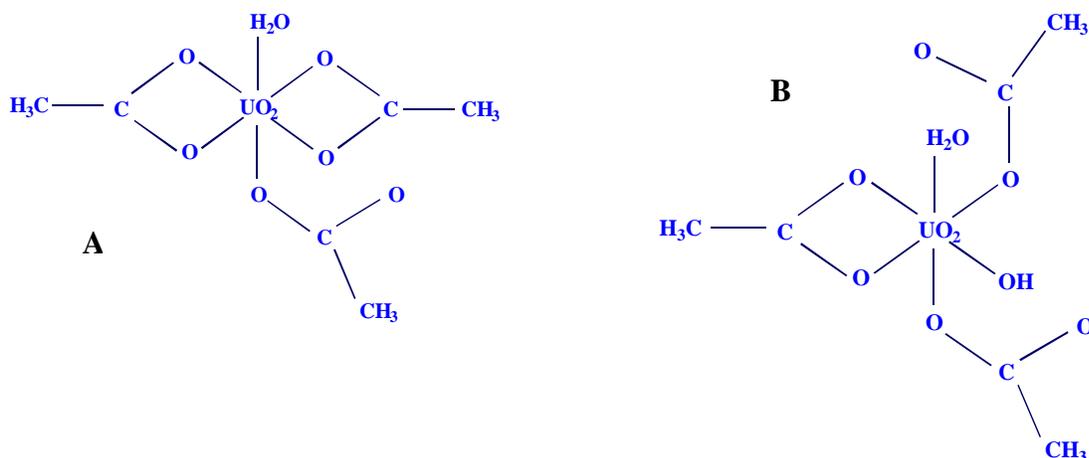


Figure 1: Resolved structures of the 1:3 uranyl:acetate complex determined by EXAFS at ambient temperature (A: pH ~ 3.9; B: pH ~ 4.5).

PLANNED ACTIVITIES

For the next fiscal year, we plan to extend our complexation studies into more alkaline pH regions. In addition, we will begin to explore the effects of complexation on the pentavalent actinides and also study systems using Pu. The use of Pu in our systems is now possible because of our experience with this kind of work, and our understanding of the effect of temperature on complexation with the various oxidation state analogs. We will also extend our studies to include multidentate organic ligands. Finally, we will continue to apply both indirect (i.e., potentiometric, calorimetric, etc.) methods and direct spectroscopic (EXAFS, NMR, fluorescence, absorption spectroscopy) methods to justify the species considered.

INFORMATION ACCESS

Publications

- P.Zanonato, P. Di Bernardo, A. Bismondo, L.Rao, G.R.Choppin; Thermodynamic studies of the complexation between neodymium and acetate at elevated temperatures (J. Solution Chemistry, accepted, 6/2000).
- J. Jiang, L.Rao, P.Zanonato, P. Di Bernardo; Thermodynamic studies of the complexation between UO_2^{2+} and acetate at elevated temperatures (manuscript in preparation).
- C. H. Gammons, and S. A. Wood, The aqueous geochemistry of the rare earth elements. VIII. Solubility of ytterbium oxalate and the stability of Yb(III)-oxalate complexes in water at 25° C to 80°C. Chemical Geology, vol 166, 2000, 103-124.
- S. A. Wood, D. J. Wesolowski, and D. A. Palmer, The aqueous geochemistry of the rare earth elements. IX. A potentiometric study of Nd^{3+} complexation with acetate in 0.1 molal NaCl solution from 25° to 225°C. Chemical Geology, vol 167, 2000, 231-253.
- “A spectroscopic investigation of temperature effects on solution complexation in the Eu^{3+} -acetate system,” M. Yeh, T. Riedener, K. Bray, and S. B. Clark, J. Alloys Compounds, vol 303-304, 2000, pp. 37-41.
- “Temperature dependence of chloride complexation for the trivalent *f*-elements”, M. Yeh, A. Maddison, S. B. Clark, J. Radioanalyt. Nucl. Chem, vol. 3, 2000, pp. 645-650.