

Understanding the Chemistry of the Actinides in HL Waste Tank Systems: The Impact of Temperature on Hydrolysis and Complexation with Organics

Project ID number 81962

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RESEARCH OBJECTIVES

The overall goal of this research plan is to provide a thermodynamic basis for describing actinide speciation over a range of tank-like conditions, including elevated temperature, elevated OH⁻ concentrations, and the presence of various organic ligands.

RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes work after 2 years of a 3-year project. An overall summary of the research progress under this project is provided in an annual report from WSU for EMSP Award # DE-FG07-98ER14922. The following gives more detailed descriptions of the progress at LBNL. In this period, we have focused on the complexation of actinides with organic ligands and the hydrolysis of actinides at variable temperatures.

Complexation of U(VI) with oxydiacetate at variable temperatures. This study is partially supported by the EMSP project and by the BES Heavy Element Chemistry Program under the project of "Chemical thermodynamics of actinide coordination under non-conventional conditions" at LBNL.

The complexation of uranium(VI) and samarium(III) with oxydiacetate in 1.05 mol kg⁻¹ NaClO₄ is studied at variable temperatures (25 - 70 °C). Three U(VI)/ODA complexes (UO₂L, UO₂L₂²⁻ and UO₂HL₂⁻) and three Sm(III)/ODA complexes (SmL_j^{(3-2j)+} with j = 1, 2, 3) are identified in this temperature range. The formation constants and the molar enthalpies of complexation are determined by potentiometry and calorimetry. The complexation of uranium(VI) and samarium(III) with oxydiacetate becomes more endothermic at higher temperatures. However, the complexes become stronger due to increasingly more positive entropy of complexation at higher

temperatures that exceeds the increase in the enthalpy of complexation. The values of the heat capacity of complexation (ΔC_p° in $\text{J K}^{-1} \text{mol}^{-1}$) are 95 ± 6 , 297 ± 14 and 162 ± 19 for UO_2L , $\text{UO}_2\text{L}_2^{2-}$ and UO_2HL_2^- , and 142 ± 6 , 198 ± 14 and 157 ± 19 for SmL^+ , SmL_2^- , and SmL_3^{3-} , respectively. The thermodynamic parameters, in conjunction with the structural information from spectroscopy, help to identify the coordination modes in the uranium oxydiacetate complexes. The effect of temperature on the thermodynamics of the complexation is discussed in terms of the electrostatic model and the change in the solvent structure.

Temperature effect on the hydrolysis of U(VI) and Np(V). The studies on actinide hydrolysis are partially supported by the EMSP project and by the BES Heavy Element Chemistry Program under the project of "Chemical thermodynamics of actinide coordination under non-conventional conditions" at LBNL in collaboration with the research group in University of Padova, Italy.

The hydrolysis of uranium(VI) in tetraethylammonium perchlorate (0.10 mol dm^{-3} at 25°C) was studied at variable temperatures ($10 - 85^\circ\text{C}$). The hydrolysis constants ($^*\beta_{n,m}$) and enthalpy of hydrolysis ($\Delta H_{n,m}$) for the reaction $m\text{UO}_2^{2+} + n\text{H}_2\text{O} = (\text{UO}_2)_m(\text{OH})_n^{(2m-n)+} + n\text{H}^+$ were determined by titration potentiometry and calorimetry. The hydrolysis constants, $^*\beta_{1,1}$, $^*\beta_{2,2}$ and $^*\beta_{5,3}$, increased by 2 - 5 orders of magnitude as the temperature was increased from 10 to 85°C . The enthalpies of hydrolysis, $\Delta H_{2,2}$ and $\Delta H_{5,3}$, also varied: $\Delta H_{2,2}$ became more endothermic while $\Delta H_{5,3}$ became less endothermic as the temperature was increased. The heat capacity of hydrolysis, $\Delta C_{p(2,2)}$ and $\Delta C_{p(5,3)}$, was calculated to be $(152 \pm 43) \text{ J K}^{-1} \text{mol}^{-1}$ and $-(229 \pm 34) \text{ J K}^{-1} \text{mol}^{-1}$, respectively. UV/Vis absorption spectra supported the trend that hydrolysis of U(VI) was enhanced at elevated temperatures. Time-resolved laser-induced fluorescence spectroscopy provided additional information on the hydrolyzed species at different temperatures. Approximation approaches to predict the effect of temperature were tested with the data from this study.

The hydrolysis of neptunium(V) was studied at variable temperatures ($10 - 85^\circ\text{C}$) in tetramethylammonium chloride (1.12 mol kg^{-1}). Two hydrolyzed species of neptunium(V), $\text{NpO}_2\text{OH}(\text{aq})$ and $\text{NpO}_2(\text{OH})_2^-$, were identified by potentiometry and Near-IR absorption spectroscopy. The hydrolysis constants ($^*\beta_n$) and enthalpy of hydrolysis (ΔH_n) for the reaction $\text{NpO}_2^+ + n\text{H}_2\text{O} = \text{NpO}_2(\text{OH})_n^{(1-n)+} + n\text{H}^+$ ($n = 1$ and 2) were determined by titration potentiometry and microcalorimetry. The hydrolysis constants, $^*\beta_1$ and $^*\beta_2$, increased by 0.8 and 3.4 orders of magnitude, respectively, as the temperature was increased from 10 to 85°C . The enhancement of hydrolysis at elevated temperatures is mainly due to the significant increase of the degree of ionization of water as the temperature is increased. The hydrolysis reactions are endothermic but become less endothermic as the temperature is increased. The heat capacities of hydrolysis, ΔC_{p1} and ΔC_{p2} , are calculated to be $-(71 \pm 17) \text{ J K}^{-1} \text{mol}^{-1}$ and $-(127 \pm 17) \text{ J K}^{-1} \text{mol}^{-1}$, respectively. Approximation approaches to predict the effect of temperature, including the constant enthalpy approach, the constant heat capacity approach and the DQUANT equation, have been tested with the data.

Temperature effect on the solubility of CeO_2 in NaNO_3 . Additional studies this past year centered around studies of the solubility of CeO_2 in NaNO_3 media as a function of pH in the absence of organic ligands and in the presence of EDTA. Detailed information on these data is provided in an annual report from WSU for EMSP Award # DE-FG07-98ER14922.

Additional thermodynamic data generated using EMSP support. Data include stability constants for the complexation of Am(III) and Eu(III) with chloride and nitrate at $10 - 75^\circ\text{C}$, and comparison of predicted and measured hydrolysis constants for Nd(III). Detailed information on these data is provided in an annual report from WSU for EMSP Award # DE-FG07-98ER14922.

PLANNED ACTIVITIES

A renewal proposal (WSU, LBNL, PNNL) has been submitted with a plan of research to address the question of actinide speciation in systems of oxalic acid. We plan to determine the coordination chemistry and thermodynamic data needed to describe actinide speciation in the $\text{Na}^+\text{-H}^+\text{-Al(III)-Fe(III)-Fe(II)-Mn(II)-NO}_3\text{-H}_2\text{C}_2\text{O}_4\text{-HC}_2\text{O}_4^-\text{-C}_2\text{O}_4^{2-}\text{-H}_2\text{O}$ system that are valid over a range of oxalic acid concentrations, acidities, ionic strengths, and temperature. This will be accomplished by using an integrated experimental and computational approach. The data will be incorporated into a chemical process model that can be used by site engineers at Hanford and Savannah River to develop appropriate processing conditions for residual treatment by oxalic acid, and that will facilitate prediction of the partitioning of the actinides when oxalic acid is applied to the tank residuals.

INFORMATION ACCESS

Journal Articles (WSU, LBNL, UI):

1. L. Rao, T. G. Srinivasan, A. Yu. Garnov, P. Zanonato, P. Di Bernardo, A. Bismondo; Hydrolysis of neptunium(V) at variable temperatures (10 - 85 °C), *Geochim. Cosmochim. Acta* (in press).
2. A. Paulenova, Z. Zhang, and S. B. Clark (submitted), "Temperature Effects on the complexation of neptunyl with simple organic ligands." *Radiochimica Acta*.
3. A. Paulenova, Z. Zhang, S. Pepper, and S. B. Clark (submitted), "The complexation of actinide cations with gluconate", *Radiochimica Acta*.
4. P. Zanonato, P. Di Bernardo, A. Bismondo, G. Liu, X. Chen, L. Rao; Hydrolysis of uranium(VI) at variable temperatures (10 - 85 °C), *J. Am. Chem. Soc.* 126, 5515-5522 (2004).
5. L. Rao, A. Yu. Garnov, J. Jiang, P. Di Bernardo, P. Zanonato, A. Bismondo; Complexation of uranium(VI) and samarium(III) with oxydiacetic acid: temperature effect and coordination modes, *Inorg. Chem.* 42, 3685-3692, 2003.
6. J. Jiang, L. Rao, P. Di Bernardo, P. Zanonato, A. Bismondo, Complexation of uranium(VI) with acetate at variable temperatures, *J. Chem. Soc., Dalton Trans.*, 2002, 1832-1836.
7. L. Rao, J. Jiang, P. Zanonato, P. Di Bernardo, A. Bismondo, A. Yu. Garnov; Complexation of uranium(VI) with malonate at variable temperatures, *Radiochimica Acta*, 90, 581-588, 2002.
8. C. H. Gammons, S. A. Wood, and Y. Li (2002). Complexation of the rare earth elements with aqueous chloride at 200°C and 300°C and saturated water vapor pressure. In Hellmann, R. and Wood, S.A., ed., *Water-rock Interaction, Ore Deposits, and Environmental Geochemistry: A tribute to David A. Crerar*. Geochemical Society Special Publication No. 7.
9. Nicholson, K.N. and Wood, S.A. (2002) Aqueous geochemistry of rare earth elements and yttrium. XII: Potentiometric stability constant determination of Bis-Tris complexes with La, Nd, Eu, Gd, Yb, Dy, Er, Lu, and Y. *Jour. Sol. Chem.* 31, 703-717.
10. Nicholson, K.N., Twamley, B. and Wood, S.A. (2001) [Bis(2-hydroxyethyl)amino]-tris(hydroxymethyl)methane (Bis-Tris), an important complexing agent. *Acta Cryst.* E57, o1133-o1135.
11. 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. Sol. Chem.* 30 (1), 1-18, 2001.

12. A. P. Maddison, M. Yeh, and S. B. Clark (2000), "The Effects of Ionic Strength and Temperature on the Complexation of the Trivalent *f*-elements with Chloride", *Journal of Radioanalytical and Nuclear Chemistry*, 243(3), 645-650.
13. M. F. Yeh, T. Riedener, K. L. Bray, and S. B. Clark (2000), "A Spectroscopic Investigation of Temperature Effects on Solution Complexation on the Eu³⁺-Acetate System", *Journal of Alloys and Compounds*, 303, 37-41.
14. Wood, S.A., Wesolowski, D.J. and Palmer, D.A. (2000) The aqueous geochemistry of the rare earth elements. IX. A potentiometric study of Nd³⁺ complexation with acetate in 0.1 molal NaCl solution from 25°C to 225°C. *Chemical Geology* 167, 231-253.
15. *Radionuclide Speciation in Real Systems* (1999), D. T. Reed, L. F. Rao, and S. B. Clark, eds., Plenum Publishing Corporation.
16. M. Yeh, A. P. Maddison, and S. B. Clark (1998) "The Effect of Elevated Temperature on the Complexation of Am³⁺ with Chloride," *Biological Trace Element Research*.
17. R Ding and Scott A. Wood: The aqueous geochemistry of the rare earth elements and yttrium. Part X. Potentiometric determination of stability constants of acetate complexes of La³⁺, Nd³⁺, Gd³⁺ and Yb³⁺ at 25-70 °C and 1 bar. In Hellmann, R. and Wood, S.A., ed., *Water-rock Interaction, Ore Deposits, and Environmental Geochemistry: A tribute to David A. Crerar*. Geochemical Society Special Publication 7.
18. S. A. Wood, D. A. Palmer, D. J. Wesolowski, and P. Bénézech: The aqueous geochemistry of the rare earth elements and yttrium. Part XI. The solubility of Nd(OH)₃ and hydrolysis of Nd³⁺ from 30 to 290°C at saturated water vapor pressure with *in-situ* pH_m measurement. In Hellmann, R. and Wood, S.A., ed., *Water-rock Interaction, Ore Deposits, and Environmental Geochemistry: A tribute to David A. Crerar*. Geochemical Society Special Publication No. 7.

ADDITIONAL INFORMATION

Post-doctoral associates and students trained under this project (WSU, LBNL, UI)

Sarah Pepper, Post-doctoral Associate, Washington State University (WSU)

A. Paulenova, Post-doctoral Associate, WSU

C. Phelps, Post-doctoral Associate, WSU

M. Yeh, Post-doctoral Associate, WSU

A. Maddison, Graduate Student, WSU

Z. Zhang, Graduate Student, WSU/LBNL

E. Finn, Undergraduate and Graduate Student, WSU

T. Oshiro, Undergraduate Student, WSU

B. Bottenus, Undergraduate Student, WSU

J. Jiang, Post-doctoral Associate, Lawrence Berkeley National Lab (LBNL)

A. Yu. Garnov, Post-doctoral Associate, LBNL

T. G. Srinivasan, Post-doctoral Associate, LBNL

L. Yates III, Post-doctoral Associate, University of Idaho (UI)

K. Nicholson, Post-doctoral Associate, UI

H. Cao, Post-doctoral Associate, UI

Z. S. Cetiner, Post-doctoral Associate, UI

A. Taunton, Graduate Student, UI

D. Koenig, Undergraduate Student, UI