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## Fundamental Chemistry of U and Pu in the TBP-Dodecane-Nitric Acid System

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## Task 26

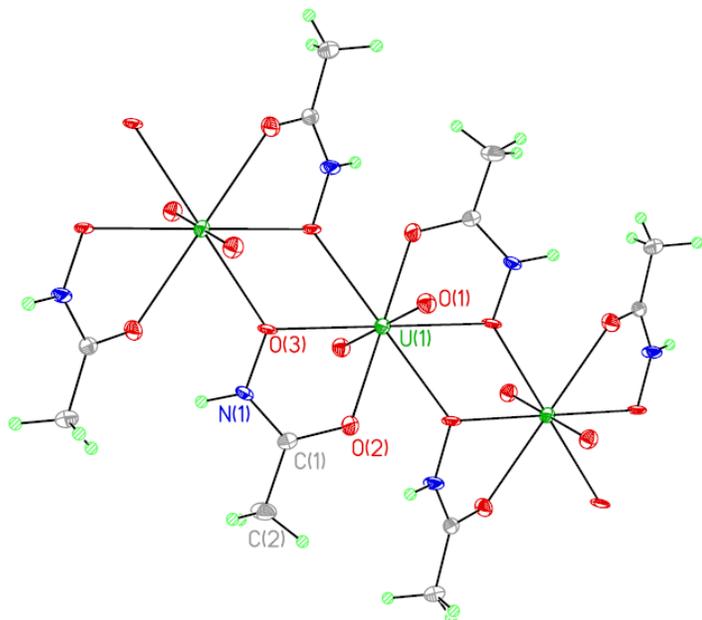
# Fundamental Chemistry of U and Pu in the TBP-Dodecane-Nitric Acid System

K. Czerwinski

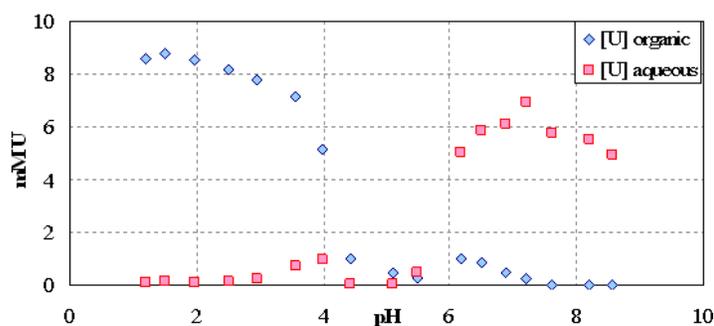
## BACKGROUND

The extraction of tetravalent Pu and hexavalent uranyl in nitric acid solution by tributylphosphate (TBP), based on the formation of organic phase neutral complexes such as  $\text{Pu}(\text{NO}_3)_4 \cdot 2\text{TBP}$  and  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ , has been the foundation of actinide purification for a number of decades. Upon reduction of Pu(IV), Pu(III) is back extracted into an aqueous phase. However, the data needed for detailed modeling of Pu extraction is not available for all conditions of concern to the Advanced Fuel Cycle Research and Development program. This proposal was developed with Dr. George Vandegrift of Argonne National Laboratory to obtain the necessary data for Pu extraction modeling.

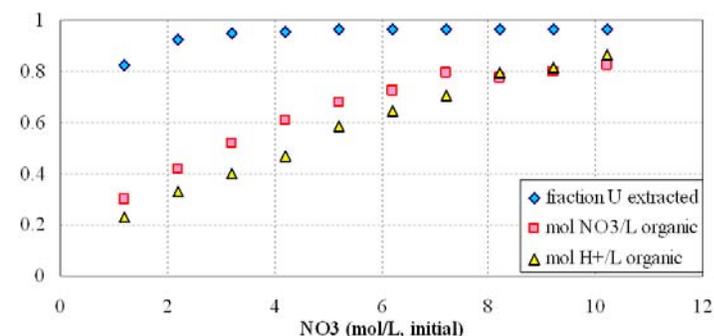
Understanding the role of nitrate in actinide speciation is important for determining the necessary data for extraction modeling. Difficulties in modeling Pu extraction under some nitrate conditions may be due to ill-defined constants of formation for the dinitrate and trinitrate species of U and Pu. The influence of pertechnetate on the speciation of U and Pu in the TBP-dodecane-nitric



Crystal Structure of Uranyl-AHA.



The measured concentrations in the organic and aqueous phases of 10 mM uranyl, 100 mM AHA extracted with TBP.



The measured concentrations of uranyl, nitrate, and acid in the organic phase extracted from 0.02 M U, 1.0 M  $\text{HNO}_3$ , and varied initial nitrate.

acid system is still poorly understood. Since pertechnetate is capable of reoxidizing reduced Pu species, it may have a profound impact on the extraction of Pu.

In the uranium extraction process, acetohydroxamic acid (AHA) is expected to be used. AHA can complex and reduce Pu, decreasing its extraction into the organic phase; the effect of uranyl-AHA on U extraction has not been quantified. AHA can reduce pertechnetate as well, initiating a redox cycle with both U and Pu. In a solvent extraction system using AHA, it is necessary to determine the complexation kinetics, redox reactions, and thermodynamics of AHA interactions with these elements.

## RESEARCH OBJECTIVES AND METHODS

The research objective is to experimentally evaluate the fundamental speciation of Pu and U in the TBP-dodecane-nitric acid-AHA system and the effect of pertechnetate, specifically:

- To determine the influence of nitrate on the speciation of U and Pu in the TBP-dodecane-nitric acid system. The aqueous and organic speciation of U and Pu are examined as a function of the nitric acid concentration, nitrate concentration, actinide ion concentration, temperature, and time.
- To determine the speciation of U and Pu with AHA in the presence and absence of TBP-dodecane organic phase. The aqueous and organic speciation of U and Pu are evaluated as a function of AHA concentration, metal ion concentration, metal ion redox state, pH, and temperature.
- To determine the interaction of AHA with pertechnetate, and the effect on the interaction of AHA and pertechnetate with U and Pu.
- To incorporate thermodynamic and kinetic data into existing modeling codes.

All of the initial experiments were performed with uranyl,  $\text{UO}_2^{2+}$ . The results obtained from U are the basis for further experiments with Pu. In extraction experiments, the aqueous and organic phases are contacted in equal volumes from 0.3 to 5.0 mL.

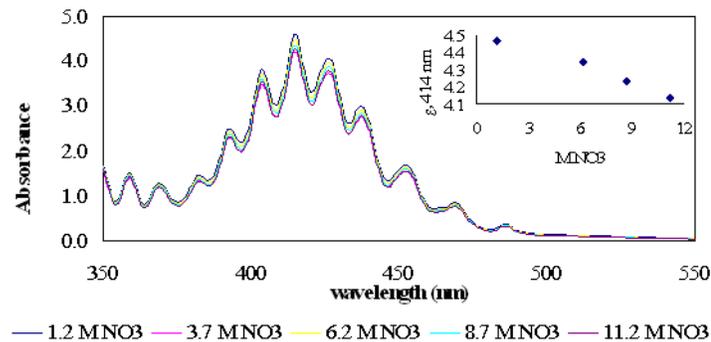
## RESEARCH ACCOMPLISHMENTS

**Uranyl Nitrate.** The complexation of uranyl (0.01 to 0.1 M) with nitrate was studied at 1 M HNO<sub>3</sub> with excess nitrate (from LiNO<sub>3</sub>) varied from 0 to 10 M. It was found that at higher nitrate concentrations, more uranyl was present in the organic phase, and, in the absence of uranyl, more HNO<sub>3</sub> extracted.

**Uranyl-AHA.** The complexation of uranyl with AHA and its effect on U extraction into TBP-dodecane was studied via ultraviolet-visible spectroscopy (UV-Vis), nuclear magnetic resonance (NMR), and Inductively Coupled Plasma-Atomic Emission Spectroscopy in perchlorate and nitrate media. The concentrations of uranyl (0.1 to 10 mM) and AHA (1 to 700 mM) and the pH (1 to 10) were systematically varied. It was determined via NMR that there are at least two species of uranyl-AHA, that the species formed is pH-dependent, and that there is little hydrolysis at 25 times or higher molar excess AHA. The low-pH species extracts from perchlorate media as well as free uranyl, and the high-pH species remains in aqueous solution. In nitrate media, the nitrate competes with and oxidizes the AHA under acidic conditions; the exact interactions remain to be explored.

In addition, methods for synthesis of the uranyl-AHA solid were developed; the solid was characterized by UV-Vis, Fourier Transform Infrared spectroscopy, NMR, laser fluorescence, melting point, and X-ray Absorption Fine-structure Spectroscopy (XAFS), and a crystal structure was obtained. The uranyl-AHA is present as a highly symmetrical polymer, in which each equatorial atom is exactly 180° from its opposite and the ligand planes are twisted within and between unit cells.

**Technetium-AHA.** Previous work failed to observe pertechnetate reduction by AHA; however, in the presence of catalytic acid (0.5 to 4 M HNO<sub>3</sub> or HClO<sub>4</sub>) and a large excess of AHA (0.5 to 4 M),



The UV-Vis spectrum of uranyl nitrate in 30% TBP varies with nitrate concentration.

pertechnetate (0.1 - 20 mM) will be reduced to the Tc<sup>II</sup>NO(AHA)<sub>2</sub> species in aqueous media. This species is highly water soluble and does not extract into 30% TBP. The presence of uranyl has no effect on the formation or extraction of this species, and up to hundredfold excess UO<sub>2</sub><sup>2+</sup> does not affect the rate of formation. There is significant evidence that the reaction is instantaneous and the change in the Tc-AHA UV-Vis spectrum is due to the increasing pH as AHA hydrolyzes to acetic acid. However, the mechanism of formation is yet to be elucidated.

## TASK 26 PROFILE

Start Date: August 2004

Completion Date: December 2007

(This work continued under Task 40, see pages 84-85.)

### Journal Articles:

C.S. Gong, W.W. Lukens, F. Poineau, and K.R. Czerwinski, "Reduction of pertechnetate by acetohydroxamic acid: Formation of [TcNO(AHA)<sub>2</sub>(H<sub>2</sub>O)]<sup>+</sup> and implications for the UREX process," *Inorg. Chem.*, 47(15), 6674-6680, 2008.

C. Gong, F. Poineau, and K. Czerwinski, "Synthesis and characterization of the solid uranium(VI) dioxo-diacetohydroxamate complex," *Radiochim. Acta*, 95(8), 439-450, 2007.

### Conference Proceedings:

A.D. Wright and K. Czerwinski, "Nitrate effects on uranium and plutonium extractions," 234<sup>th</sup> ACS National Meeting, Boston, MA, August 2007.

C.S. Gong, F. Poineau, and K. Czerwinski, "Reduction of Technetium by Acetohydroxamic Acid in Nitric and Perchloric Acids and its Effects on Extraction into Tributylphosphate-dodecane," Actinide Separations Conference, Las Vegas, NV, June 2007.

A. Wright and K. Czerwinski, "Nitrate effects on uranium and plutonium extractions," 233rd ACS National Meeting, Chicago, IL, March 2007.

C. Gong, F. Poineau, and K. Czerwinski, "Synthesis and characterization of the solid uranyl-acetohydroxamic acid complex," 233rd ACS National Meeting, Chicago, IL, March 2007.

K. Czerwinski, A. Wright, N. Smith, L. Wright, and G. Cerefice, "Fundamental Chemistry of Uranium in Extraction for use in Enhanced Separations and Proliferation Resistance," MRS Scientific Basis for Nuclear Waste Management XXX, Boston, MA, November-December 2006.

A. Wright, N. Smith, F. Poineau, and K. Czerwinski, "Nitrate effects on uranium and plutonium extractions in the tributylphosphate-dodecane system," 232nd ACS National Meeting, San Francisco, CA, September 2006.

A.D. Wright and K. Czerwinski, "Nitrate effects on uranium and plutonium extractions in the tributylphosphate-dodecane system," 231<sup>st</sup> ACS National Meeting, Atlanta, GA, March 26-30, 2006.

### Research Staff

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