

Task 26

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

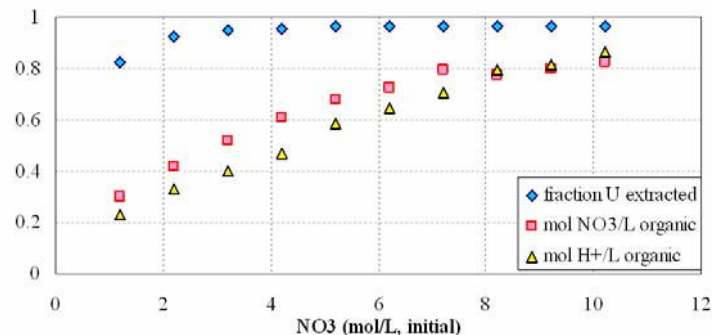
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BACKGROUND

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 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-



The measured concentrations of uranyl, nitrate, and acid in the organic phase extracted from 0.02 M U, 1.0 M HNO₃, and varied initial nitrate.

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

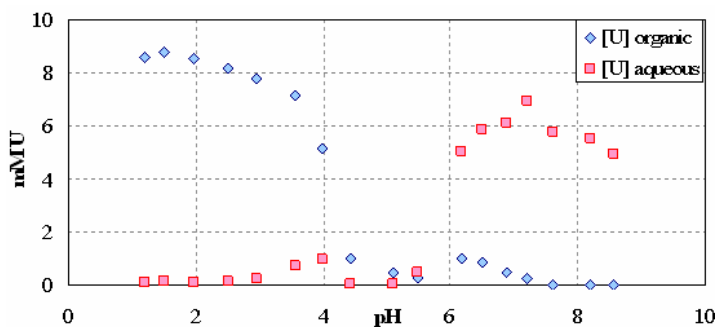
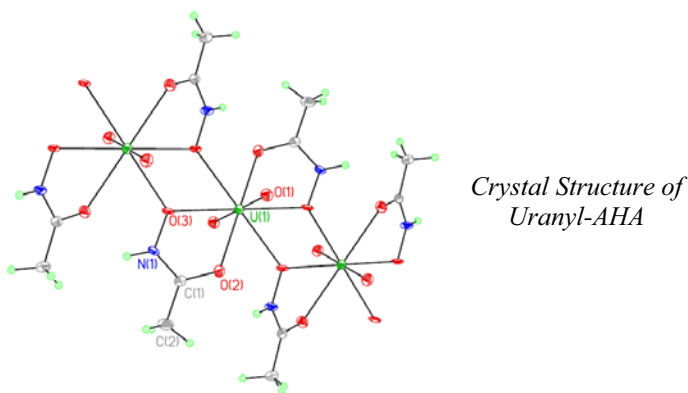
The research objective is to experimentally evaluate the fundamental speciation of Pu and U in the TBP-dodecane-nitric acid-AHA system and the effect of pertechnetate, specifically:

- 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, 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 HNO₃ with excess nitrate (from Li-NO₃) varied from 0 to 10 M. It was found that at higher nitrate



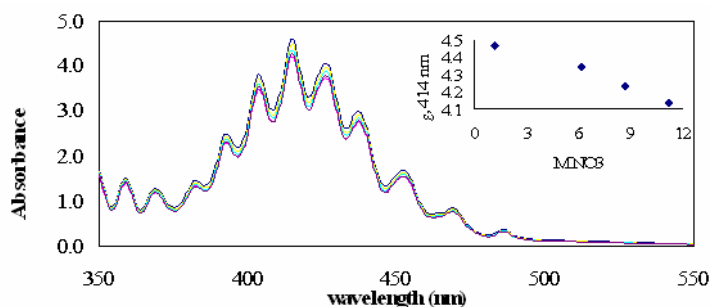
The measured concentrations in the organic and aqueous phases of 10 mM uranyl, 100 mM AHA extracted with TBP.

concentrations, more uranyl was present in the organic phase, and, in the absence of uranyl, more HNO₃ 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 HNO₃ or HClO₄) and a large excess of AHA (0.5 to 4 M), pertechnetate (0.1 to 20 mM) will be reduced to the Tc^{II}NO(AHA)₂ 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 UO₂²⁺ does not affect the rate of formation. There is significant evidence that the reaction is in-



— 1.2 MNO₃ — 3.7 MNO₃ — 6.2 MNO₃ — 8.7 MNO₃ — 11.2 MNO₃
 The UV-Vis spectrum of uranyl nitrate in 30% TBP varies with nitrate concentration.

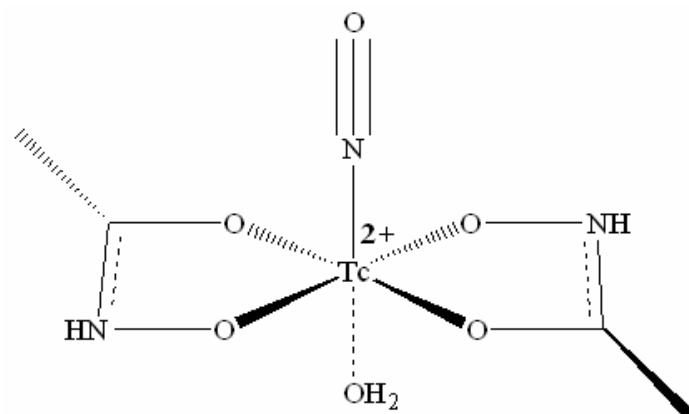
ACADEMIC YEAR HIGHLIGHTS

- ◆ 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).
- ◆ 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. Cereface, "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

stantaneous 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.

FUTURE WORK

The stability constants of the higher nitrate species of uranyl have yet to be determined; preliminary UV-Vis and laser fluorescence studies have been performed. The stability constant of the uranyl-AHA species is also unknown; UV-Vis and NMR studies are underway. The mechanism of Tc-AHA formation and its effect on Pu redox and extraction will be explored.



XAFS Structure of Technetium(II)-nitrosyl-AHA.

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