

Task 40

Evaluation of Fundamental Radionuclide Extraction Data for UREX

K. Czerwinski

BACKGROUND

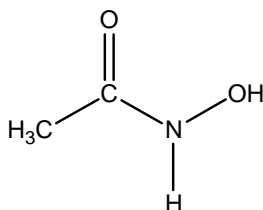
The speciation of technetium and actinides in advanced solvent extraction systems is the basis for their manipulation in separations. The ability to understand and predict radionuclide speciation is paramount to successful modeling of proposed separation systems. This project will examine the speciation of radionuclides in different stages of the uranium extraction (UREX) separation scheme, providing data useful to modeling. The areas to be examined include the speciation of uranium and plutonium with tributylphosphate and the kinetics and thermodynamics of lanthanides and actinides in the TALSPEAK (Trivalent actinide lanthanide separation by phosphorous reagent extraction from aqueous complexes) system. The complexation constants of uranium and plutonium with tributylphosphate (TBP) will be evaluated. In the TALSPEAK system, studies will elucidate the difference in complexation kinetics for the lanthanides and actinides. Computational studies based on density functional theory will be performed for both systems.

RESEARCH OBJECTIVES AND METHODS

Tributylphosphate-Based Extractions

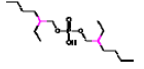
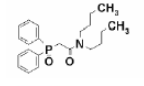
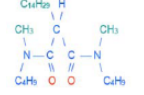
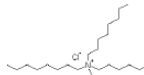
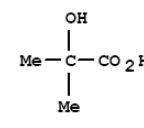
The extraction of tetravalent Pu in nitric acid solution by TBP is well known and has been the basis of Pu purification for a number of decades. However, the data needed for detailed modeling of Pu extraction is not available for all conditions of concern to the Advanced Fuel Cycle Initiative.

Understanding the role of nitrate in plutonium speciation is important for determining the necessary data for plutonium extraction modeling. Data indicates the dinitrate complex of plutonium is strong and may account for difficulties in modeling plutonium extraction under some nitrate conditions. The formation of hydrolysis products may also form an extractable species that will need to be included in modeling. In the UREX process, acetohydroxamic acid (AHA, see figure below) is expected to be used. For the separation of Pu in a solvent extraction system using acetohydroxamic acid, it is necessary to determine the complexation kinetics and thermodynamics. In addition, since plutonium is a redox sensitive element, the change in speciation due to oxidation-reduction reactions upon complexation needs to be evaluated. This project will experimentally evaluate the fundamental speciation of plutonium and uranium in the TBP-dodecane-nitric acid system, with the main emphasis on nitrate speciation and subse-



Acetohydroxamic acid.

Examples of ligands for actinide and lanthanide separations.

	Bis(2-ethylhexyl)phosphoric acid (HDEHP) for TALSPEAK
	Diphenyl-N,N-dibutylcarbamoyl phosphine oxide (CMPO) for TRUEX
	N,N'-dimethyl-N,N'-dibutyl-2-tetradecyl-malonamide (DMDBTDMA) for DIAMEX
	Quaternary ammonium salts (Aliquat 336)
	α -hydroxyisobutyrate

quent third phase formation at high nitric and metal ion conditions. Experiments on the AHA systems will be conducted in collaboration with Argonne National Laboratory (ANL) with input from the U.S. Department of Energy Separations Working Group. For this project the focus will be on the evaluation on U and Pu complexation constants with TPB.

Lanthanide-Actinide Separations

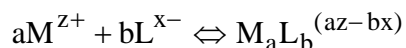
The separation of trivalent lanthanides from trivalent actinides, and americium from curium, has been identified as a topic for investigations by the Global Nuclear Energy Partnership (GNEP). These separations are based on slight differences in ionic radii, small variations in Lewis acidity between the lanthanides and actinides, and redox state speciation.

Numerous ligands have been examined for actinide and lanthanide separations, some of which are the basis of separation schemes. In this work efforts will focus on the TALSPEAK process through the determination of thermodynamic and kinetic data necessary for separation modeling. The TALSPEAK conditions include an aqueous phase with 1 M lactic acid and 0.1 M diethylenetriamine-pentaacetic acid (DTPA). In the original work, the lanthanides are extracted from the aqueous phase at pH 3 with an organic phase of 0.3 M Bis(2-ethylhexyl)phosphoric acid (HDEHP). The actinides americium and curium are then extracted into 0.3 M HDEHP at pH 1.5. The actinides can be removed from the organic phase with dilute mineral acid. Recent GNEP related results have focused on evaluating kinetic and thermodynamic parameters for the extraction of actinides and lanthanides in the TALSPEAK process. While complexation data is available for the interaction of americium and curium with some ligands used in the TALSPEAK process, further efforts are necessary to complete the appropriate dataset for modeling separations in AMUSE (Argonne Model for Uni-

versal Solvent Extraction). Acquiring the necessary kinetic and thermodynamic data for AMUSE modeling of lanthanide and actinide extractions will be an important element of this project.

Evaluation of Chemical Thermodynamic and Kinetic Data

The goal of our plutonium and uranium speciation studies will be to obtain data for modeling the behavior of the actinides under a range of extraction conditions, including acid concentration, metal ion concentration, and temperature. Speciation calculations can be performed if the stability and solubility constants for the chemical species formed under the examined conditions are known. If conditions under which precipitation of the actinide occurs, solubility studies of the precipitated species will be included. A general chemical reaction is described as:



for complexation where M is the metal ion and L is a ligand. In the case of the extraction system under investigation, two ligands may be considered, namely nitrate and TBP. The kinetics of the reaction can be measured to establish conditions needed for equilibrium. For the extraction system under study the kinetics are expected to be rapid. However, kinetic evaluation of third phase formation may be needed.

Enthalpy and entropy will be investigated by evaluating the stability constant as a function of temperature. For a system with different species, if the stability constants are known, then all the species can be calculated at any given pH. The thermodynamic data can also easily be incorporated into existing codes such as AMUSE or the geochemical code CHESS.

Computational studies

Density functional theory (DFT) calculations will be performed to



TBP-HNO₃-Np⁴⁺ third phase appearance..

ACADEMIC YEAR HIGHLIGHTS

- ◆ C.S. Gong, F. Poineau, W.W. Lukens, and K.R. Czerwinski, "Something New From Something Old: Acetohydroxamic Acid for Complete and Efficient Separation of Technetium from Uranium Using Liquid-Liquid Extraction," *Atalante 2008, Nuclear Fuel Cycles for a Sustainable Future*, Montpellier, France, May 2008.

evaluate the electronic structure of the radionuclide species in the extraction system. Initial DFT calculations on the actinides have been performed using an all electron relativistic calculation rather than a relativistic effective core potential. The DFT calculations will provide a means to compare experimental spectroscopy data that investigates structure and electron transitions, providing a basis for examining and comparing the role of 5f electron mechanisms involved in the crucial species in separation systems.

RESEARCH ACCOMPLISHMENTS

- Extractions were performed at constant ionic strength. Aqueous solutions contained HNO₃, UO₂(NO₃)₂, LiNO₃, and the ionic strength was adjusted using NaClO₄. The organic phase consisted of pre-equilibrated 30% TBP/dodecane. It was mixed for 2 minutes, centrifuged, and separated for analysis. Diluted samples were analyzed by IC and ICP-AES.
- Four sets of extractions were performed for determining Eu-DTPA complexation constant for TALSPEAK separations studies. In the aqueous phase, DTPA varied from 1x10⁻⁷ to 5x10⁻⁷ M, ionic strength was 0.1M, pH of 3.60, and trace amount of ¹⁵²Eu. In the organic phase, 2x10⁻⁴ M HDEHP in dodecane pre-equilibrated three times. Analysis was performed on organic and aqueous phases by Liquid Scintillation Counting. The pH was measured in the aqueous phase after equilibration. The electrode was calibrated and adjustments were made in order to determine H⁺ concentration.
- A slug flow problem was identified that affected UV-Vis spectra. The physical positions of the instrumentation was changed to alleviate issue.
- Steady-state conditions were successfully demonstrated in the contactors with a non-radioactive feed solution (after repairing leaks and checking flow rates via mass balances and flowmeters). The radioactive feed solution used after this steady state was achieved, and the data acquired shows hot feed growing in as cold feed is pushed out.
- DFT calculations were performed of the possible equilibrium structures of the UO₂²⁺/NO₃⁻/H₂O system for various concentrations of NO₃⁻ with determination of the corresponding molecular orbital energy levels and population analysis.

Research Staff

Ken Czerwinski, Principal Investigator, Associate Professor, Department of Chemistry
Philippe Weck, Computational Chemist, Department of Chemistry
Cynthia Gong and Frederic Poineau, Post-Doctoral Researchers, Harry Reid Center for Environmental Studies

Students

Amber Wright and Jamie Warburton, Graduate Students, Department of Chemistry (Radiochemistry Ph.D. Program)
Solenne Michaud, Graduate Student, French Internship, École Nationale Supérieure de Chimie de Paris

Collaborator

George Vandegrift, Argonne National Laboratory