

Evaluation of fundamental radionuclide extraction data for UREX

Professor Ken Czerwinski
Department of Chemistry and Harry Reid Center
Department of Chemistry
University of Nevada, Las Vegas
E-mail: czerwin2@unlv.nevada.edu

Student: Amber Wright, Jamie Warburton
Post doctoral researchers: Cynthia Gong
Computational Research Professor: Phil Weck
DOE Collaborator: Dr. George Vandegrift, ANL
Technical Focus Area: Separations

Abstract

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 UREX separation scheme, providing data useful to modeling. The areas to be examined include the speciation of U and Pu with tributylphosphate and the kinetics and thermodynamics of lanthanides and actinides in the TALSPEAK system. The complexation constants of U and Pu with tributylphosphate 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.

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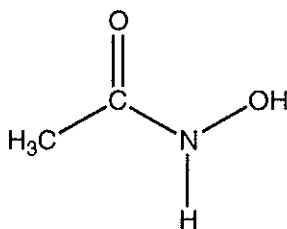
1. Background and Rational

1.1. Tributylphosphate based extractions

The extraction of tetravalent Pu in nitric acid solution by tributylphosphate (TBP) is well known and has been the basis of Pu purification for a number of decades. The extraction is based on the formation of an organic phase neutral complexes such as $\text{Pu}(\text{NO}_3)_4 \cdot 2\text{TBP}$. Upon reduction, the trivalent Pu species 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 AFCI. Based on the direction from Dr. George Vandegrift of ANL, this proposal was developed to obtain the necessary data for Pu extraction modeling.

Understanding the role of nitrate in Pu speciation is important for determining the necessary data for Pu extraction modeling. Data indicates the dinitrate complex of Pu is strong and may account for difficulties in modeling Pu 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) is expected to be used (Figure 1). The interaction of AHA with tetravalent Pu decreases extraction into the organic phase by either complex formation or reduction of Pu to the trivalent state. For the separation of Pu in a solvent extraction system using acetohydroxamic acid, it is necessary to determine the complexation kinetics and thermodynamics [1]. In addition, since Pu 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 Pu and U in the TBP-dodecane-nitric acid system, with the main emphasis on nitrate speciation and subsequent third phase formation at high nitric and metal ion conditions. Experiments on the AHA systems will be conducted in collaboration with the and with input from DOE separations group. For this project the focus will be on the evaluation on U and Pu complexation constants with TPB.

Figure 1. Acetohydroxamic acid



1.2. Lanthanide-Actinide Separations

A schematic of a proposed UREX separation (Figure 2) demonstrates the desired separations of actinides and fission products for the advanced fuel cycle. Some of the separations are well developed (i.e., UREX, essentially a modified PUREX step) while others require further investigation. The separation of trivalent lanthanides from trivalent actinides, and even the actinides Am from Cm, has been identified as a topic for investigations by 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 (Figure 3). 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 [2] include an aqueous phase with 1 M lactic acid and 0.1 M diethylenetriaminepentaacetic 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 Am and Cm 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 [3]. While complexation data is available for the interaction of Am [4] and Cm [5] with some ligands used the TALSPEAK process, further efforts are necessary to complete the appropriate dataset for modeling separations in AMUSE (Argonne Model for Universal 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.

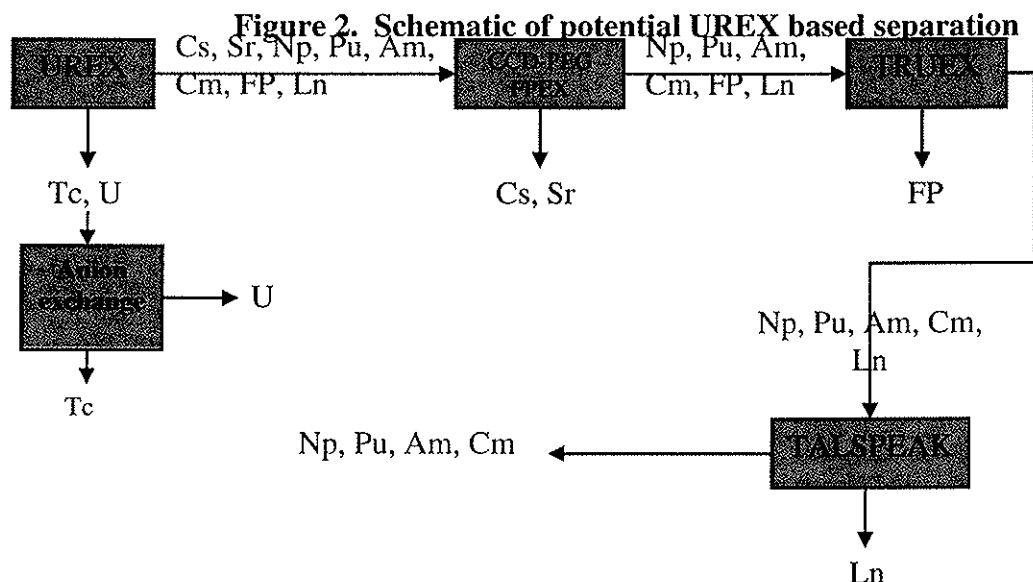
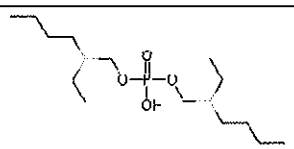
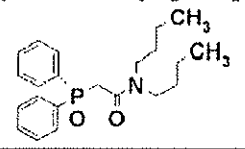
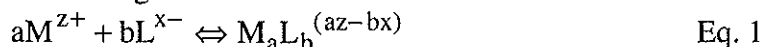


Figure 3. Examples of ligands for actinide and lanthanide separations

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

1.3. Evaluation of Chemical Thermodynamic and Kinetic Data

The goal of our Pu and U 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. For the extraction system under study precipitation is not expected, therefore solubility data can be neglected. 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. The change in actinide and ligand concentration can drive the formation of various chemical species.

From Eq. 1, the stability constant to describe speciation at equilibrium can be written as:

$$\beta_{MaLb} = \frac{[M_aL_b^{(az-bx)}]}{[M^{z+}]^a [L^{x-}]^b} \quad \text{Eq. 2}$$

In actuality, the constants should include activity coefficients. If the constant is measured as a function of ionic strength, the specific ion interaction theory or the Pitzer equation can be used to evaluate constants at different ionic strengths. Temperature variations are explained by second law extrapolations with Gibbs free energy. Enthalpy and entropy will be investigated by evaluating the stability constant as a function of temperature through the following equations (using standard nomenclature) [6]:

$$\Delta G = -RT \ln \beta \quad \text{Eq. 3}$$

$$R \ln \beta = -\frac{\Delta H}{T} + \Delta S \quad \text{Eq. 4}$$

For a system with different species, if the stability constants are known, then all the species can be calculated at any given pH by:

$$[M]_{\text{total}} = 10^{-pM} + \sum 10^{-(apM - bpL - \log \beta_{MaLb})} \quad \text{Eq. 5}$$

where pM is $-\log[M]$ and pL is $-\log[L]$. The thermodynamic data can also easily be incorporated into existing codes such as AMUSE or the geochemical code CHESS.

1.4. Computational studies

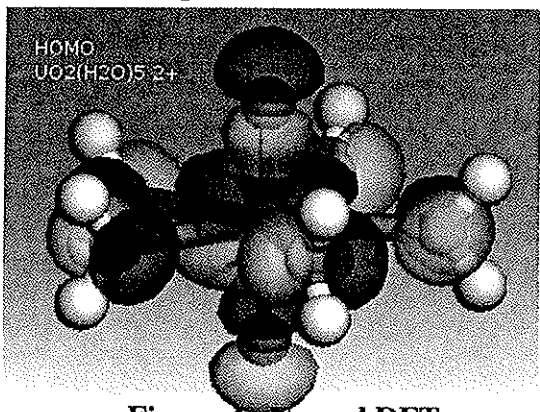


Figure 4. Uranyl DFT

Density functional theory calculations will be performed to 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 (Figure 4). 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.

First-principles all-electron relativistic calculations of the total energies and optimized geometries will be performed using the spin-polarized density functional theory (DFT) [7]. The exchange correlation energy are calculated using the generalized gradient approximation (GGA) with the parametrization of Perdew and Wang [8] (PW91). Double numerical basis sets including polarization functions on all atoms (DNP) will be used in the calculations. The DNP basis set corresponds to a double- ζ quality basis set with a d -type polarization functions added to atoms heavier than hydrogen. The DNP basis set is comparable to 6-31G** Gaussian basis sets [9] with a better accuracy for a similar basis set size [7, 10]. In the generation of the numerical basis sets, a global orbital cutoff of 5.9 Å can be used. The energy tolerance in the self-consistent field calculations will be set to 10^{-6} Hartree. Optimized geometries can be obtained without symmetry constraints using an energy convergence tolerance of 10^{-5} Hartree and a gradient convergence of $2 \cdot 10^{-3}$ Hartree/Å. The Monkhorst-Pack special k -point scheme [11] will be employed with a 4x4x4 mesh for structural optimizations and electronic properties calculations.

2. Research Objectives and Goals

- Determination of complexation constants for U and Pu with tributylphosphate (Task 1)
 - The aqueous and organic speciation of U and Pu will be examined as a function of the following conditions
 - nitric acid concentration
 - nitrate concentration (by the addition of NaNO₃)
 - actinide ion concentration
 - temperature
- Speciation of U and Pu with AHA in the presence and absence of TBP-dodecane organic phase (Task 2)
 - The aqueous and organic speciation of U and Pu will be evaluated under the following conditions
 - AHA concentration
 - Metal ion concentration
 - Metal ion redox state
 - pH
 - temperature
 - experiment will initially examine the aqueous phase then examine the two phase system
- Computations (Task 3)
 - DFT calculations on actinide species in the separation system
- Experimental techniques
 - The following experimental techniques will be used in the evaluation of U and Pu speciation
 - UV-Visible spectroscopy
 - Time resolved laser fluorescence spectroscopy
 - NMR spectroscopy
 - IR spectroscopy
 - Raman spectroscopy
 - Titrations

- ICP-MS
- ICP-AES
- XAFS
- Electrochemical

3. Technical Impact

The research will address an important area within AFCI by providing data useful for modeling the extraction of U, Pu, lanthanides, and trivalent actinides. The data will expand the utility of existing codes and provide fundamental data on the chemical behavior of Pu in nitric acid. This will permit the modeling of novel extractions under a variety of TBP-nitric acid conditions as well as evaluate the influence of AHA. Furthermore, the formation of third phase will be understood based on speciation data.

4. Research Approach

In extraction experiments, the aqueous and organic phases will be equal volumes and range from 0.5 mL to 5.0 mL. The actinide ion concentration will be varied from $\mu\text{mol/L}$ to the mmol/L range. Nitrate concentration will be varied from the concentration due to nitric acid by the addition of NaNO_3 . The nitric acid concentration will be varied from 14 M to the pH range in experiments with AHA. The temperature will be varied from 20 °C to 80 °C. The results will be used to determine thermodynamic and kinetic parameters.

4.1. Determination of complexation constants for the U and Pu TBP system

In Task 1 the influence of nitrate and pertechnetate on the speciation of hexavalent U and tetravalent Pu in the TBP-dodecane-nitric acid system will be examined. The TBP concentration in the organic phase will be 30 % and the TBP will be purified by washing with carbonate prior to use. The following parameters will be varied:

Nitric acid: 2-14 M

Metal ion concentration: 1 $\mu\text{mol/L}$ to 500 mmol/L

Nitrate: 2.5-14 M, increased by the addition of NaNO_3

Pertechnetate (up to 0.001 M)

Temperature: 20-80 °C

The distribution of the actinide will be determined to permit comparison with existing data and the determination of complexation constants. The chemical form for the actinide in the aqueous and organic phase will be examined by UV-Visible spectroscopy, time resolved laser fluorescence spectroscopy (for hexavalent U), and with indicator dyes or chromatography at lower concentrations. XAFS spectroscopy will be used to determine oxidation state and coordination environment around the metal center. The nitrate in the organic phase will be evaluated by ion chromatography or Raman spectroscopy. The concentration of the acid in the organic phase will be determined by titration with base and the addition of ammonium oxalate to complex metal ion from an organic sample back extracted with an aqueous phase. We expect to obtain data to describe the formation of actinide-nitrate-TBP species and determine complexation constants based on the equations in section 1.2.

4.2. Collection of thermodynamic and kinetic data for TALSPEAK

The UNLV program is currently engaged in this task with Dr. Art Guelis of Argonne National Laboratory on TALSPEAK studies. The data generated within this proposed work will allow for the generation of a module of the AMUSE code capable of accurately predicting the

behavior of trivalent lanthanides and actinides within the TALSPEAK process. The work will proceed through two main efforts:

- Determination of lanthanide and actinide complexation constants under TALSPEAK process conditions
- Determination of lanthanide and actinide extraction kinetics under TALSPEAK process conditions

The experiments proposed below will examine the behavior of La, Nd, Eu, Lu, Am, and Cm in simulated extraction and stripping steps of the TALSPEAK process. The lanthanides were selected to represent the range of light and heavy lanthanides as well as including the least extractable lanthanide (Nd). The lighter lanthanides are expected to exhibit slightly faster extraction kinetics than the heavier lanthanides and actinides. In both tasks, experiments will be performed using either stable lanthanide species with analysis via ICP-MS, electrochemical measurements or radiotracers with analysis via gamma spectroscopy. The actinide elements can be evaluated by alpha scintillation, gamma spectroscopy for ²⁴¹Am, or laser spectroscopy for Cm.

The stability constants of lanthanide and actinide complexes with HDEHP under TALSPEAK conditions will be determined for inclusion in the AMUSE code. The complexation constants will be determined using the distribution coefficients measured during batch liquid-liquid extractions. The magnitude of the distribution coefficient is related to the thermodynamic favorability of the extracted complex relative to the strength of aqueous complexes as noted in equation (1):[12]

$$D = \frac{[ML_x]_{org}}{([M^{x+}](1 + \beta_1[X^-] + \beta_2[X^-]^2 + \dots))} = \frac{K_{ex}[H^+]^x}{([HL]^x(1 + \beta_1[X^-] + \beta_2[X^-]^2 + \dots))} \quad (1)$$

where D is the distribution coefficient, K_{ex} is the complexation constant of the extracted complex, β_i are the stability constants of the soluble aqueous-metal complexes (MX), $[ML_x]$ is the concentration of the extracted complex, $[H^+]$ is the concentration of free hydrogen ions, $[HL]^x$ is the concentration of the protonated ligand, and $[M^{x+}]$ is the concentration of the free metal ion. The complexation constants needed to determine the aqueous lanthanide-DTPA and lanthanide-lactic acid complexation are available [13]. The concentration of HDEHP will be varied to determine the stoichiometry of the extracted complex. The lanthanides La, Nd, Eu, and Lu along with Am and Cm will be examined. The data generated within this task will allow for a more accurate and reliable thermochemical database for use with the AMUSE code.

Since the TALSPEAK process involves separations using a two phase (aqueous and organic) system, understanding the phase transfer kinetics will support and enhance process simulations. Using a series of batch and flow-through experiments, the kinetics of lanthanide and actinide extraction by HDEHP will be examined. These experiments will provide preliminary data that will verify previous results [14] and aid in the design of more detailed experiments described above. The concentration of HDEHP, DTPA, and lactic acid will slightly varied but maintained within the range of concentrations of the TALSPEAK process. In an effort to understand the dynamics at the liquid-liquid interface, the kinetics of the extractant distribution between the aqueous and organic phases will also be monitored. These interfacial reactions are of utmost importance in understanding the rates of phase transfer reactions.

Preliminary experiments will also be performed to understand the kinetics of backextraction of the lanthanides into 1M HNO₃ and 1M HCl. Following extraction and separation from the actinides, the lanthanides must be stripped from the organic phase. The kinetics of lanthanide

stripping from 0.3 M HDEHP into 1.0 M HNO₃ and 1 M HCl will be determined using batch experiments.

4.3. Task 3. Computational Studies

High-accuracy DFT calculations will be performed and the data will be used to interpret the electronic structure of the resulting species and focus on the role played by 5f electrons. 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 in mechanisms involved in speciation.

Computation of reaction kinetics will be investigated by means of classical molecular dynamics (MD) simulations driven by force fields. While the level of agreement between experimental structures and dynamics is in general acceptable, discrepancies subsist between different models and between models and experiments. This is particularly true in the case of systems, such as anion-hydrogen distributions, affected by directional interactions that involve some degree of local polarization or even charge transfer between molecules. This major shortcoming of force-field based MD methods stems from the fact that most force fields use fixed partial charges and Buckingham or Lennard-Jones interaction centers on the atomic positions. The *ab initio* MD simulations will be performed using the Car-Parrinello method [15] with periodic boundary conditions applied in order to model the bulk behavior with a limited number of molecules. Using MD simulations, data will be obtained for comparison to experimental kinetic results.

4.4. Capabilities

The PI has a transuranic chemistry laboratories for performing radiochemical and spectroscopic experiments. For determining actinide speciation and concentration, the main experimental methods can be divided into spectroscopic and separation followed by detection. XAFS (XANES and EXAFS) will also be used. XAFS experiments will be performed with DOE collaborators at ANL or SRTC. Separation/Detection experiments divide species based on size, charge, or a combination of the two. The amount of each species is quantified by radiation detection or analytical techniques. Speciation by spectroscopy relies upon the differences between the absorption or emission of different species. Through controlled experiments, spectra are collected and deconstructed to analyze the contribution from each species. The PI can also utilize electrochemical methods to evaluate the speciation of Pu with acetohydroxamic acid. Electrochemistry is a powerful tool for the determination of formal redox potentials, detection of chemical reactions that precede or follow the electrochemical reaction and the evaluation of electron transfer kinetics. XAFS experiments are to be performed at Stanford or ANL facilities with partners from ANL or SRTC. The PI has already used these XAFS facilities for examining actinide containing solutions and solid phases. XAFS is well suited to actinide speciation studies [16]. This is because X-ray absorption originates from an atomic process, and an element will always exhibit XAFS regardless of its speciation (i.e., species are never spectroscopically silent). Since XANES and EXAFS provide average local electronic and structural information about specific atomic species, they are well suited to the study of actinide ions in many forms (e.g. molecular ions, An³⁺, An⁴⁺, AnO₂²⁺; complexes AnO₂(OH)₂, An(CO₃)₄²⁻; and solids AnO₂CO₃, AnO_s, where An=U or Pu).

5. Project Timeline

Reports will be produced as specified. It is anticipated that presentations at annual scientific meeting will result from this research. The project will be 3 years in length. The time frame and expected results for each task are below.

Task 1: Determination of complexation constants for the U and Pu TBP system (Months 0-15)

- Determination of the U-TBP complexation constant
- Determination of the Pu-TBP complexation constant
- Investigating the influence of Tc on the system

Task 2: Collection of thermodynamic and kinetic data for TALSPEAK (Months 6-33)

- Set up of 2 phase diffusion system for kinetic studies
- Determination of lanthanide complexation constants under TALSPEAK process conditions
- Determination of actinide complexation constants under TALSPEAK process conditions
- Determination of lanthanide extraction kinetics under TALSPEAK process conditions
- Determination of actinide extraction kinetics under TALSPEAK process conditions

Task 3: Computational Studies (Project Months 3-36)

- Examination of the U system
- Examination of the Pu system
- Examination of the Am and Cm system with ligands for the TALSPEAK system

5.1. Year 1 Tasks

Task 1: Determination of complexation constants for the U and Pu TBP system

- Determination of the U-TBP complexation constant
- Initial studies on the Pu-TBP system
- Initial studies on the influence of Tc and the U-TBP system

Task 2: Collection of thermodynamic and kinetic data for TALSPEAK

- Set up of 2 phase kinetic diffusion apparatus
- Initial studies with lanthanides

Task 3: Computational studies

- Studies on the U system
- Studies on the influence of Tc on the U TBP system

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