

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 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 Argonne National Laboratory, 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. 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.

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 experimentally evaluates 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 are conducted in collaboration with input from the AFCI separations group.

RESEARCH OBJECTIVES AND METHODS

The research objectives of this project are as follows:

- 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 (by the addition of NaNO_3), 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. Experiments will initially examine the aqueous phase then examine the two phase system.

- To incorporate thermodynamic and kinetic data into existing modeling codes.

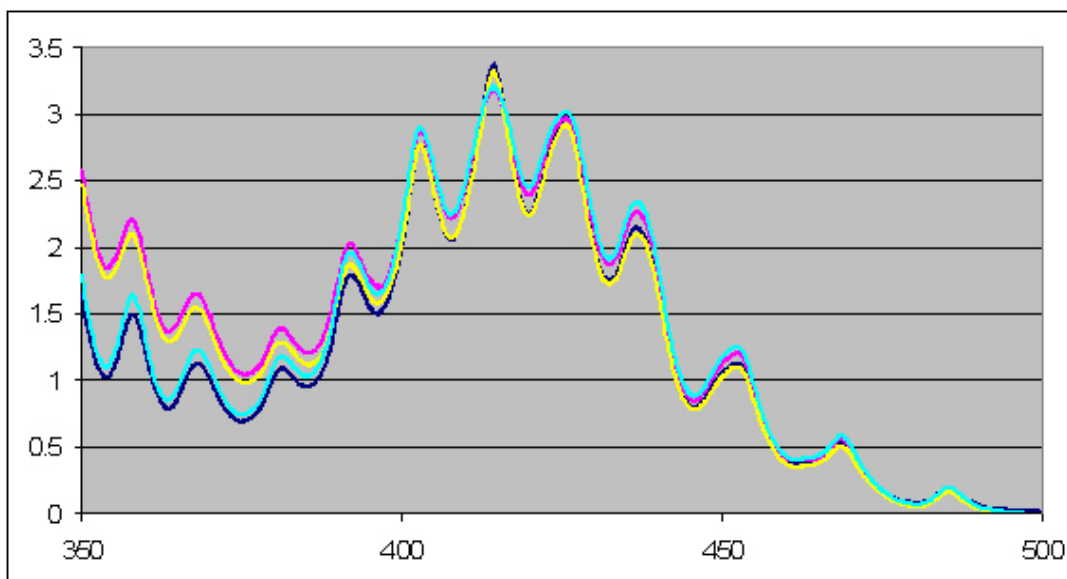
The following experimental techniques are used in the evaluation of U and Pu speciation: UV-Visible spectroscopy, Time resolved laser fluorescence spectroscopy, NMR spectroscopy, IR spectroscopy, Raman spectroscopy, Titrations, ICP-MS, ICP-AES, XAFS, and Electrochemical.

Initial experiments are performed with UO_2^{2+} . The initial results obtained with UO_2^{2+} are the basis for further experiments with Pu. In extraction experiments, the aqueous and organic phases are equal volumes and range from 0.5 mL to 5.0 mL. The actinide ion concentration varies from mmol/L to the mmol/L range. Nitrate concentration varies from the concentration due to nitric acid by the addition of NaNO_3 . The nitric acid concentration varies from 14 M to the pH range in experiments with AHA. The temperature varies from 20 °C to 80 °C. The results will be used to determine Gibbs free energy.

RESEARCH ACCOMPLISHMENTS

Studies were performed on the extraction of uranium from nitric acid into 30 % TBP in dodecane as a function of nitrate concentration. Stock solutions of uranyl nitrate were prepared at constant nitric acid concentration by dissolution of known quantities of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck) in nitric acid solutions. Organic extraction phases were prepared using 30 vol. % tributyl phosphate (Aldrich 97 %) with n-dodecane (Prolabo). Nitrate concentration was adjusted by the addition of concentrated LiNO_3 . Equal volumes of 5 mL organic and aqueous phases were contacted and vigorously mixed for 5 minutes then allowed to mix on a shaker table for 5 hours. After centrifuging, samples of each phase were drawn off and spectra taken using a Cary UV-visible spectrometer with precision quartz cuvettes (1 cm path length) measured against a deionized water reference cell. Four sets of spectra were collected for each sample and the average used in analysis performed with Microsoft Excel™ software.

Improvement of the extraction methods was undertaken. The volume of aqueous and organic phase used was reduced to 1.6 mL. Spectroscopy is still possible with these volumes and waste volume is minimized. The determination of nitrate concentration in the organic phase has been measured by ion specific electrode and ion chromatography. For the ion specific electrode the system is found to be highly dependent upon the total acid concentration. Up to 5 % drift with same standards and 12



Comparison of quartz to PMMA cuvettes: Blue and yellow are quartz; teal and fuschia are PMMA.

% drift with variations in total acid concentration was observed. Nitrate ion chromatography shows accuracy of 5% and no acid effects are observed. UV-visible spectra were collected for a number of TBP/dodecane extractions of uranium (see figure above).

A number of different nitrate concentrations were examined. The following conditions were found for third phase formation as measured at 18°C:

- For 1 M U, need $[\text{NO}_3]_{\text{tot}} \geq 10.2 \text{ M}$, $[\text{HNO}_3] > 5 \text{ M}$
- For 0.5 M U, need $[\text{NO}_3]_{\text{tot}} > 11 \text{ M}$, $[\text{HNO}_3] > 7 \text{ M}$,
- For 10 M HNO_3 , no nitrate need $[\text{U}] \sim 0.57 \text{ M}$
- For 12 M HNO_3 , no nitrate need $[\text{U}] \sim 0.185 \text{ M}$
- For 13 M HNO_3 , no nitrate need $[\text{U}] \sim 0.08 \text{ M}$
- For 14 M HNO_3 , no nitrate need $[\text{U}] \sim 0.022 \text{ M}$
- For 14 M $[\text{NO}_3]_{\text{tot}}$ and 10 M $[\text{HNO}_3]$, need $[\text{U}] \sim 0.062 \text{ M}$
- For 12 M $[\text{NO}_3]_{\text{tot}}$ and 8 M $[\text{HNO}_3]$, need $[\text{U}] \sim 0.42 \text{ M}$

The results on nitrate organic concentration at 12 M HNO_3 , 12 M total nitrate, and 14 M HNO_3 show that the bulk of the nitrate remains in the aqueous phase. The total nitrate extracted appears independent of initial uranium, nitrate, and nitric acid concentrations.

When the organic phase splits, the heavy phases has about 2 –

2.5 M $[\text{NO}_3]$ and the light phases have about 1-1.2 M $[\text{NO}_3]$. Single phases have about 1.3-1.5 M $[\text{NO}_3]$, similar to the light 2nd phase. High $[\text{NO}_3]$ is found to encourages complete extraction of U into a heavy phase. Kinetic effects on third phase formation were observed.

Work also focused on 3rd phase formation studies with the uranyl system. which happens with the organic phase spontaneously splits into a light and a heavy phase. This phenomenon occurs when the uranium and nitric acid concentrations exceed a certain threshold. Current theories include that the third phase forms gradually in small reverse micelles when uranyl and nitric acid reach a certain limiting organic concentration (LOC) that makes it thermodynamically favorable to separate and form a different structure. This is analogous to the critical micelle concentration (cmc) in surfactant micelle formation. The third phase formation *is* quite dependent on temperature. There has been some work indicating that the UV-visible spectrum changes at certain wavelengths as the system approaches third phase, indicating a variation in the uranyl electronic structure as this third phase begins to form.

Furthermore, the role of nitrate vs. nitric acid in third phase formation was evaluated. To this end, hundreds of samples were generated over a spectrum of concentrations for U, LiNO_3 , and HNO_3 .

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