

## 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 organic phase neutral complexes. 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.

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.

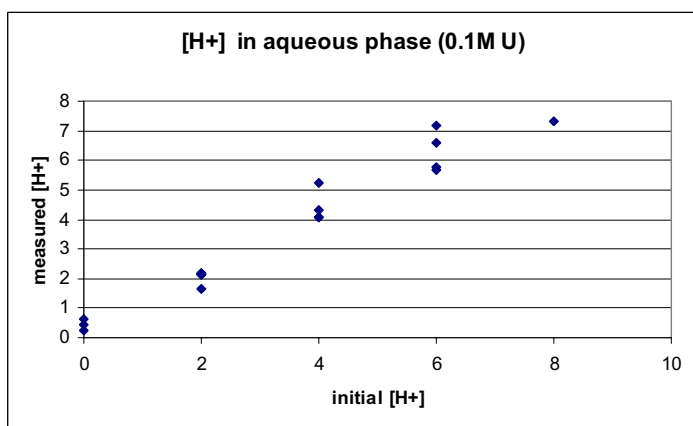
In the UREX process, acetohydroxamic acid (AHA) is expected to be used. The interaction of AHA with tetravalent Pu decreases extraction into the organic phase by either complex formation or reduction of Pu to the trivalent state. For the separation of Pu in a solvent extraction system using acetohydroxamic 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.

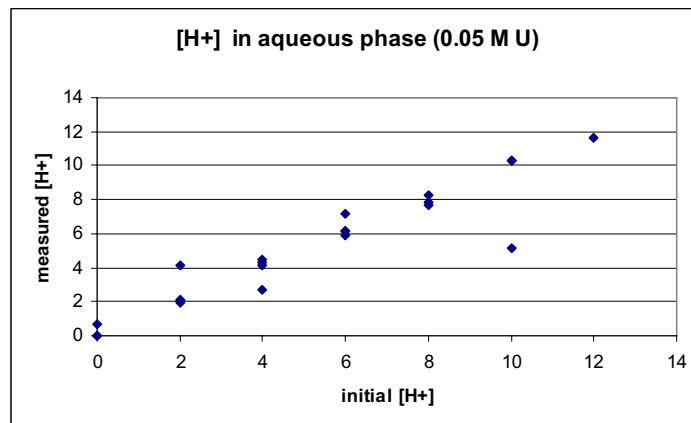
## RESEARCH OBJECTIVES AND METHODS

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  $\text{NaNO}_3$ ), actinide ion concentration, temperature, and time.



Measured aqueous acid concentration with varied initial acid.



Measured aqueous acid concentration with varied initial acid.

- 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  $\text{UO}_2^{2+}$ . The initial results obtained with  $\text{UO}_2^{2+}$  are the basis for further experiments with Pu.

## RESEARCH ACCOMPLISHMENTS

Efforts focused on methods for the determination of nitrate concentration in the experimental system. Ion Chromatography (IC) was examined as a method for nitrate determination and was found to be suitable.

Analysis of XAFS data was completed during year. Different hypotheses were proposed in the literature concerning the nature of the U species in the heavy organic phase examined:

- formation of the compound  $\text{HUO}_2(\text{NO}_3)_3 \cdot x\text{TBP}$
- formation of U(VI) polymer
- modification of nitrate bonding and formation of hydrogen bond with water or acid nitric present in the third phase

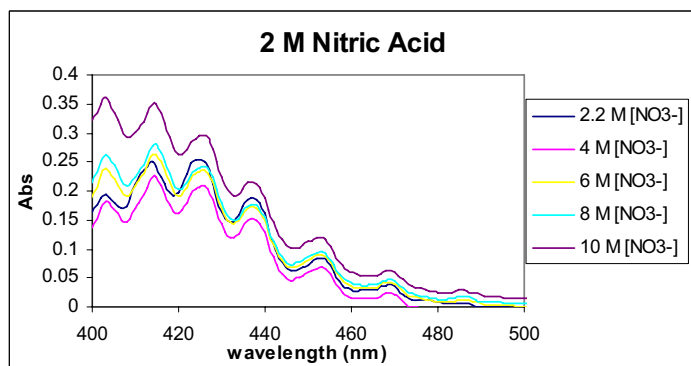
According to EXAFS result obtained in this study the following was found for the different theories. Hypothesis (i) was rejected since the formation of an eventual  $\text{HUO}_2(\text{NO}_3)_3 \cdot x\text{TBP}$  will lead 6

O(N) atom at 2.50 Å, and this was not found. Hypothesis (ii) cannot be completely rejected, and it might be possible that  $[\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}]_2$  and  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$  are simultaneously extracted in the heavy third phase. Hypothesis (iii) corroborates the observation from 15 M  $\text{HNO}_3$  media but is not verified in 8M and 12 M  $\text{HNO}_3$  media.

Extraction studies on samples containing two different uranium concentrations were performed. The organic phase of each sample consisted of a pre-equilibrated solution of 30% TBP (tributylphosphate) in dodecane. The aqueous phase consisted of nitric acid (0-12M), lithium nitrate (0-12M), uranyl nitrate (0.1 and 0.05M) and water. After contact the phases were separated and analyzed for nitrate and uranium concentrations by IC (ion chromatography) and LSC (liquid scintillation counting), respectively. The amount of nitrate extracted into the organic phase was surveyed. The data shows a slightly increasing trend as nitric acid and total nitrate increase though, generally the amount of nitrate extracted stays between 0.5 M and 1.5 M regardless of the varying initial nitrate, acid or uranium concentrations. The distribution ratio for uranium has shown a general decrease with increasing acid concentration and an increasing trend with increasing nitrate concentration. Both of these effects seem to level off around a  $K_d$  value of 10 which occurs around 10 M acid and nitrate.

The acid concentrations of the samples were determined by titration in order to have more complete information about the phases. Also UV-Vis spectroscopy was done on the organic phases of the samples.

The organic phases of the samples were examined with UV-Visible spectroscopy. There are not noticeable peak shifts as the nitrate increases, but the relative peak heights do change. The peak around 403nm gets larger while the peak at 425nm gets



Uranium absorbance with varied nitrate.

## ACADEMIC YEAR HIGHLIGHTS

- ◆ J. Plaué, S. Goeur, J. Petchsaiprasert, M. Drayé, J. Foos, and K. Czerwinski, "Comparison of Uranyl Third-Phase Formation in 30 % TBP-Nitric Acid in Dodecane and HPT using UV-Visible Spectroscopy," *ACS Symposium Series 933, Separations for the Nuclear Fuel Cycle in the 21st Century*, Gregg Lumetta et al. editors, 119-134 (2006).
- ◆ J. Plaué, A. Gelis, and K. Czerwinski, "Actinide Third Phase Formation in 1.1 M TBP/Nitric Acid/Alkane Diluent Systems," *Sep. Sci. and Techn.*, 41, 1-10 (2006).
- ◆ J. Plaué, A. Gelis, K. Czerwinski, P. Thiagarajan, and R. Chirizia, "Small-angle neutron scattering study of plutonium third phase formation in 30% TBP/ $\text{HNO}_3$ /alkane diluent systems," *Solv. Extr. Ion Exch.* 24(3), 283-298, (2006).
- ◆ J. Plaué, A. Gelis, and K. Czerwinski, "Plutonium third phase formation in the 30% TBP/nitric acid/hydrogenated polypropylene tetramer system," *Solv. Extr. Ion Exch.*, 24(3), 271-282 (2006).

smaller. The trends in this spectrum are very similar to the other spectra taken when holding acid concentration constant. Similar effects are not seen when holding total nitrate concentration constant. This suggests that as nitrate concentration increases there may be a difference in the bonding around uranium with a change in speciation to the nitrate form.

The interaction of uranium with AHA was reinvestigated. The ionic strength was held constant at 1.003 M using  $\text{NaClO}_4$  with a constant 4:1 ratio AHA to uranium and the pH varied from approximately 0 to 10. There was a noticeable optical variation with pH and an accompanying change in absorbance. Further experiments were performed at pH 5 with a constant uranium concentration and the AHA varied. Kinetic experiments were also performed and showed rapid complexation of uranium to AHA.

## FUTURE WORK

The influence of nitrate and pertechnetate on the speciation of U and Pu in the TBP-dodecane-nitric acid system will be examined. The nitrate research is a continuation of previous studies. The pertechnetate studies will include experiments with perhenates. The speciation of U and Pu with AHA in the presence and absence of TBP-dodecane organic phase will be continued, with an emphasis on the impact of the organic system.

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