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## Fundamental Chemistry of U and Pu in the TBP-Dodecane-Nitric Acid System: Quarterly Report January - March, 2006

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

Quarterly Report

January 2006-March 2006

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Technical Focus Area: Separations

## 1. Project Abstract

The speciation of hexavalent U and tetravalent Pu will be examined in the Tributylphosphate (TBP)-dodecane-nitric acid systems. This topic is chosen based on data needs for separation modeling identified by the APCI. Emphasis will be placed on studying the influence of nitrate and acetohydroxamic acid on U and Pu speciation as well as conditions where a third phase forms in the organic phase. The organic phase will be 30 % TBP in dodecane. Equal volumes of aqueous and organic phase will be used. The speciation of the actinides in the aqueous and organic phase will be determined by a number of different spectroscopic and radiochemical techniques. Additionally the actinide distribution between the phases as a function of conditions will be determined. The project data will be incorporated into models to evaluate separations under a variety of conditions.

## 2. Work performed in previous quarter (October 2005 to December 2005)

Efforts in the past quarter focused on methods for the determination of nitrate concentration in the experimental system. The HPLC primarily used and was found to be precise but not very reliable. Ion Chromatography (IC) was examined as a method for nitrate determination and was found to be suitable. The IC to be used is a Dionex ICS 2000 for measuring cations, and a Dionex ICS 2500 for the anions. It has an autosampler and dual injection system in order to run both at the same time. The 2000 is able to measure  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ , and  $\text{Mg}^{2+}$ . The 2500 can measure  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ . Both have conductivity suppressors which the samples go through before reaching the detectors.

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

- i) formation of the compound  $\text{HUO}_2(\text{NO}_3)_3 \cdot x\text{TBP}$  [1]
- ii) formation of U(VI) polymer [2]
- iii) modification of nitrate bonding and formation of hydrogen bond with water or acid nitric present in the third phase [3]

According to EXAFS result obtained in this study the following was found for the different theories. The hypothesis i is 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 can not 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. In 8 M and 12 M nitric acid media, in the light and heavy phase, EXAFS measurement show that the environment around  $\text{UO}_2^{2+}$  is the same and constituted by 2  $\text{NO}_3$  and 2 TBP group.

### **3. Work performed in current quarter (January 2006 to March 2006)**

This quarter involved work on extraction samples containing two different uranium concentrations. The samples were analyzed for nitrate and uranium concentrations by IC (ion chromatography) and LSC (liquid scintillation counting), respectively. This data will be helpful in understanding how nitrate and uranium are distributing between the two phases and the dependence of this effect on total nitrate concentration.

#### **Sample Generation**

The samples were made of an aqueous phase and an organic phase. The aqueous phase consisted of nitric acid, lithium nitrate, uranyl nitrate and water. The concentrations of nitric acid varied from 0 M to 12 M. The total nitrate concentration varied by addition of  $\text{LiNO}_3$  and ranged from the acid concentration to 12 M. There were two sets of uranium concentrations investigated; they were 0.1 M and 0.05 M  $\text{UO}_2(\text{NO}_3)_2$ . The organic phase of each sample consisted of a pre-equilibrated solution of 30% TBP (tributylphosphate) in dodecane. Volumes of 0.75 mL of each phase were contacted by mixing for 2 minutes with a vortexor. Then the samples were centrifuged for 3 minutes to ensure complete separation of the two phases. Each phase was extracted and stored separately. The analyses were run on both the organic and aqueous phases.

#### **Nitrate Determination**

The concentration of nitrate in the samples was determined by IC. The IC was run with an eluent of 30mM KOH on a dionex anion exchange column. This was done on both the aqueous and the organic phases. The only difference is that the conductivity detector was used on the aqueous samples while the UV detector was used on the organics. The data collected is summarized below. Figures 1 and 2 show how the amount of nitrate in the organic phase varies with initial acid concentration. Figures 3 and 4 show how the amount of nitrate in the organic phase varies with initial nitrate concentration. The nitrate concentration for 0 M  $\text{NO}_3^-$  listed in the figures excludes the nitrate contribution from the uranyl nitrate. The data demonstrates a slightly increasing trend, but generally the amount of nitrate extracted into organic phase stays between 0.5 M and 1.5 M regardless of the varying initial nitrate, acid or uranium concentrations.

Figure 1. Nitrate Distribution in the organic phase with 0.1 M Uranium

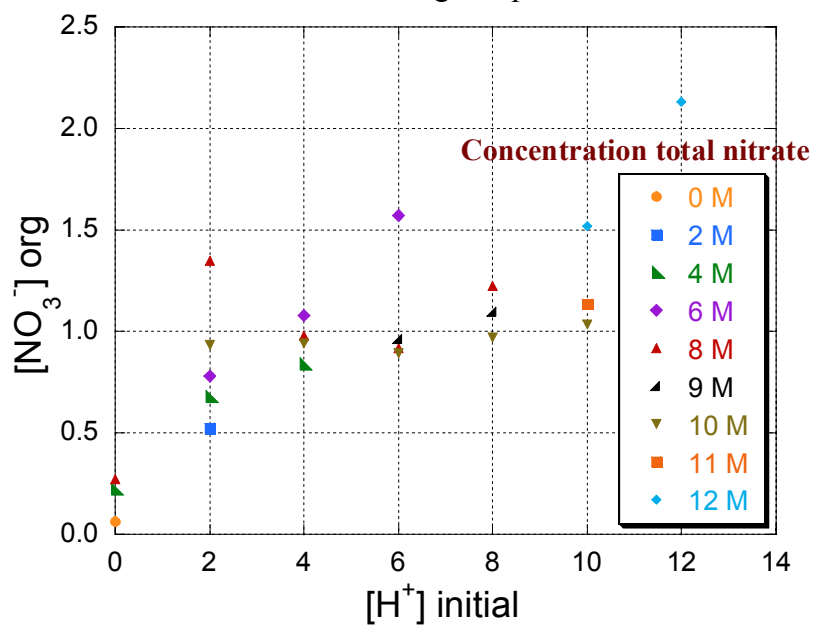


Figure 2

### Nitrate Distribution (0.05 M U)

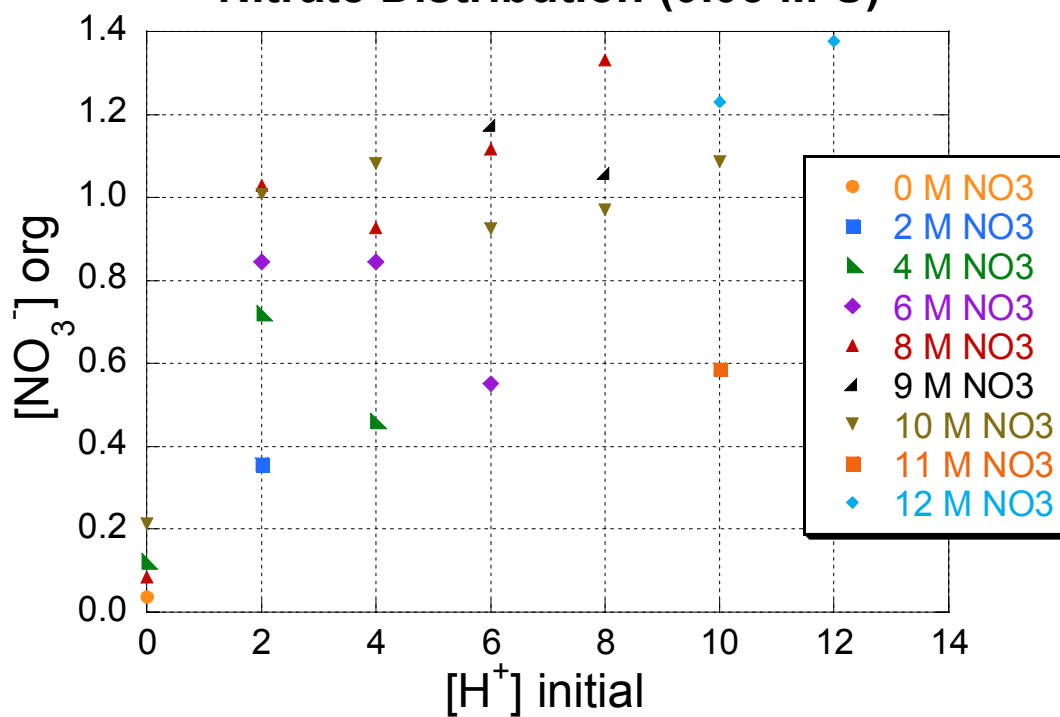


Figure 3

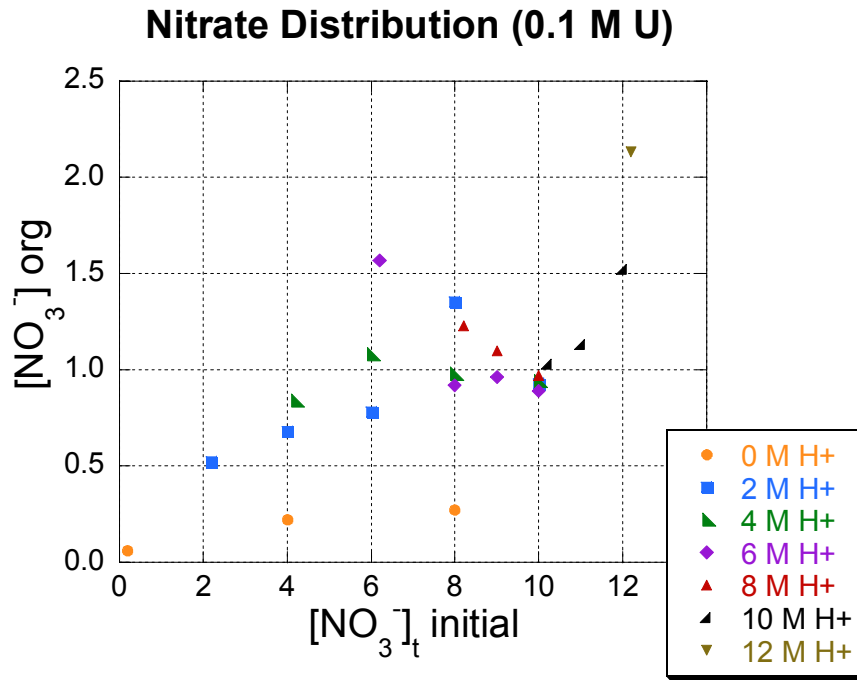
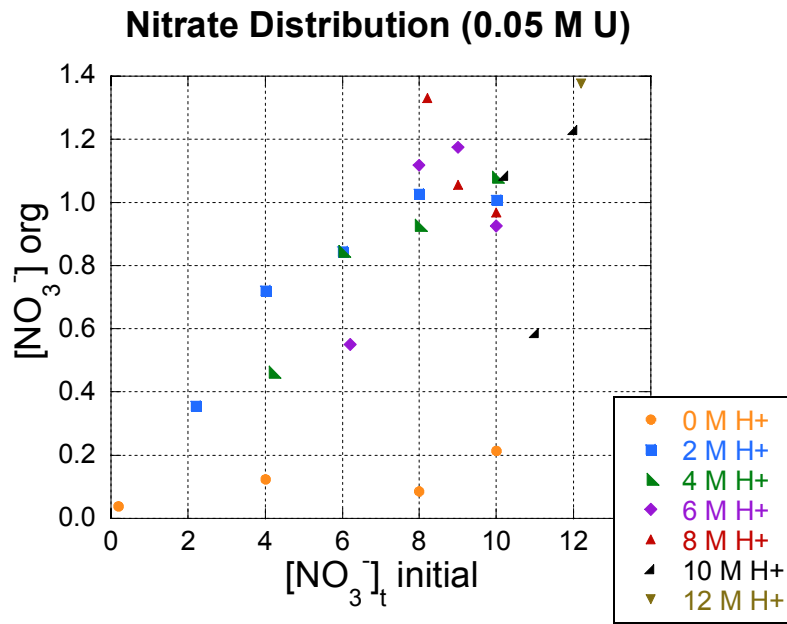


Figure 4



### Uranium Determination

The uranium concentration of the samples was measured using LSC. The count time was one hour, and the amount of sample was 0.1mL in 10mL of scintillation fluid.

Both the aqueous and organic phases were analyzed for uranium concentration. The distribution ratio,  $K_d$ , was found by the following:

$$K_d = [U]_{\text{organic}} / [U]_{\text{aqueous}}$$

The data is summarized in the following graphs. Figures 5 and 6 show how  $K_d$  varies with initial acid concentration.

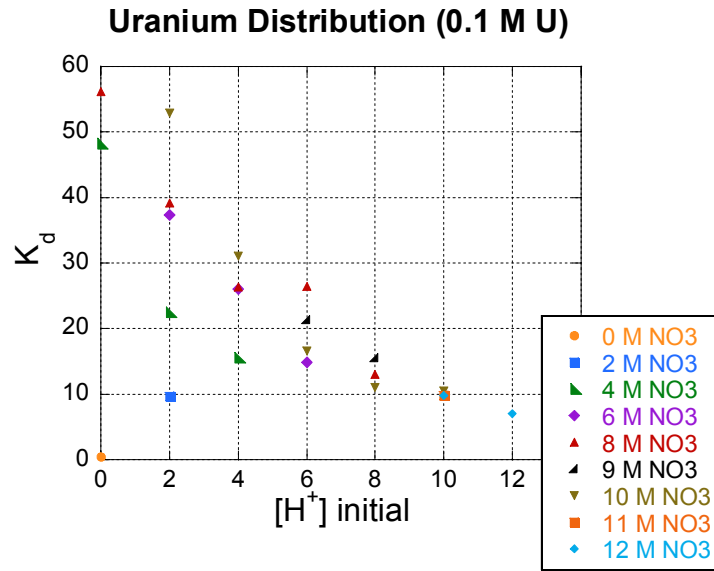


Figure 5.

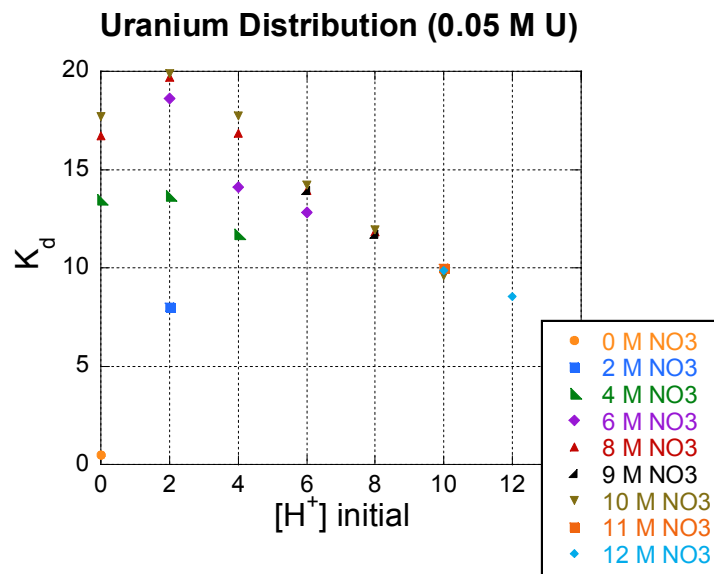


Figure 6.

Figures 7 and 8 show how  $K_d$  varies with initial nitrate concentration.

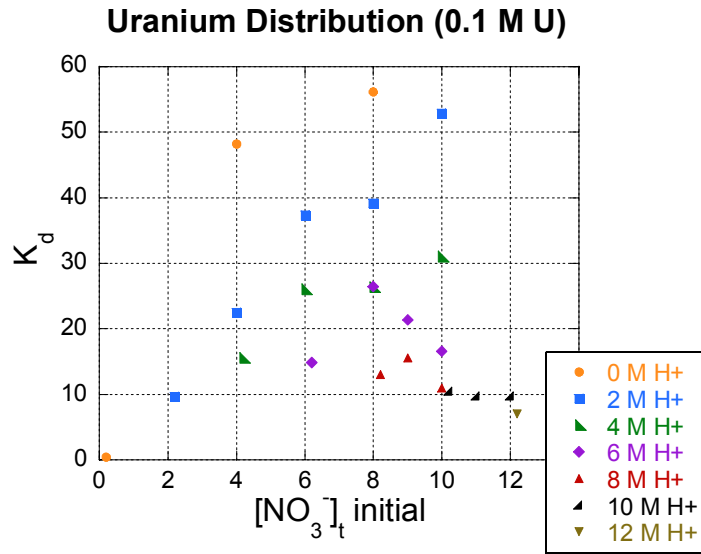


Figure 7.

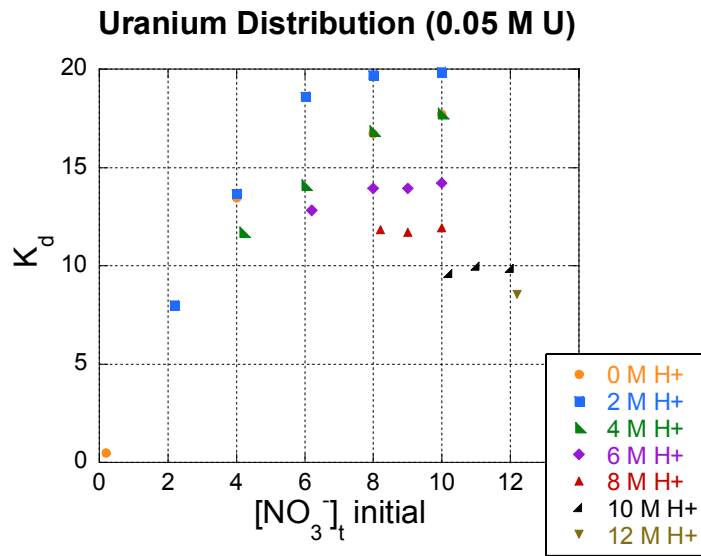


Figure 8.

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.

#### Other Accomplishments

The titrator that will be used to measure acid concentration has been repaired and now has autosampling capabilities. The new NMR is operational, and methods for using

this on radioactive samples must now be determined. A new FT-IR has been ordered and should be arriving soon.

In March, a presentation on this research project was given at the 231<sup>st</sup> ACS (American Chemical Society) National Meeting in Atlanta, Georgia.

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<sup>1</sup> Solovkin, A. S.; Povitskii, N. S.; Lunichkina, K. P. Formation of a third phase in the system  $\text{UO}_2(\text{NO}_3)_2\text{HNO}_3\text{-H}_2\text{O}$ -tributyl phosphate-kerosine. *Zhurnal Neorganicheskoi Khimii* (1960), 5 2115-18.

<sup>2</sup> Nemodruk, A. A.; Karyakin, A. V.; Muradova, G. A. Formation of polymeric compounds with uranyl nitrate in tributyl phosphate extracts. *Radiokhimiya* (1969), 11(2), 229-32.

<sup>3</sup> R. Chiarizia, M. P. Jensen, M. Borkowski, J. R. Ferraro, P. Thiyagarajan, and K. C. Third Phase Formation Revisited: The U(VI),  $\text{HNO}_3$  - TBP, *n*-Dodecane System *Littrell Solvent Extr. and Ion Exch.* 21 (1), 1-27 (2003)