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Fundamental Chemistry of U and Pu in the TBP-Dodecane-Nitric Acid System: Quarterly Report

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

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Technical Focus Area: Separations

Project Abstract

The speciation of hexavalent U and tetravalent Pu will be examined in the TBP-dodecane-nitric acid systems. This topic is chosen based on data needs for separation modeling identified by the AFCL. 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.

Work performed in previous quarter (January 2005 to March 2005)

Studies were performed 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 % 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.

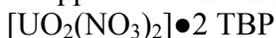
Work performed in current quarter (April 2005 to June 2005)

Work in this quarter 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.

One theory about the mechanism of formation is that the uranyl begins to gather excess nitrate or nitric acid around itself. The third phase only forms at high [U] and/or high [HNO₃]. One of our questions is whether the complex formed is dependent on [H⁺], [NO₃⁻], or [HNO₃]. The current prevailing theory is that the complex formed is:



as opposed to the “normal phase” or “single phase” complex, which is purported to be:



What this formula indicates is that the uranyl pulls in nitrate and TBP and an additional nitrate that is itself still coordinated to a proton. Further research using the aforementioned SANS technique, among others, seemed to indicate a slightly different structure:



Previous work in this project found that at 12 M HNO₃, the organic phase split with an initial [U] around 0.16 M U, and afterwards the concentration of U in the light phase stayed constant around 10 M while the concentration of U in the heavy phase increased fairly linearly with increasing initial [U]_i; this split decreased to 0.05 M [U]_i for 13 M HNO₃ and all the way down to 0.01 M [U]_i for 14 M HNO₃. Using the scaled down method in the plastic tubes, similar results were found at 17-18 °C, validating the method.

Conc. HNO ₃	[U] _i (5 mL)	[U] _i (0.8 mL)
10 M	N/A	0.472 M
12 M	0.17	0.162 M
13 M	0.06	0.065 M
14 M	0.01	0.020 M

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, LiNO₃, and HNO₃. The raw data are condensed below:

Conc. [U] _i	Conc. HNO ₃	Total NO ₃ ⁻
1.6 M	≥ 5 M	≥ 8.2 M
0.8 M	≥ 5 M	≥ 10.2 M
0.4 M	≥ 8 M	≥ 11.8 M
0 M		
≥ 0.32 M	8	12 M
≥ 0.056 M	10	14 M

A catalytic amount of acid is needed to form the third phase with uranium. Acid can even form third phase on its own without uranium, but much higher concentrations are needed. As the concentration of U decreases, the amount of acid and nitrate needed for third phase formation increases. Conversely, as the concentration of HNO₃ increases, the amount of U necessary for third phase formation decreases. EXAFS experiments on third phase were performed and data analysis initiated. Data analysis should be complete by the next quarter.

A definite kinetic component was observed in third phase formation. This was especially true for material near the cusp of the third phase; often material just above the putative LAC would not separate for several hours, or material just below will separate after waiting for several hours. Part of this is due to the exquisite sensitivity of third phase to small changes in temperature as shown below.

Sample	17 C	30 C	40 C	60 C
10 M HNO ₃	0.472 M U	0.800 M U	≥ 1 M U	≥ 1 M U
12 M HNO ₃	0.162 M U	0.400 M U	0.6 M U	0.8 M U
12N/8H	0.320 M U	0.630 M U	0.8 M U	1 M U
13 M HNO ₃	0.065 M U	0.10 M U	0.1 M U	≥ 0.2 M U
14 M HNO ₃	0.020 M U	≥ 0.2 M U	≥ 0.2 M U	≥ 0.2 M U
14N/10H	0.056 M U	0.20 M U	0.2 M U	0.3 M U
0.4 M U	H ≥ 8 N ≥ 11.8	H ≥ 9 N ≥ 13	H ≥ 11 N ≥ 13	H ≥ 12 N ≥ 13

Above and below, 12N/8H means 12 M total nitrate, 8 M acid; 14N/10H is defined similarly.

The kinetics problem may easily be seen in the change in aqueous concentration over time. Initially, more U is extracted than ultimately ends up after equilibrium is reached; these numbers were reached by making duplicate samples and separating the organic and aqueous after about 1 hour and then after over 24 hours.

Sample:	12 M HNO ₃	12N/8H	14 M HNO ₃	14N/10H
A2/A1	1.117	1.169	1.087	N/A
		1.154		
L2/L1	0.958	0.997	0.958	N/A
		0.865		
H2/H1	1.090	1.081	1.054	N/A
		1.198		

These ratios reflect the ratio of the concentrations of sample before and after separation. With this quick and dirty experiment, we can see that the concentrations in

the aqueous phase generally increase by about 10% over time (U is extracted quickly, then re-equilibrates as water is taken up into the organic system) while the concentrations in the organic phases hold fairly steady. It has already been seen that the concentration in the light and single phases does not change much with changes in nitrate, uranium, or acid concentration, but the heavy phase is affected in both volume and concentration. A more systematic study of the kinetics of the solutions on the cusp is needed.

Liquid Scintillation Counting

The liquid scintillation counter was used with known aqueous standards of U and organic samples that were counted on the ICP-AES. Since there are at least four daughter products in secular equilibrium with ^{238}U including ^{234}U one can only expect about half of the activity to be due to uranium. In addition, the solvent extraction purifies the U from the daughter products; the ~ 250 keV ^{234}Th beta peak takes about 170 days to grow into secular equilibrium with U, so the amount of time between the extraction and liquid scintillation counting will affect the overall radiation; after purification and seven Th half-lives (170 days), Th will be in secular equilibrium with the U; however, since the U-234 daughter is long-lived, it will not contribute significantly to the radiation. Thus the uranium can be expected to contribute to two thirds of the activity. By knowing the time and counting the spectrum, one may then figure out what of the activity is due to the uranium and the daughter products. However, since the U has a much higher energy than the Th daughter, an easier route would be to gate the LSC so that it only integrates under the U peak, around 40-110 keV for the aqueous and about 50-105 keV for the cleaner organic. Gating on this peak only yields a calibration curve of $y = 6.8x$ with an R^2 value of 0.990, where y = concentration (in μM) and x = counts per minute (cpm). The detection limit will be about 1 ppm (about 8 cpm above background).