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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 (October 2004 to December 2004)

In the previous quarter initial experiments on the extraction of uranium from 3 M nitric acid as a function of total nitrate was examined. The slope to evaluate the nitrate stoichiometry was determined from the concentration data and was found to be 2.1 ± 0.1 at 3 M HNO_3 with a total nitrate concentration up to 10 M.

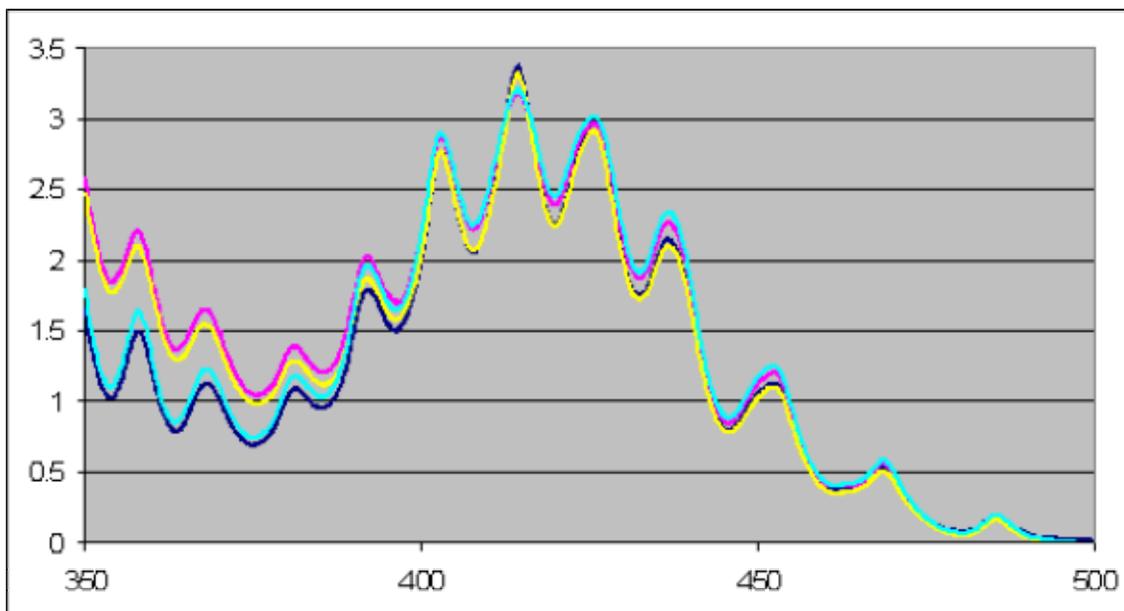
Work performed in current quarter (January 2005 to March 2005)

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 (Figure 1).

Figure 1. Comparison of quartz to PMMA cuvettes: Blue and yellow are quartz; teal and fuschia are PMMA



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 shows 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.