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

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Fundamental Chemistry of U and Pu in the TBP-Dodecane-Nitric Acid System
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DOE Collaborator: Dr. George Vandegrift, ANL
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 AFCI. 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 this quarter (July 2004 to September 2004)

In this quarter work was 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 UO₂(NO₃)₂·6H₂O (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 LiNO₃. 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. Sample analysis will be performed this quarter. Samples were returned, and a small volume of aqueous uranyl ion was titrated into the system at constant acid molarity. The same solution was evaluated with a nitrate specific electrode to determine nitrate concentration in the organic phase. Phase volumes were determined by mass using density measurements. Extinction coefficients for aqueous phase uranyl nitrate were determined using laboratory prepared samples. Acid concentration in each phase was determined by titration with a Metrohm titration apparatus. The organic phase was washed twice with water to remove the acid and oxalate was added to aqueous phase to bind the uranium and prevent complexation with hydroxide during the titration. Material balance
calculations enabled determination of total organic phase metal content, from which extinction coefficients for the normal and light organic phases were determined. The aqueous uranium concentration was determined by ICP-AES. An example of the uranium data is provided below. 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 HNO₃.

\[
\begin{array}{ccc}
\text{[NO3-] M} & \text{[UO2 2+]aq} & \text{[UO2 2+] org} \\
3.4 & 1.44E-02 & 1.86E-01 \\
4 & 5.22E-03 & 1.95E-01 \\
5 & 2.90E-03 & 1.97E-01 \\
6 & 2.00E-03 & 1.98E-01 \\
7 & 1.58E-03 & 1.98E-01 \\
8 & 1.18E-03 & 1.99E-01 \\
9 & 2.09E-03 & 1.98E-01 \\
10 & 1.97E-03 & 1.98E-01 \\
\end{array}
\]

\[
y = m1 + m2 \cdot M0
\]

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<thead>
<tr>
<th></th>
<th>Value</th>
<th>Error</th>
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<tbody>
<tr>
<td>m1</td>
<td>0.32115</td>
<td>0.091891</td>
</tr>
<tr>
<td>m2</td>
<td>2.1212</td>
<td>0.1189</td>
</tr>
<tr>
<td>Chisq</td>
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<td>NA</td>
</tr>
<tr>
<td>R</td>
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