

2004

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


Kenneth Czerwinski

University of Nevada, Las Vegas, czerwin2@unlv.nevada.edu

Byron Bennett

University of Nevada, Las Vegas

Follow this and additional works at: https://digitalscholarship.unlv.edu/hrc_trp_separations

 Part of the [Analytical Chemistry Commons](#), [Chemical Engineering Commons](#), [Oil, Gas, and Energy Commons](#), and the [Physical Chemistry Commons](#)

Repository Citation

Czerwinski, K., Bennett, B. (2004). Fundamental Chemistry of U and Pu in the TBP-Dodecane-Nitric Acid System: Quaterly Report. 1-2.

Available at: https://digitalscholarship.unlv.edu/hrc_trp_separations/86

This Report is protected by copyright and/or related rights. It has been brought to you by Digital Scholarship@UNLV with permission from the rights-holder(s). You are free to use this Report in any way that is permitted by the copyright and related rights legislation that applies to your use. For other uses you need to obtain permission from the rights-holder(s) directly, unless additional rights are indicated by a Creative Commons license in the record and/or on the work itself.

This Report has been accepted for inclusion in Separations Campaign (TRP) by an authorized administrator of Digital Scholarship@UNLV. For more information, please contact digitalscholarship@unlv.edu.

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

Professor Ken Czerwinski
Harry Reid Center
Department of Chemistry
University of Nevada, Las Vegas

Department of Chemistry and

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 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 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 $\text{UO}_2(\text{NO}_3)_2 \cdot 62\text{O}$ (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. 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 HNO_3 .

[NO ₃ ⁻] M	[UO ₂ ²⁺]aq	[UO ₂ 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

