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Separation Science and Technology

Publication details, including instructions for authors and subscription information:

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J. Plaue^a; A. Gelis^b; K. Czerwinski^c

^a Defense Nuclear Facilities Safety Board*, Washington DC, USA ^b Chemical Engineering Division, Argonne National Laboratory, Argonne, IL, USA ^c Department of Chemistry, University of Nevada, Las Vegas, Nevada, USA

To cite this Article Plaue, J. , Gelis, A. and Czerwinski, K.(2006) 'Actinide Third Phase Formation in 1.1 M TBP/Nitric Acid/Alkane Diluent Systems', *Separation Science and Technology*, 41: 10, 2065 – 2074

To link to this Article: DOI: 10.1080/01496390600745362

URL: <http://dx.doi.org/10.1080/01496390600745362>

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J. Plaue

Defense Nuclear Facilities Safety Board*, Washington DC, USA

A. Gelis

Chemical Engineering Division, Argonne National Laboratory,
Argonne, IL, USA

K. Czerwinski

Department of Chemistry, University of Nevada, Las Vegas,
Nevada, USA

Abstract: Additional information on the organic phase speciation of Np and Pu was obtained in order to further understand the impact on third phase formation. In the Np(VI) extraction system, indications of the presence of a species associated with the absorbance at 1210 nm appears to be consistent with an increased tendency for third phase formation. Attempts to couple this absorption peak to a higher order nitrate species were inconclusive, and further study is required. For Pu(VI), continued evidence has emerged suggesting a role of higher order nitrate species in third phase formation.

Keywords: Third phase, plutonium, neptunium, speciation, tri-*n*-butyl phosphate

Received 23 October 2005, Accepted 10 March 2006

*The views expressed are solely those of the author and no official support or endorsement of this manuscript by the Defense Nuclear Facilities Safety Board or the federal government is intended or should be inferred.

Address correspondence to J. Plaue, Defense Nuclear Facilities Safety Board, 625 Indiana Ave, Washington DC, 20004, USA. E-mail: jplaue@alum.mit.edu

INTRODUCTION

Third phase formation is the solvent extraction phenomenon known to occur under certain conditions resulting in a spilt of the organic phase into a heavy phase and a light phase. The heavy phase consists mostly of extractant, acid, and metal salt, while the light phase is mainly diluent. The PUREX process, which extracts plutonium dissolved in nitric acid into an organic phase consisting of tri-*n*-butyl phosphate (TBP) mixed with a diluent (1), is a common solvent extraction system with the potential to form third phase. When separating actinides from fission products, formation of the heavy third phase can lead to a number processing and safety concerns, such as an increased potential for criticality or runaway decomposition reactions (e.g., Red Oil). For these reasons, a deeper understanding of the chemistry involved in third phase formation can be useful for integrating safety into process design.

For example, the U.S. Department of Energy is currently pursuing research in advanced separations to reduce the impact of nuclear waste on a future geological repository. Many of the flowsheets under study build upon the fundamental chemistry of the PUREX process, but lead to different final product streams (e.g., Pu/Np) which may eventually support advanced fast reactor fuels (2). Increased study of the organic phase chemistry, since the third phase behavior in these systems is largely unknown, is therefore necessary.

Historically, third phase formation has been studied through the determination of the organic phase conditions (i.e., temperature, acid and metal concentrations) which lead to formation of the heavy phase. The impact of these conditions on the limiting organic concentration (LOC), the maximum organic phase metal concentration prior to a observation of phase splitting, has been extensively reviewed (3).

More recently, several investigations have examined third phase formation from the perspective of surfactant and colloid science (4–8). Small angle neutron scattering techniques have been used to probe third phase formation, resulting in evidence that suggests the formation of the heavy phase results from the interaction of small reverse micelle-like aggregates of 3 to 4 TBP molecules per metal nitrate complex. Specifically, these studies have noted this reverse micelle behavior in TBP extraction of nitric acid systems containing Zr(IV), Th(IV), U(VI), and Pu(IV). It is well known that each of these cations has different tendencies to induce third phase, as observed by the variation in LOCs (3). However, an explanation linking third phase to properties of the metal has been lacking. In their paper focusing on Zr(IV), Chiarizia et al. attempted to correlate the potential energy of interaction, $-U(r)$, with fundamental properties of the cations (7). They were able to demonstrate a reasonably linear relationship between the derivative of $-U(r)$ with respect to the total nitrate concentration in the organic phase and the cation hydration enthalpy or ionization potential.

With this finding, a detailed understanding of actinide speciation in the organic phase becomes even more important, given that the total organic nitrate concentration appears to be closely related to third phase formation. Classically, both tetravalent and hexavalent nitrate actinide species have been known to form disolvate complexes with TBP ($\text{An}^{m+}(\text{NO}_3)_m \cdot 2\text{TBP}$) (9). These stoichiometries were also recently confirmed at the hundredth molar metal concentration in pure TBP using x-ray absorption spectroscopy (10). Generally, there is a paucity of experimental data at higher metal concentrations in the organic phase. For example, the conditions of these two referenced experiments differed substantially from the regions near the LOC.

This manuscript attempts to build upon the link between the speciation of the actinides in the organic phase and the tendency to form third phase. Additional information on the speciation of Np and Pu in the extracted TBP phase is presented in order to increase the fundamental understanding of the extraction process.

METHODS

Methods used in these experiments are described in detail elsewhere (7, 11, 12). Stock aqueous solutions of purified ^{237}Np and ^{242}Pu were prepared using nitric acid dissolution and anion exchange purification techniques. Organic phases were prepared using 1.1 M TBP (Aldrich 99+%) in dodecane (Aldrich) without further purification. Generally, samples consisting of 500 to 1000 μL of each phase were vigorously contacted for 5 minutes using a vortex mixer and then centrifuged to assist phase separation to completion. This procedure resulted in distinct two and three phase solutions, which were sampled for further analysis. All work was performed at room temperature (22°C).

Samples with increasing organic phase metal concentrations were prepared and then analyzed (e.g., UV-visible spectroscopy, titration, radio-nuclide counting, etc.). Consistent with the literature practice, the LOC was determined by visual observation as the highest metal concentration in the organic phase prior to any obvious phase splitting or cloudiness. The general methodology for identification of LOC was confirmed through the approach to LOC with small additions of concentrated metal solution at the desired acidity into the aqueous phase, until formation of a third phase, as well as dilution of a loaded organic phase using pristine organic, until dissolution of the third phase.

RESULTS AND DISCUSSION

In order to motivate the experiments discussed below, trends in the LOC data obtained from the literature and experiments for tetravalent and hexavalent

forms of U, Np, and Pu at constant conditions (7 M HNO₃, 1.1 M TBP/dodecane, 20–25°C) are presented in Fig. 1 (12). For the tetravalent species, U(IV) has the strongest propensity to form a third phase, followed by Np(IV) and then Pu (IV). The order is reversed for the hexavalent actinides, with U(VI) not forming a third phase under the described conditions. Given these trends, an attempt was made to further elucidate the chemistry behind them.

Neptunium Third Phase Boundaries

The third phase formation boundaries for Np(IV) and Np(VI) oxidation states were determined and the conditions, including organic phase nitric acid concentrations, are reported in Table 1. In terms of the magnitude of the LOCs, neptunium behaves similarly to uranium in lower molarity acid systems, with the hexavalent state generally less susceptible to third phase formation than the tetravalent. However, in systems with acid concentrations above approximately 7 M, the two valence states behave very similarly with respect to third phase formation. This behavior is unique to neptunium, and appears to support a trend observed by these authors of the increased ability of hexavalent actinides to form third phase as one progresses from uranium to plutonium (12).

The results of the titration studies of the organic phase at LOC can be used to determine the role of nitric acid in the extracted Np species. Using a mass balance of the available TBP and assuming a solvation number of 2 for the Np species, the nitric acid species can be determined. For the tetravalent system, based on material balance of available TBP, the data suggest a mixture of the

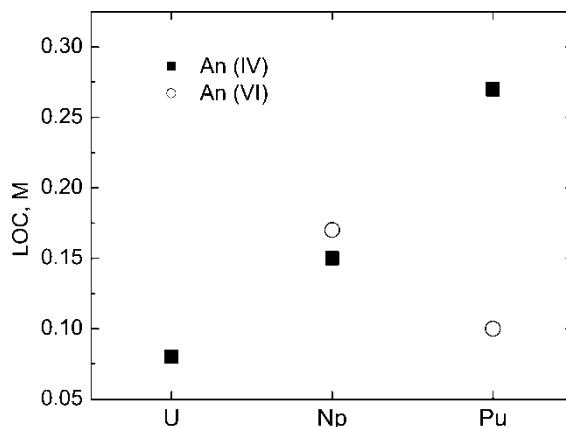


Figure 1. Actinide LOC values in 7 M HNO₃/1.1 M TBP/dodecane, M at T = 20–25°C (Data reproduced from Reference 12).

Table 1. Concentrations at the LOC boundary for neptunium, M

| [HNO ₃] _{aq} | Np(IV) | [H ⁺] _{org} | Error | Np(VI) | [H ⁺] _{org} | Error |
|-----------------------------------|--------|----------------------------------|-------|--------|----------------------------------|-------|
| 4 | 0.10 | 1.39 | 0.03 | 0.27 | 1.01 | 0.01 |
| 6 | 0.12 | 1.49 | 0.02 | 0.23 | 1.20 | 0.02 |
| 7 | 0.15 | 1.51 | 0.01 | 0.17 | 1.51 | 0.17 |
| 8 | 0.10 | 1.62 | 0.02 | 0.14 | 1.46 | 0.02 |
| 10 | 0.10 | 1.52 | 0.06 | 0.08 | 1.72 | 0.02 |

Note: Error values represent the 95% confidence level of duplicate analysis. For the metal concentrations, error is conservatively estimated at $\pm 10\%$.

monosolvate (TBP · HNO₃) and hemisolvate (TBP · 2HNO₃) acid species. For the hexavalent species, the data indicate the dominance of the hemisolvate acid species. These results are in agreement with previous studies that have examined the extraction of nitric acid with Th(IV) and U(VI) (13, 14).

Spectroscopic Study

Some early work on third phase formation (15, 16) suggested the presence of the uranyl trinitrato complex, UO₂(NO₃)₃⁻, as the source of third phase formation. Such a large charged complex would act similarly to perchloric acid, which has a strong tendency to form third phase (17). However, subsequent detailed infrared spectroscopy and x-ray absorbance investigations on the uranyl system did not find evidence to support the existence of the trinitrato species in organic TBP phase (18). With respect to third phase formation, no further detailed studies of the actinide organic phase speciation have been performed for either Np or Pu.

Small reverse micelles in similar actinide-TBP-nitrate solutions have been experimentally determined to have hard sphere diameters of 10–20 Å (5, 6, 8). This size particle would not generally be expected to interfere with the UV-visible spectra of its constituent molecular complexes (TBP-actinide-nitrate). The work here attempts to examine the spectra of the organic phase as the chemical conditions are changed in order to elucidate whether there are particular species driving the formation of the reverse micelles. Experimentally, direct examination of the heavy phase by UV-visible spectroscopy becomes prohibitively difficult, due to the near-saturated absorbance produced from the high metal concentrations.

As an extension of our earlier work (12), selected organic phase samples were evaluated for spectral changes to correlate speciation variations to third phase formation. Spectra taken at the Np(VI) LOC condition at various initial aqueous nitric acid concentrations are presented in Fig. 2. The main features are two prominent absorption peaks at approximately 1120 and 1210 nm. The minor peak near 1000 nm is attributed to trace Np(V) formed from the

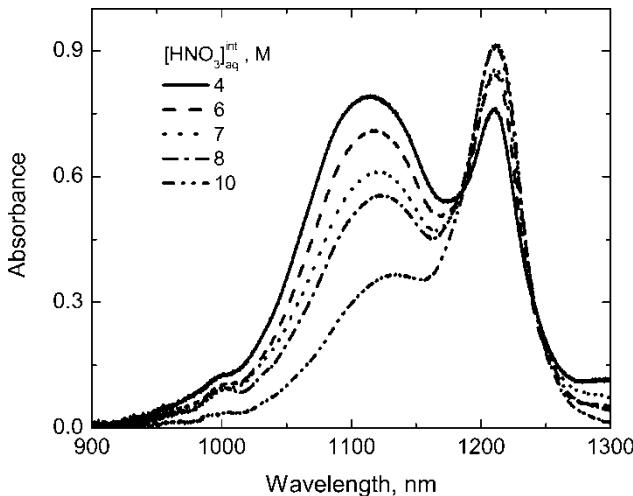


Figure 2. UV-Visible spectra of Np(VI) in 1.1 M TBP/dodecane as a function of LOC varying with initial aqueous HNO_3 at 22°C.

reduction of the hexavalent state upon extraction. The spectra reveal a definite increase of the peak near 1210 nm as the acid concentration is increased. This suggests the formation of a possible different organic phase species as a function of the organic phase metal and nitric acid concentrations. The variation in nitric acid concentration can lead to either an addition of nitrate or nitric acid to the extracted moiety.

A similar experiment was performed on the Np(IV) LOC samples and no notable features were observed. In fact, the trend observed in Np(VI) is the first report of significant changes in TBP-actinide spectra. For example, Pu(IV) has been widely studied and found to exhibit nearly stable spectra under various acid conditions (19). Spectra of the heavy and light phases for both valences were examined, but useful information could not be obtained due to high absorbance at the necessary metal concentrations.

Based on the initial interesting observations in the Np(VI) system, further attempts to elucidate the species involved in spectral changes were performed. The effect of nitrate concentration is shown in Fig. 3 for both the organic and aqueous phases. Both sets of spectra were taken from an initial solution containing a Np(VI) concentration of 0.03 M and an aqueous nitric acid concentration of 4 M. Four sets of solutions, with total nitrate concentration varied by adding sodium nitrate solid to the systems, were equilibrated with the organic phase and examined using UV-visible spectrometry.

The spectral trends in each system were contradictory. For the aqueous system, as nitrate is increased, the species associated with the 1120 nm absorption increases, while the 1225 nm absorption decreases. In addition, an isobestic point was observed at 1142 nm. In the organic phase the opposite

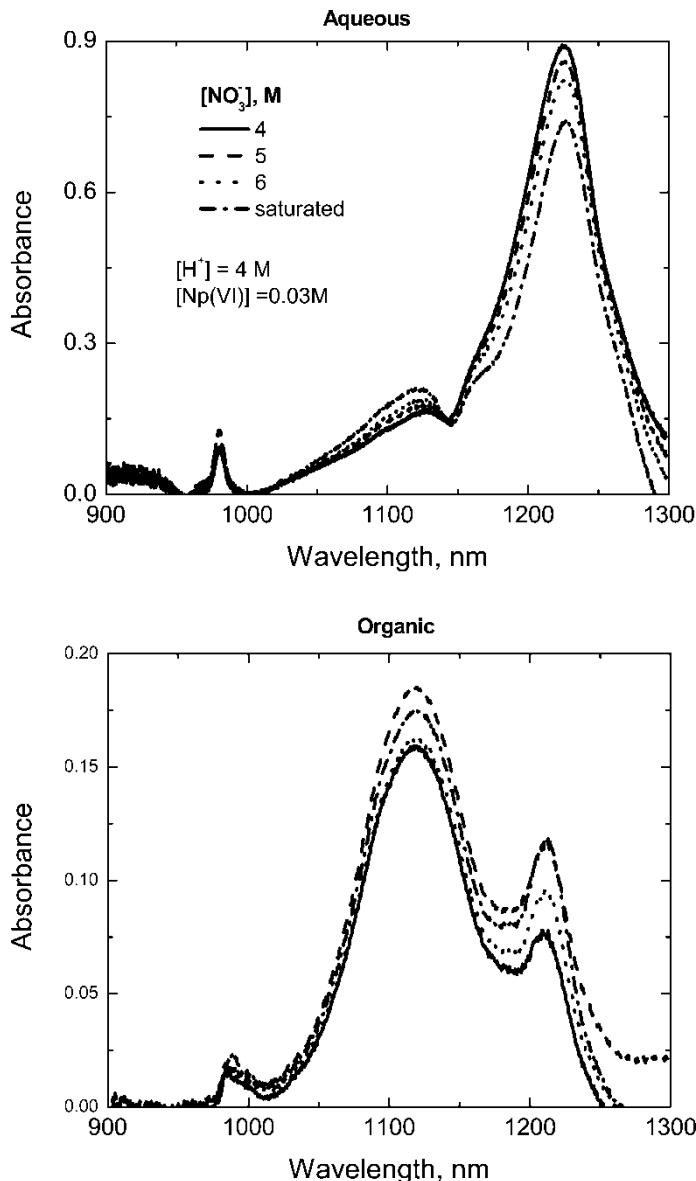


Figure 3. Effect of nitrate concentration on Np(VI) UV-Visible spectra for initial aqueous phase and resulting organic phase of 1.1 M TBP in dodecane at 22°C.

trend was observed; as nitrate is increased, the absorbance at 1120 nm decreases, though there appears to be an aberration in the data associated with the 4 M nitrate sample. Also, the peak previously observed at 1225 nm in the aqueous phase has now shifted to 1210 nm.

Based on the findings indicating a significant impact of the presence of Pu(VI) on increased third phase susceptibility (8, 11), further spectroscopic investigations on the organic phase were performed. Spectroscopic evidence for anionic plutonyl trinitrato species, $\text{PuO}_2(\text{NO}_3)_3^-$, has been found in nitric acid aqueous phases with a characteristic peak at 812 nm (19). However, others performing similar research in acetone media, have attributed the occurrence of this peak simply from a shift from the free PuO_2^{2+} to the dinitrato complex, $\text{PuO}_2(\text{NO}_3)_2$ (21).

The results of our Pu(VI) metal loading experiment in 7 M HNO_3 into 1.1 M TBP in dodecane are presented in Fig. 4. Unfortunately, the high extinction coefficient of Pu(VI) prevented study of higher metal concentrations on order of the LOC. Under the conditions studied, three absorption peaks are observed at 809, 820, and 835 nm. As Pu(VI) increases, an increase in the prominence of the 809 and 820 nm peaks is observed, in addition to the disappearance of the shoulder associated with the 835 nm peak. It is possible that the increase associated with the 809 nm absorption, assuming a shift due to TBP complexation, may be related to the plutonyl trinitrato species as previously suggested.

CONCLUSIONS

Based on the observation of differences in the tendencies for U, Np, and Pu to form third phases, additional information on the organic phase speciation of

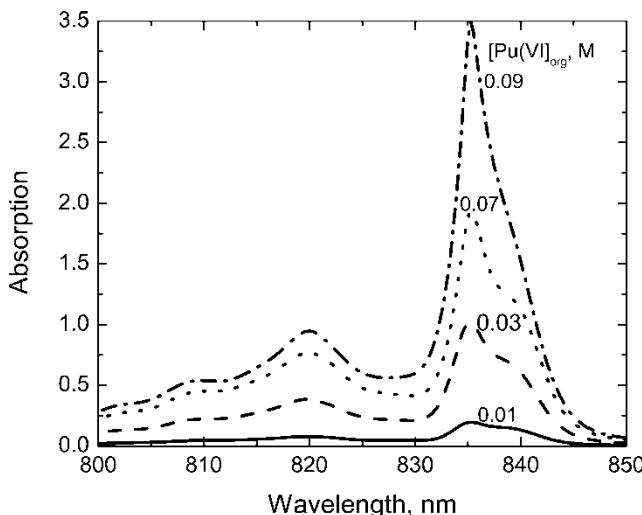


Figure 4. UV-Visible spectra of Pu(VI) extracted into 1.1 M TBP/dodecane from 7 M HNO_3 at 22°C.

Np and Pu was obtained in order to further understand the third phase formation mechanism. The third phase boundary for both Np(IV) and Np(VI) was measured. In the Np(VI) system, a study of the UV-visible spectra at the LOC revealed indications of a species associated with the absorbance at 1210 nm to be consistent with an increased tendency for third phase formation (lower LOC). Attempts to couple this absorption peak to a higher order nitrate species were inconclusive, and further study is required. For Pu(VI), a spectroscopic study of the impact of nitrate concentration, continues to suggest a key role for higher order nitrate species in third phase formation.

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