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Actinide Third Phase Formation in 1.1 M TBP/Nitric Acid/Alkane Diluent Systems

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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.

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46 **INTRODUCTION**

47

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

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

69 Historically, third phase formation has been studied through the determi-
70 nation of the organic phase conditions (i.e., temperature, acid and metal con-
71 centrations) which lead to formation of the heavy phase. The impact of these
72 conditions on the limiting organic concentration (LOC), the maximum organic
73 phase metal concentration prior to a observation of phase splitting, has been
74 extensively reviewed (3).

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

Actinide Third Phase Formation

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91 With this finding, a detailed understanding of actinide speciation in the
92 organic phase becomes even more important, given that the total organic
93 nitrate concentration appears to be closely related to third phase formation.
94 Classically, both tetravalent and hexavalent nitrate actinide species have
95 been known to form disolvate complexes with TBP ($An^{m+}(NO_3)_m \cdot 2TBP$)
96 (9). These stoichiometries were also recently confirmed at the hundredth
97 molar metal concentration in pure TBP using x-ray absorption spectroscopy
98 (10). Generally, there is a paucity of experimental data at higher metal concen-
99 trations in the organic phase. For example, the conditions of these two referen-
100 ced experiments differed substantially from the regions near the LOC.

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

METHODS

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110 Methods used in these experiments are described in detail elsewhere
111 (7, 11, 12). Stock aqueous solutions of purified ^{237}Np and ^{242}Pu were
112 prepared using nitric acid dissolution and anion exchange purification techni-
113 ques. Organic phases were prepared using 1.1 M TBP (Aldrich 99+%) in
114 dodecane (Aldrich) without further purification. Generally, samples consisting
115 of 500 to 1000 μL of each phase were vigorously contacted for 5 minutes
116 using a vortex mixer and then centrifuged to assist phase separation to com-
117 pletion. This procedure resulted in distinct two and three phase solutions,
118 which were sampled for further analysis. All work was performed at room
119 temperature (22°C).

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

RESULTS AND DISCUSSION

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

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

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145 Neptunium Third Phase Boundaries

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

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

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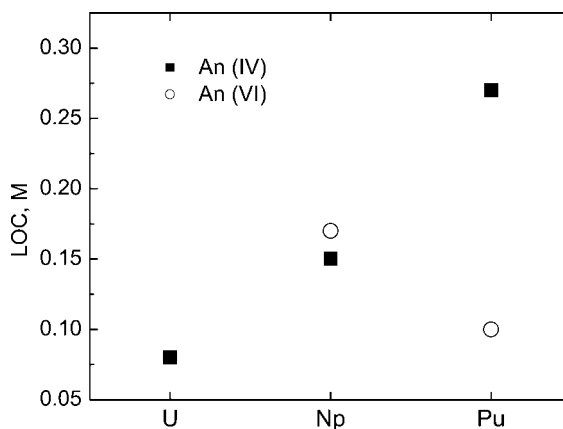
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179 **Figure 1.** Actinide LOC values in 7M HNO₃/1.1M TBP/dodecane, M at
180 T = 20–25°C (Data reproduced from Reference 12).

Actinide Third Phase Formation

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

182	[HNO ₃] _{aq}	Np(IV)	[H ⁺] _{org}	Error	Np(VI)	[H ⁺] _{org}	Error
184	4	0.10	1.39	0.03	0.27	1.01	0.01
185	6	0.12	1.49	0.02	0.23	1.20	0.02
186	7	0.15	1.51	0.01	0.17	1.51	0.17
187	8	0.10	1.62	0.02	0.14	1.46	0.02
188	10	0.10	1.52	0.06	0.08	1.72	0.02

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

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 192
 193 monosolvate (TBP · HNO₃) and hemisolvate (TBP · 2HNO₃) acid species. For
 194 the hexavalent species, the data indicate the dominance of the hemisolvate
 195 acid species. These results are in agreement with previous studies that have
 196 examined the extraction of nitric acid with Th(IV) and U(VI) (13, 14).

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199 **Spectroscopic Study**

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

210 Small reverse micelles in similar actinide-TBP-nitrate solutions have
 211 been experimentally determined to have hard sphere diameters of 10–20 Å
 212 (5, 6, 8). This size particle would not generally be expected to interfere
 213 with the UV-visible spectra of its constituent molecular complexes (TBP-
 214 actinide-nitrate). The work here attempts to examine the spectra of the
 215 organic phase as the chemical conditions are changed in order to elucidate
 216 whether there are particular species driving the formation of the reverse
 217 micelles. Experimentally, direct examination of the heavy phase by
 218 UV-visible spectroscopy becomes prohibitively difficult, due to the near-
 219 saturated absorbance produced from the high metal concentrations.

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

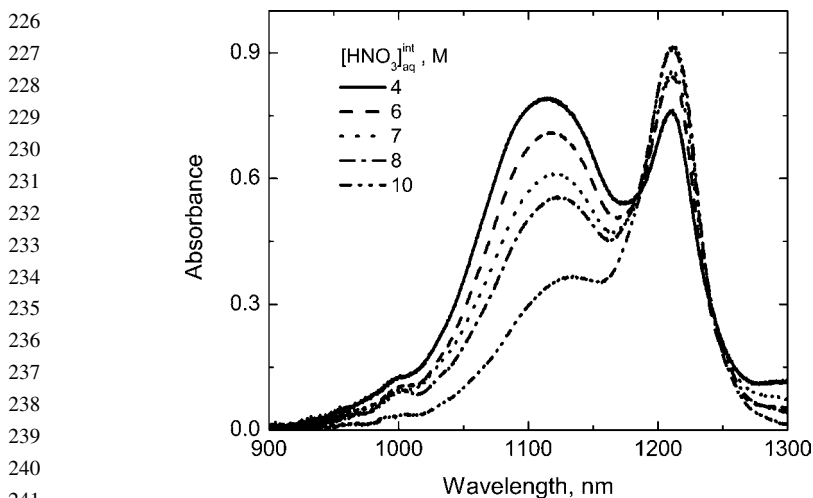


Figure 2. UV-Visible spectra of Np(VI) in 1.1 M TBP/dodecane as a function of LOC varying with initial aqueous HNO_3 at 22°C .

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

Actinide Third Phase Formation

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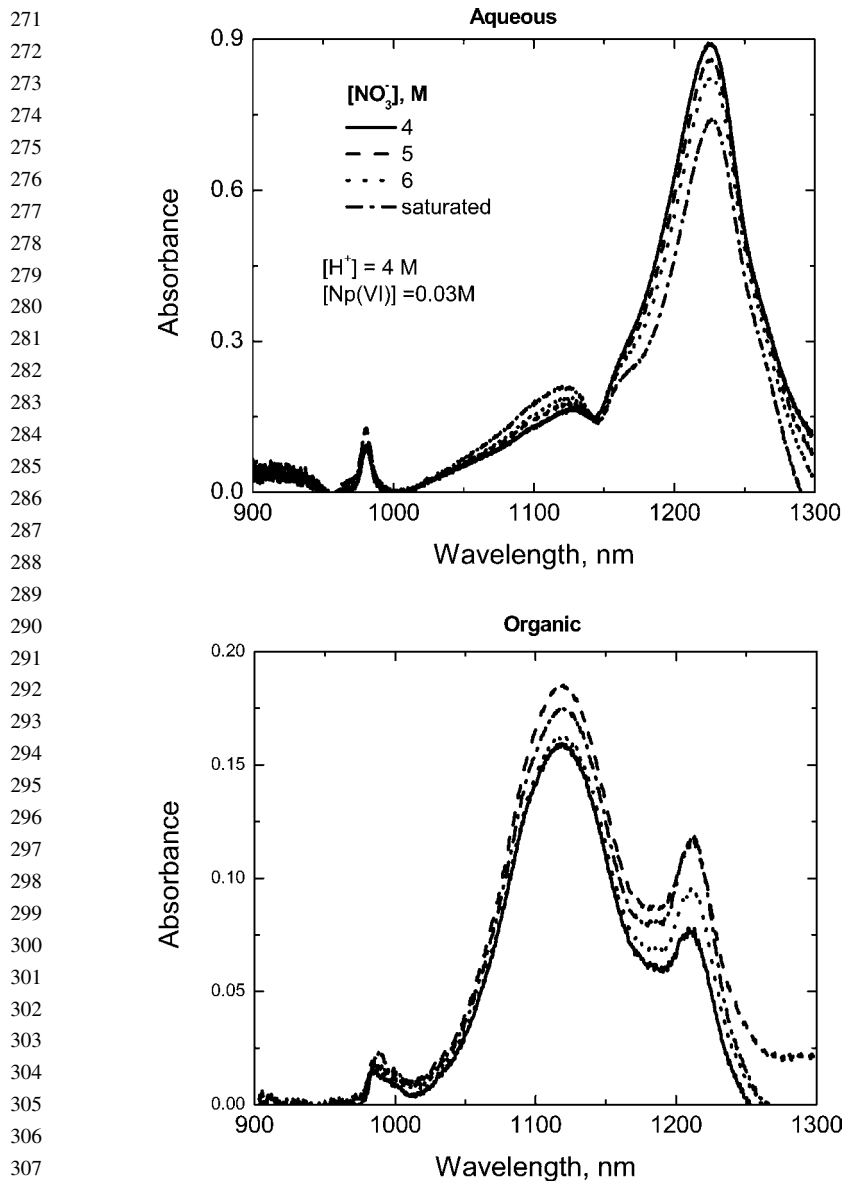


Figure 3. Effect of nitrate concentration on Np(VI) UV-Visible spectra for initial aqueous phase and resulting organic phase of 1.1 M TBP in dodecane at 22°C.

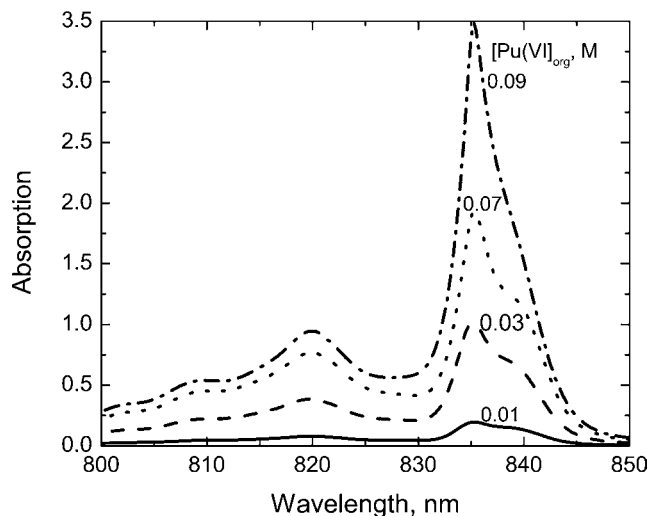
trend was observed; as nitrate is increased, the absorbance at 1120 nm decreases, though there appears to be an aberration in the data associated with the 4 M nitrate sample. Also, the peak previously observed at 1225 nm in the aqueous phase has now shifted to 1210 nm.

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

324 The results of our Pu(VI) metal loading experiment in 7 M HNO_3 into
325 1.1 M TBP in dodecane are presented in Fig. 4. Unfortunately, the high extinction
326 coefficient of Pu(VI) prevented study of higher metal concentrations on
327 order of the LOC. Under the conditions studied, three absorption peaks are
328 observed at 809, 820, and 835 nm. As Pu(VI) increases, an increase in the
329 prominence of the 809 and 820 nm peaks is observed, in addition to the
330 disappearance of the shoulder associated with the 835 nm peak. It is
331 possible that the increase associated with the 809 nm absorption, assuming a
332 shift due to TBP complexation, may be related to the plutonyl trinitrato
333 species as previously suggested.

336 CONCLUSIONS

338 Based on the observation of differences in the tendencies for U, Np, and Pu to
339 form third phases, additional information on the organic phase speciation of
340



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

Actinide Third Phase Formation**9**

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

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