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Plutonium Third Phase Formation in the 30% TBP/Nitric Acid/Hydrogenated Polypropylene Tetramer System

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Abstract: A study on plutonium third phase formation in 30% TBP/nitric acid/hydrogenated polypropylene tetramer (HPT) was performed. Characterization studies of HPT indicate its composition to be a mixture of many highly branched alkanes with a volatility close to *n*-undecane. This composition results in about a factor of two better resistance to Pu(IV) third phase formation than dodecane. At 7 M nitric acid in the aqueous phase, the presence of Pu(VI) was observed to substantially reduce the organic phase metal concentration necessary to induce phase splitting in both diluents. Spectroscopic investigation of mixed valence systems also suggest a prominent role for Pu(VI) in the formation of the dense organic phase. Accumulation of Pu(VI) in the heavy phase, as well as certain spectral features, suggest that Pu(VI) is

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forming a different species, possibly a plutonyl trinitrato, with a strong tendency to form third phase.

INTRODUCTION

It is well known that under certain conditions in solvent extraction, the organic phase may split into a heavy phase rich in extractant, acid, metal; and a light phase consisting of mostly diluent (see Fig. 1). This phenomenon, known as third phase formation, is especially problematic in systems involving metal ions with higher valence states, such as the actinides. The PUREX process, which extracts plutonium dissolved in nitric acid, into an organic phase of
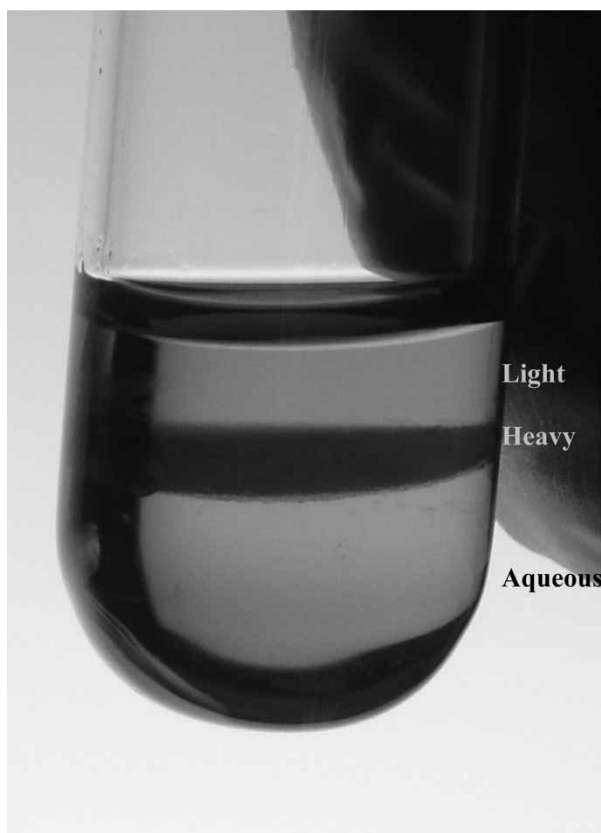
Figure 1. Third phase formation in 1.1 M TBP/HPT. Note the dark color of the metal enriched heavy phase. Sample in the photograph was for mixed plutonium oxidation state.

tri-n-butyl phosphate (TBP) mixed with a diluent,[1] is one common solvent extraction system with the potential to form third phase. A complete understanding of third phase formation is necessary for several key safety issues. Third phase formation has been shown to lead to organic phases with densities higher than the aqueous phase, thus creating a phase inversion. While problematic from a simple material handling prospective, the phase inversion can also be a criticality concern. The formation of the third phase presents issues with organic/aqueous phase separators and can lead to carry over of high concentration organics to undesired unit operations such as an evaporator. It has been suspected that third phase formation contributed to the 1993 Red Oil event at Tomsk in Seversk, Russia.[2]

Vasudeva Rao and Kolarik[3] have extensively reviewed third phase formation in nuclear solvent extraction systems with TBP. Typically, results are reported as a limiting organic concentration (LOC), which is the maximum concentration of metal found in the organic phase prior to a visual observation of phase splitting. For systems involving plutonium, the effects of several variables (nitric acid and extractant concentrations, temperature, diluent and extractant types, and ionic strength) have been studied on the third phase formation boundaries.[4−8]

These works provide some useful basic information on third phase formation in plutonium systems. No published information is available on the chemical properties or third phase behavior of hydrogenated polypropylene tetramer (HPT), which may also be known as 4,4 dipropyl heptane or tétrapropylène hydrogéné. It may be assumed to be somewhat similar in nature to other commercial branched diluents such as Amsco™, Shellsol-T™, and Hyfrane™. HPT is commonly used in the French reprocessing industry, specifically because of its resistance to third phase formation.

The composition is nominally considered to be a branched dodecane. While branching is known to increase resistance to third phase formation,[9] there are several tradeoffs which must be considered during process design. First, branched mixtures typically have flashpoints at about 60°C,[10] while that of pure dodecane is 74°C.[11] Second, branching of organic molecules has been known to reduce radiation and chemical stability.

While more advanced techniques to study third phase formation have been demonstrated,[12] the intent of this paper was to determine: (i) the phase separation boundary for Pu(IV) in HPT, and (ii) the impact of Pu(VI) on the phase boundary. The HPT was examined by gas chromatography-mass spectrometry (GC-MS) to provide information on the general molecular structure. The acid concentration in the organic phase was determined by titration. This data was used in combination with UV-Visible spectroscopy to evaluate the speciation, primarily oxidation state, of the extracted Pu organic complex as a function of experimental conditions. The experiments were conducted using phase volumes from 0.5 mL to 1.0 mL, as this work was also meant to demonstrate that small volumes can be used in the examination of third phase phenomena.

METHODS

Work was performed at the Chemical Engineering Division at the Argonne National Laboratory (ANL). Plutonium nitrate solutions were prepared from the nitric acid dissolution of ANL plutonium oxide stocks. All plutonium used was ^{242}Pu (99.9% by mass), which minimized radiolysis effects in the organic phase, and reduced the radiological hazards involved with the experiments. The stock solution was freshly purified using anion exchange on a Reillex HPQ resin column. The pure tetravalent state was prepared by reduction with hydrogen peroxide.[14] Mixed ratios of valence states were produced through various degrees of heating with concentrated nitric acid. The pure hexavalent state was prepared by fuming perchloric acid taken to a wet salt, and redissolved in 7M nitric acid. Valence adjustments were verified by UV-Visible spectroscopy at the characteristic absorptions for Pu(IV) and Pu(VI).[13]

Organic phases were prepared using TBP (Aldrich 99+%), HPT (Panchim, France), and dodecane (Aldrich) without further purification. Without published signatures for the pristine HPT organic phase, the potential for impurities could not be precluded. Because of the industrial relevance, this work only investigated 30 volume percent TBP (1.1 M) in the organic phase. Prior to extraction experiments, all organic phases were pre-equilibrated with equal volumes of the appropriate nitric acid concentration.

Generally, samples consisting of 500 μL per phase (1000 μL for certain spectroscopic investigations) were vigorously contacted for 5 min using a vortex mixer and then centrifuged. Consistent with the literature practice,[3] 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 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. All work was performed at room temperature, which was observed to be an approximately stable 22°C at the laboratory work station.

Plutonium concentrations were determined using liquid scintillation counting of triplicate 10 μL aliquots of a sample of organic phase further diluted in dodecane. Organic phase acid concentrations were determined in duplicate by stripping 10 μL aliquots diluted with dodecane into an equal volume of 0.1 M ammonium oxalate, followed by a contact with deionized water. The aqueous phases were combined and titrated against 0.0098 N sodium hydroxide using an automated Metrohm 716 titrator with a semi-micro Orion, sealed, gel combination electrode. Absorption spectra were taken on a Cary 5 UV-Visible-Near Infrared spectrometer using 5 mm path length quartz cells.

Characterization of HPT was performed using a Varian Saturn-III GC-MS with a 30 meter, DB5 column, 0.25 micron surface coating using a He carrier gas. Samples were run from 40 to 280°C at a rate of 2°C/min. Major components were identified by elution time on GC based upon calibration with known straight chain C_8-C_{12} alkanes. Information on branching was obtained by evaluation of mass fragments at each major elution peak. Standard interpretation assumed fragmentation was most likely at a carbon-carbon branch, with the positive charge remaining with the molecular fragment.

RESULTS AND DISCUSSION

HPT Characterization

GC-MS analysis was performed on a sample of HPT in order to ascertain information on its structure and composition. The gas chromatogram (Fig. 2) reveals greater than 40 different types of molecules with the bulk approximately near the linear C_{11} calibration point. While the large peak near the linear C_{11} standard undoubtedly contains branched dodecane, as well as branched undecane, the peaks with retention times less than 15 min represent HPT components of lower molecular mass. No significant concentrations of molecules below the linear C_9 calibration or greater than the linear C_{12} calibration were found. In addition, infrared, proton NMR, and ^{13}C NMR spectra were taken and were negative for alcohols or other functionalities. The NMR spectra showed the presence of CH_3, CH_2, and CH groups
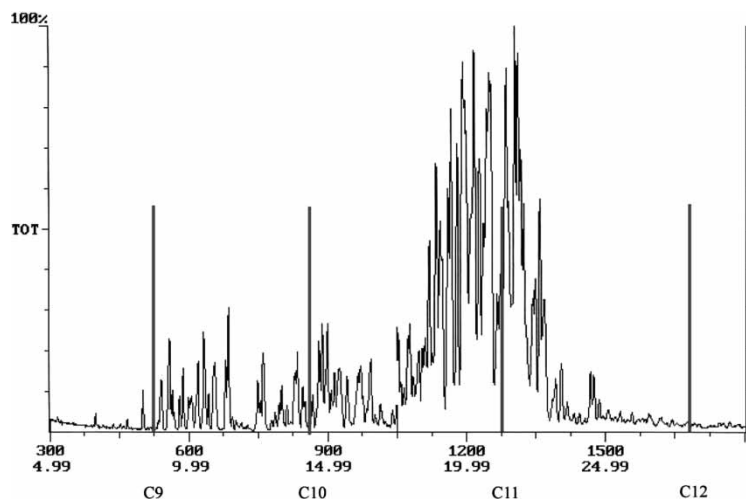
Figure 2. Gas chromatogram of HPT sample injection. The solid lines represent the retention times for linear standards.

with no spectral indication of conjugated ring systems. Mass spectra at major peaks show high percentage of fragments at 57 and 71 amu, suggesting 4 and 5 carbon branches in the parent molecule. Overall, these results indicate that HPT is not a single type of branched molecule, but rather a mixture of highly branched molecules with the volatility of the major fraction similar to the linear C_{11} standard. As expected the volatility of the HPT is less than linear C_{12}.

Third Phase Boundary

Basic information on the metal and acid composition of the third phase boundary was obtained over the range of initial aqueous nitric acid concentrations from 1 to 7 M. In samples below 6 M HNO_3, the visual observation technique was difficult to utilize due to the dark brown coloration of the lower Pu(IV) nitrate complexes in such high concentrations in the HPT systems. In addition, a time dependence on phase splitting was noted, as some LOC samples were found split after a period of time (stable greater than 4 h, but less than 24 h). It is possible this behavior was due to slight temperature variations following centrifugation. For consistency, the values reported here represent LOC as observed immediately following 5 min of centrifugation. In general, the similarity of the dodecane data with other published results suggests confidence in the experimental methods.

Composition values are presented in Table 1, with the error value reported in the table at the 95% confidence limit for triplicate analysis of Pu and acid concentration. Consistent with literature practice, the initial aqueous phase HNO_3 values presented in Table 1 reflect pre-equilibrated organic phases. It is estimated that the equilibrium acid concentrations were approximately 10 to 30% higher due to displacement of HNO_3 in the organic phase with plutonium nitrate. No third phase was observed to form in systems greater than 5 M nitric acid at loadings below the stoichiometric limit of 0.55 M Pu assuming the classical $Pu(NO_3)_4 \cdot 2$ TBP complex.[15] Examination of the

Table 1. Third phase boundary data for Pu(IV)/30% TBP/HPT at 22°C

| $[HNO_3]_{aq,}$ M	LOC, M	Error	$[H^+]_{org}$, M	Error
1	0.27	0.01	0.97	0.06
2	0.31	0.01	0.93	0.05
3	0.39	0.01	1.02	0.02
4	0.45	0.01	1.05	0.02
5	0.50	0.04	0.92	0.02
7	>0.52	0.09	ND	ND

ND means not determined.

extraction of nitric acid concentrations suggests of the monosolvate ($HNO_3 \cdot$ TBP) as the predominate species. This is consistent with other studies of tetravalent actinides.[16] For comparison purposes, the Pu(IV) LOC boundary for various diluents is presented in Fig. 3. Both branched diluents afford similar resistance to third phase of approximately 2 to 3 times the values for dodecane over a range of conditions.
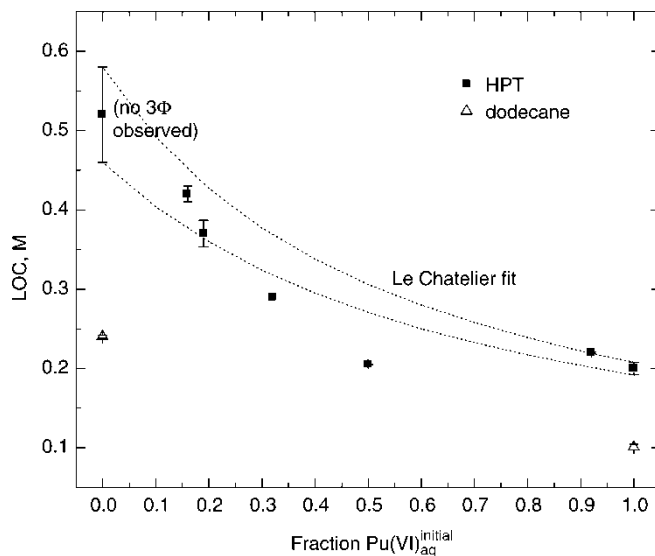
Effect of Pu(VI)

The impact of Pu(VI) in the initial aqueous phase on third phase formation was studied. Typically in industrial processes, care is taken to maintain plutonium in the tetravalent state because of its substantially higher distribution ratio values.[17] However, there are conceivable conditions (i.e., evaporators) where plutonium oxidation may occur and it is therefore necessary to evaluate the impact of the hexavalent state.

For the 1.1 M TBP/HPT system, several stock solutions were prepared at 7 M HNO_3 with varying percentages of Pu(VI), and then the LOC determined. The acid conditions were chosen solely for ease of experimentation. The results (Fig. 4) show an impact of the presence of Pu(VI). The LOC is related to the sum of Pu(IV) and Pu(VI). Pure Pu(IV) does not form third phase (to the stoichiometric limit) in the HPT system at 7 M or greater
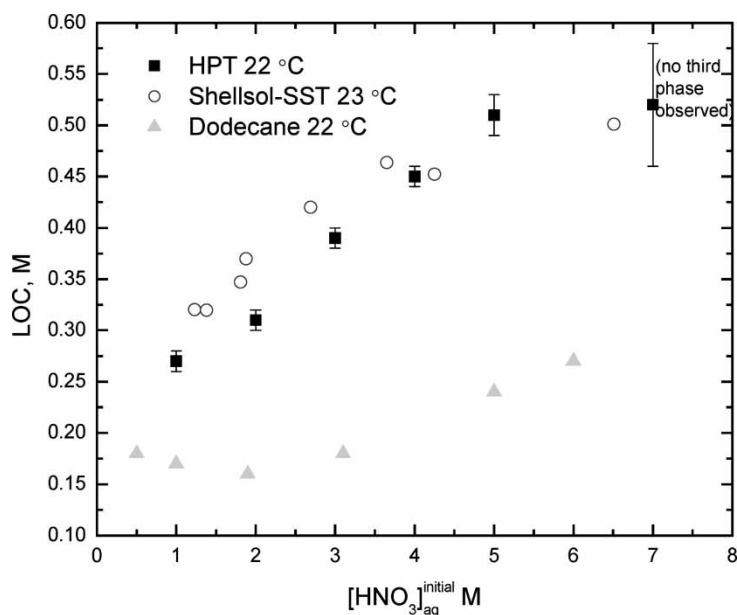
Figure 3. Comparison of Pu(IV) LOC values for various diluents. Other curves based on literature for Shellsol (8) and dodecane (3). Error bars represent 95% confidence levels.

Figure 4. Effect of Pu(VI) on third phase formation in 1.1 M TBP from 7 M HNO$_3$.
Error bars represent 95% confidence levels of triplicate samples.

HNO$_3$. However, it was found that 16% Pu(VI) in the original Pu composition
can reduce the LOC to 0.42 M. The data also seem to suggest a region from 0
to 50% Pu(IV), where the LOC is approximately equivalent to the pure Pu(VI)
system determined in this work to be 0.20 M in HPT. The data resemble a fit
similar to that described by Le Chatelier's principle according to the following
equation.

$$LOC_{system} = \left[\frac{x_{Pu(VI)}}{LOC_{Pu(VI)}} + \frac{1 - x_{Pu(VI)}}{LOC_{Pu(IV)}} \right]^{-1}$$

where $x_{Pu(VI)} =$ fraction of Pu(VI), $LOC_{Pu(VI)} =$ limiting organic concen-
tration of system with pure Pu(VI), $LOC_{Pu(IV)} =$ limiting organic con-
centration of system with pure Pu(IV).

The curves in Fig. 4 were generated using the 95% confidence level
values for the LOCs in each of the pure systems. While the general
behavior is similar, further experimentation in the 25 to 75% Pu(VI) region
is necessary to support a firm conclusion on the behavior of mixed valence
systems of the same metal.

For reference purposes, the LOC values for each pure valence state were
also measured in dodecane and presented in Fig. 4. Under both conditions, the
LOC for the dodecane system remained significantly lower than the HPT. For
the dodecane system the Pu(VI) trend of LOC being less than Pu(IV) is in
agreement with a previous comparison of each valence state in 20% TBP/
odorless kerosene.[7] However, this behavior contradicts the trends widely

reported for the analog uranium systems which show U(IV) as having a lower LOC than U(VI).[3]. Based on these previous third phase formation studies, this reversal in the U and Pu oxidation state behavior is unexpected and may be related to metal ion charge density. Further investigation of this finding is warranted and ongoing.

Spectral Examination

Selected organic phases were examined via UV-Visible spectroscopy. For the pure Pu(IV) system, spectral features of each phase (normal, light, and heavy) were indistinguishable. The spectrum was characterized by the strong absorption peak at 490 nm. Previous investigations have reported an analytical determination of Pu(IV) at 492 nm[18] with a molar extinction coefficient of 62 ± 2 $(M^{-1} cm^{-1})$. This study determined the molar extinction coefficient to be 85 ± 3 $(M^{-1} cm^{-1})$ with no evident changes as a result of changes in organic phase metal and/or acid loading.

Spectra of the three organic phases produced in a mixed valence system are presented in Fig. 5. There appear to be observable changes in the spectra in the Pu(VI) absorption region especially for the heavy phase. The relative ratios of the oxidation states in each phase were calculated based on a mass balance between the absorption attributed to Pu(IV) at 490 nm and the total Pu concentration. High absorbance at the Pu(VI) peak at 835 nm prevented
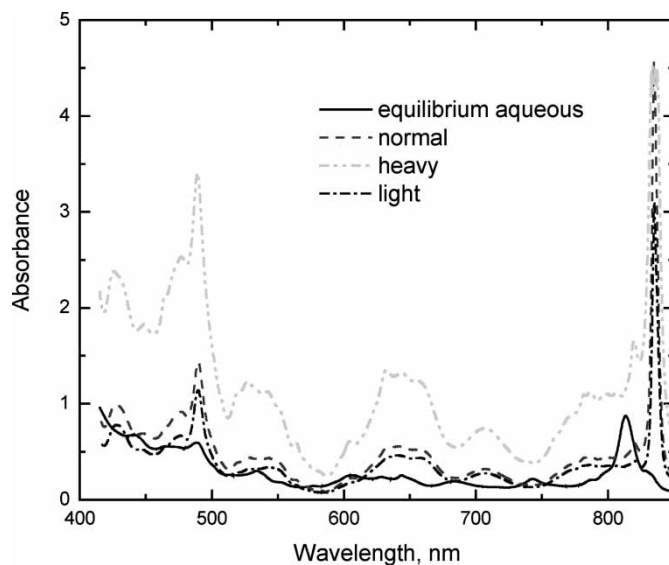
Figure 5. UV-Visible absorption spectra of three phase system for mixed valence Pu in 1.1 M TBP/HPT. Aqueous phase was 13 M HNO₃.

quantitative direct spectroscopic determination in these phases. Heavy phases examined in 7 and 13 M nitric acid systems both showed enriched concentration of Pu(VI). For initial aqueous phases consisting of approximately 30% Pu(VI), the heavy phases were found to be approximately 70% Pu(VI). These findings suggest that third phase formation is highly preferential to the Pu(VI) organic species and supports the earlier observation on the lower LOC value for the hexavalent state, at this acidity.

Further investigations are planned to ascertain what aspect of the Pu(VI)-TBP complex is responsible for this propensity. One possibility is the presence of the anionic plutonyl trinitrato species, $PuO_2(NO_3)_3^-$. Spectroscopic evidence for this complex has been found in the nitric acid aqueous phases with a characteristic peak at 812 nm.[19] However, other authors performing similar research in acetone media, have attributed the occurrence of this peak simply to a shift from the free PuO_2^{2+} to the dinitrato complex, $PuO_2(NO_3)_2$.[20] Other possible explanations include an interaction between Pu(VI) and Pu(IV) species, or various bridged species involving nitric acid or TBP similar to the one observed in the U(VI)-TBP system.[21]

Whatever the species, the organic phase spectra indicate a feature near 820 nm that is very similar to those reported for dinitrato peaks. Unfortunately, the high absorption at 835 nm prevented a quantitative comparison of the relative ratios of these peaks, but it appears the heavy phase may contain a higher proportion of it. Also of note, the equilibrium aqueous phases reveal a noticeable peak remaining near 812 nm, but with the disappearance of the major peak at 830 nm. Taken together, this would suggest the preferential extraction of the dinitrato species, with a subsequent formation of a new species represented at 820 nm, which could be either the trinitrato or a bridged nitric acid species.

CONCLUSIONS

A study on plutonium third phase formation in 30% TBP/HPT was performed. Basic characterization studies of HPT reveal it is a mixture of many highly branched alkanes with retention times near linear C_{11}. This composition results in a substantial resistance to third phase formation in the Pu(IV) system. This resistance may be the result of both the smaller chain lengths and the high degree of branching. The addition of Pu(VI) into the system significantly affects third phase formation. This effect appears more pronounced in HPT than dodecane, yet the HPT remains more resistant to third phase. Spectroscopic investigation show no differences in speciation between the three phases (normal, light, and heavy) in the pure Pu(IV) system. However, investigation of mixed valence systems revealed an enrichment of Pu(VI) in the heavy phase, as well as different spectral features. These features suggest that Pu(VI) is forming a species, possibly a plutonyl trinitrato

complex, with a strong tendency to form third phase. Further work is planned to elucidate the source of the Pu(VI) effect.

ACKNOWLEDGEMENTS

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