

Small-Angle Neutron Scattering Study of Plutonium Third Phase Formation in 30% TBP/HNO₃/Alkane Diluent Systems

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

P. Thiyagarajan

Intense Pulsed Neutron Source, Argonne National Laboratory, Argonne,
IL, USA

R. Chiarizia

Chemistry Division, Argonne National Laboratory, Argonne, IL, USA

Abstract: Third phase formation in the extraction of Pu(IV) nitrate by 30% tri-*n*-butyl phosphate (TBP) dissolved in *n*-dodecane or in the highly branched diluent hydrogenated polypropylene tetramer (HPT), which may also be known as 4,4 dipropyl

Received 22 June 2005, Accepted 31 October 2005

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

***Work performed at Argonne National Laboratory was supported by Duke Cogema Stone & Webster under interagency agreement, through U.S. Department of Energy contract W-31-109-Eng-38.

Address correspondence to J. Plaue, Defense Nuclear Facilities Safety Board**, 625 Indiana Ave, Washington, DC 20004-290, USA. E-mail: jplaue@alum.mit.edu

heptane or tétrapropylène hydrogéné, was investigated through small-angle neutron scattering (SANS) measurements. The SANS data were interpreted using the Baxter model for hard-spheres with surface adhesion. According to this model, the increase in scattering intensity observed when increasing amounts of $\text{Pu}(\text{NO}_3)_4$ are extracted into the organic phase, is due to interactions between small reverse micelles containing three to five TBP molecules. In *n*-dodecane, the micelles interact through attractive forces between their polar cores with a potential energy of up to $-2.6 k_B T$. This strong intermicellar attraction leads to organic phase splitting with the separation of most of the solutes of the original organic phase into a distinct phase containing interspersed layers of *n*-dodecane. When HPT is the diluent, the intermicellar attraction energy calculated from the SANS data is much lower, and no third phase formation is observed under comparable chemical conditions. However, when a significant amount of the initial aqueous plutonium is in the form of plutonyl ions, PuO_2^{2+} , the critical energy potential is reached even in HPT. A potential explanation of the effect of Pu(VI) involves the formation of a plutonyl trinitrato complex.

Keywords: Plutonium third phase formation, HPT, SANS, Baxter model

INTRODUCTION

It is well known that under certain conditions, solvent extraction systems may undergo what is known as third phase formation. Basically, the organic phase splits into a heavy phase rich in extractant, mineral acid, and metal; and a light phase consisting of mostly diluent. This occurrence in an industrial setting, involving fissile materials, can be especially problematic to safety. For example the PUREX process,^[1] which involves the extraction of plutonium dissolved in nitric acid, into an organic phase of tri-*n*-butyl phosphate (TBP) dissolved in a suitable diluent, may create the necessary conditions for third phase formation. The safety implications of third phase formation for plutonium processing have been discussed elsewhere.^[2]

Third phase formation in nuclear solvent extraction systems with TBP has been thoroughly reviewed by Vasudeva Rao and Kolarik.^[3] With respect to plutonium, several authors have presented data covering many of the common important variables.^[4–8] Typically, in third phase studies, data for the phase splitting boundary are reported as a limiting organic concentration (LOC). This value is the maximum concentration of metal found in the organic phase prior to a visual observation of phase splitting.

Several recent advances have been made in the study of third phase formation. Beginning with the work of Osseo-Asare,^[9,10] third phase formation in TBP systems has come to be viewed from a reverse micelle microemulsion approach. Subsequently, many of the concepts and techniques of colloid and surfactant chemistry have been shown to be effective tools in

studying aspects of third phase formation. In particular, small-angle neutron scattering (SANS) has been demonstrated as an effective probe of the morphology of organic phase species.^[11,12]

Interpretation and analysis of the SANS scattering data has been largely based on the pioneering work on small-angle X-ray scattering measurements of the interactions between small reverse micelles in the *N,N'*-dimethyl-*N,N'*-dibutyl-2-tetradecylmalonamide (DMDBTDMA)-dodecane- HNO_3 solvent extraction system.^[13,14] These works modeled the reverse micelle interaction via the Baxter model for hard-spheres with surface adhesion, also known as the “sticky spheres” model.^[15] The Baxter model allows the calculation of the energy of interaction between small reverse micelles assumed as incompressible spheres.

The reverse micelle approach and the Baxter interaction model have been successfully employed in the study of the TBP- HNO_3 system,^[16] as well as systems involving U(VI) and Th(IV) extraction by TBP in alkanes.^[17-19] These works have shown that in a 20% TBP system, third phase formation can be modeled as resulting from the interaction between small reverse micelles consisting of 3 to 4 TBP molecules which, under suitable conditions, attract to form the third phase.

To date, no investigations utilizing SANS on a 30% TBP system containing Pu have been reported. In addition, very little structural information exists on the role of the diluent in the reverse micelle interactions. It is well known that the diluent plays a crucial role in third phase formation.^[3] Increased branching provides greater resistance to third phase formation,^[20] though tradeoffs such as increased flash points can be associated with these materials.

The use of hydrogenated polypropylene tetramer (HPT), which may also be known as 4,4 dipropyl heptane or tétrapropylène hydrogéné, as the diluent in PUREX-type processes has been proposed. Nominally considered a branched dodecane, HPT is commonly used in the French reprocessing industry, specifically because of its resistance to third phase formation. A study characterizing HPT and its third phase resistance was recently performed.^[2] HPT was determined to be a highly branched mixture of pure alkanes ranging in molecular mass from C_9 to C_{12} , with the average mass slightly below that of dodecane. With respect to third phase formation, HPT was confirmed to be highly resistant to Pu(IV) third phase. However, it was noted that the presence of Pu(VI) can substantially lower the LOC of the system.^[2]

The objective of this work was to utilize the SANS technique for a comparison of third phase formation in the extraction of Pu(IV) nitrate from aqueous HNO_3 solutions into 30% TBP dissolved in *n*-dodecane and HPT. The results were compared with previously published systems for other actinides and, within the constraints imposed by the limited availability of beam time; an attempt was made to develop further information on the enhanced phase splitting effect of the plutonyl ion.

EXPERIMENTAL

A series of five samples were prepared with organic phase loadings of Pu(IV) at predetermined fractions (0.5, 0.75, and 1.0) of the LOC for Pu(IV) in the 30%TBP/*n*-dodecane. The third phase sample in *n*-dodecane was prepared at approximately 1.5 LOC. Samples of both the heavy and light phases were analyzed. A corresponding series of samples was made using the same initial aqueous Pu concentrations, but with HPT as the diluent. No third phase was observed at 1.5 LOC (*n*-dodecane) in the HPT diluent. Background samples were also prepared containing each of the pure diluents, as well as each diluent-TBP mixture pre-equilibrated with 7 M HNO₃. Additionally, one sample was prepared using a mixture of Pu IV-VI valence states in HPT at the previously determined corresponding LOC condition. The sample matrix is shown in Table 1.

SANS Sample Preparation

Organic phases were prepared using deuterated TBP (C₁₂D₂₇O₄P₃, 98%, CDN Isotopes) as received, in order to enhance neutron contrast and have a common comparison between diluents. The HPT (Novasep SAS, France) and *n*-dodecane (Aldrich) were used without further purification. The organic phases were prepared using 30% (v/v) d-TBP (referred to as simply TBP hereafter) and twice pre-equilibrated with an equal volume of 7 M HNO₃ prior to extraction.

Plutonium nitrate solutions were prepared from the nitric acid dissolution plutonium oxide stocks obtained from Argonne National Laboratory. All plutonium used was ²⁴²Pu (99.9% by mass) determined via alpha spectroscopy, which minimized radiolysis effects in the organic phase, and

Table 1. Sample list

Sample #	Contents
H-0	HPT-30% TBP, pre-equilibrated with 7 M HNO ₃
H-50	HPT-50% LOC for <i>n</i> -dodecane
H-75	HPT-75% LOC for <i>n</i> -dodecane
H-100	HPT-100% LOC for <i>n</i> -dodecane
H-150	HPT-150% LOC for <i>n</i> -dodecane
H-Mix	HPT-LOC with mixed Pu valence
D-0	<i>n</i> -Dodecane, 30% TBP, pre-equilibrated with 7 M HNO ₃
D-50	50% LOC
D-75	75% LOC
D-100	100% LOC
D-Hvy	150% LOC-heavy phase
D-Lgt	150% LOC-light phase

reduced the radiological hazards involved with the experiments. The stock solution was purified using anion exchange on an AG-MP1 resin column. After taking to dryness, the material was dissolved in 7 M HNO₃. A small addition of hydrogen peroxide^[21] was used to ensure tetravalent oxidation state, which was confirmed using UV-Visible spectroscopy by the absence of the strong 830 nm absorption line of Pu(VI).^[22] Individual solutions of Pu were prepared for extraction experiments by further dilution of the common stock to achieve the desired initial aqueous phase concentration.

Samples consisting of 0.5 mL per phase were vigorously contacted for 5 minutes using a vortex mixer, and then centrifuged for approximately 5 minutes. Sample cells, 1 mm thick quartz discs (Helma USA) were filled, capped, and wrapped with ParafilmTM. Individual cells were then loaded into a custom made, gasket-sealed, aluminum cassette.

Determination of Sample Compositions

Plutonium concentrations were determined using liquid scintillation counting of triplicate 10 μ L aliquots of organic phase further diluted in dodecane. Organic phase acid concentrations were determined by stripping duplicate 10 μ L aliquots diluted with dodecane into an equal volume of 0.1 M (NH₄)C₂O₄, followed by a contact with deionized water. The aqueous phases were combined and titrated against 0.0098 N NaOH using an automated Metrohm 716 titrator with a semi-micro Orion, sealed, gel combination electrode. Heavy and light phase TBP concentrations were determined using the distribution ratio method described previously.^[11] The concentration of water in the organic phases was not determined. Previous studies, however, have shown that water extraction does not play a major role in TBP-HNO₃ systems.^[23,24]

SANS Experiments

The SANS measurements were performed at the time-of-flight small-angle neutron diffractometer (SAND) at the Intense Pulsed Neutron Source (IPNS) of Argonne National Laboratory.^[25,26] For each sample the data were collected as scattered intensity, $I(Q)$ (cm^{-1}) versus momentum transfer, $Q = (4\pi/\lambda) \sin(\theta)$ (\AA^{-1}), where θ is half the scattering angle and λ is the wavelength of the probing neutrons. The SAND instrument provides a Q range of $0.004 - 0.7 \text{\AA}^{-1}$.

Data Analysis

The methodology and derivations of the approaches used here have been discussed in detail elsewhere.^[11,12,17-19] The purpose of this paper was not

to develop new approaches to the analysis of SANS data, but rather to apply demonstrated techniques to a new system. However, for clarity, a brief overview of the specific application to this data is provided.

In this analysis, organic phase aggregates, considered as reverse micelles (consisting of TBP in the lipophilic shell, and plutonium nitrate, nitric acid and minor amounts of water in the polar core) are treated as spherical particles for the purpose of interpreting the neutron scattering data. Two models were examined, where the changes in scattering intensities observed when increasing amounts of $\text{Pu}(\text{NO}_3)_4$ were transferred into the organic phase, were attributed to either:

1. Growth of non-interacting particles (Guinier analysis), or
2. Interaction between small particles (Baxter model).

For a volume fraction of solute particles, η , each with a volume, V_p (cm^3) the scattering intensity function can be expressed as:

$$I(Q) = (\Delta\rho)^2 \eta V_p P(Q) S(Q) + I_{\text{inc}} \quad (1)$$

where I_{inc} is the incoherent scattering background of the solvent (cm^{-1}) and $(\Delta\rho)^2$ is the contrast factor (cm^{-4}) representing the difference in neutron scattering properties of the deuterated TBP and diluent. The structure factor, $S(Q)$, accounts for interparticle interactions. The form factor, $P(Q)$, provides information on the shape and size of the solute particles.

For the Guinier analysis,^[27] the data were plotted as the natural logarithm of corrected scattering intensity, $\ln(I(Q))$, versus the square of the momentum transfer, Q^2 . From the slope and y-intercept of these plots, information was obtained on the radius of gyration of the spherical particles and their molecular mass. This information was then used with the known mass and molar volumes of the particle components (TBP, plutonium nitrate, and nitric acid) to determine the number of TBP molecules, or aggregation number, n_{TBP} , in each particle. The procedure for these calculations has been described in detail elsewhere.^[11,12,19]

The scattering data were also subjected to analysis via the Baxter model, following the previously demonstrated procedure.^[17-19] The Baxter model treats the reverse micelle aggregates as hard (incompressible) spheres interacting through a narrow square potential well with an attractive potential. An approximate value of the potential energy of attraction (which is negative by convention) between two hard spheres, $U(r)$, is given by the following equation:

$$U(r) = \lim_{\delta \rightarrow d_{\text{hs}}} \ln \left[12\tau \left(\frac{\delta - d_{\text{hs}}}{d_{\text{hs}}} \right) \right] \quad (2)$$

where d_{hs} is the diameter of the hard spheres, $(\delta - d_{\text{hs}})$ represents the width of the narrow square attractive well, and the reciprocal of τ , τ^{-1} , is the

“stickiness parameter” and its value is higher when the adhesion between particles is stronger. When the distance between the left rims of two particles is larger than d_{hs} but smaller than δ (i.e., for $d_{hs} < r < \delta$), the particles experience attraction. The limit in Eq. (2) indicates that the calculation of the interparticle attraction potential energy is valid only when the attractive well is extremely narrow, i.e., with a width within 10% of the particle diameter ($(\delta - d_{hs})/d_{hs} \leq 0.1$). Both τ^{-1} and $U(r)$ are expressed in $k_B T$ units, where k_B is the Boltzmann constant and T is the absolute temperature. A very useful feature of Baxter’s model approximation is that analytical expressions have been derived for the structure factor $S(Q)$ in terms of the parameters τ and d_{hs} .^[14,28]

RESULTS AND DISCUSSION

The sample compositions and their respective solute volume fractions, η , are presented in Table 2. Based on visual observations, the heavy phases for both diluents appeared to be slightly more than one third of the total organic phase volume. The values for η were calculated from the sum of the molar volumes for the plutonium nitrates, HNO_3 , and TBP. These values were obtained from the densities and molecular weights of the respective compounds. For Pu(IV), a literature value of 2.977 g/cc for the density of $Pu(NO_3)_2 \cdot 5H_2O$ was used with a correction for the water molecules.^[29] For the mixed valence sample, the ratios of each oxidation state were determined by UV-Visible spectroscopy of the aqueous phase before and after equilibration. Literature data was not available for $PuO_2(NO_3)_2$, subsequently the molar volume calculated for $UO_2(NO_3)_2$ was used.^[17]

Table 2. Sample compositions and solute volume fractions

Sample #	[HNO_3], M	St. Dev	[Pu], M	St. Dev	[TBP], M ^a	η	Error
H-0	1.06	0.06	0.00	0.000	0.99	0.342	0.015
H-50	0.71	0.01	0.13	0.01	0.99	0.342	0.015
H-75	0.68	0.03	0.19	0.01	0.99	0.347	0.015
H-100	0.57	0.01	0.25	0.01	0.99	0.349	0.015
H-150	0.40	0.01	0.35	0.03	0.99	0.353	0.015
H-Mix	0.70	0.04	0.18 ^b	0.01	0.99	0.344	0.015
D-0	1.07	0.02	0.00	0.00	0.99	0.343	0.015
D-50	0.76	0.01	0.14	0.01	0.99	0.345	0.015
D-75	0.66	0.02	0.20	0.01	0.99	0.347	0.015
D-100	0.56	0.01	0.25	0.01	0.99	0.349	0.015
D-Hvy	0.80	0.02	0.76	0.05	2.31	0.809	0.035
D-Lgt	0.20	0.01	0.15	0.01	0.28	0.108	0.004

^aEstimated accuracy of $\pm 5\%$.

^b[Pu(VI)] = 0.08 M.

In general, the compositional data is consistent with the expected classical stoichiometry of the $\text{Pu}(\text{NO}_3)_4 \cdot 2\text{TBP}$ solvate^[30] and the $\text{HNO}_3 \cdot \text{TBP}$ solvate for a tetravalent extraction system.^[31] The heavy phase composition is also consistent with these solvates. The light phase appears to exhibit slightly different component ratios, likely due to the low concentration of TBP. Also of note, within experimental error, there were no observable differences in extracted Pu concentrations (distribution values) between the two diluents.

The intensity values, I_0 , from the y-intercepts of the Guinier analysis are presented in Fig. 1. The increase in I_0 with increasing Pu concentration indicates either a particle growth phenomenon or particle interaction in the organic phase. When the effect is solely attributed to particle growth, the results show substantial growth in the aggregation number. Most strikingly, as the plutonium organic phase concentration is increased, there is a substantial growth in the TBP aggregation number, n_{TBP} . Typically, for amphiphiles in nonaqueous media, such as TBP in *n*-dodecane, physical limitations and free energy arguments have demonstrated aggregates numbers of less than 10.^[32] Based on the findings here, at the LOC condition in *n*-dodecane, the n_{TBP} is approximately 130. Clearly these results appear unrealistic, and therefore suggest that a simple aggregation model is not a valid explanation of third phase formation in this plutonium system. This conclusion is in agreement with previous SANS investigations on Th(IV) and U(VI).^[17–19]

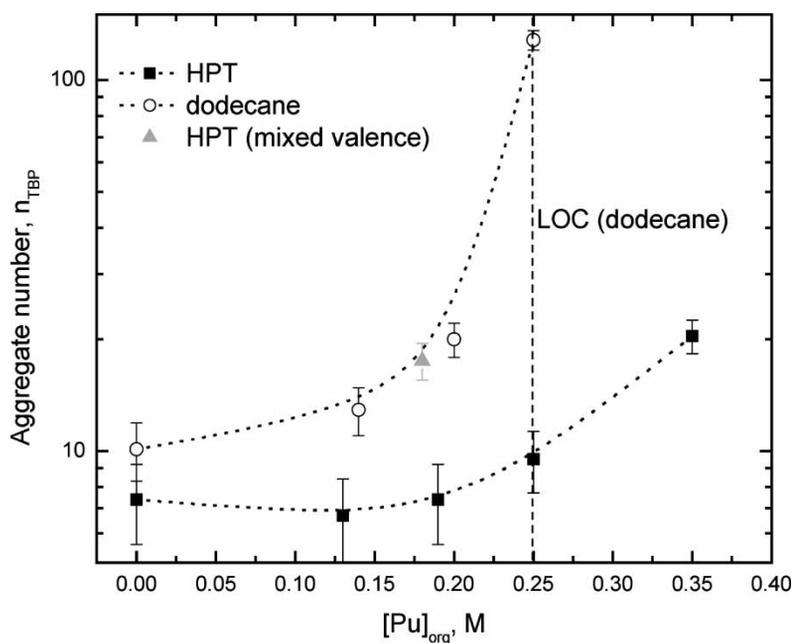


Figure 1. Results of Guinier analysis.

However, the results from the particle growth model do show a substantial difference in the behavior of the two diluents. In the HPT system, there is relatively no aggregate growth from a HNO_3 pre-equilibrated system all the way to the LOC condition for *n*-dodecane. Higher values of n_{TBP} are only seen for the H-150 concentration. The analysis also shows the strong effect of the plutonyl ion in the aggregate behavior. The mixed valence LOC exhibits a factor of 2 higher n_{TBP} over a similar concentration of pure Pu(IV).

For the particle interaction model calculations, Eq. (1) was used in conjunction with the previously reported equations for the structure factor $S(Q)$,^[14,17–19,28] and expressing $P(Q)$ as the form factor of a sphere with a radius $R = d_{\text{hs}}/2$.^[33] In the calculations, $3.90 \times 10^{21} \text{ cm}^{-4}$ and $3.91 \times 10^{21} \text{ cm}^{-4}$ were used as the contrast factors for *n*-dodecane and HPT, respectively, and the η values for each sample were taken from Table 2. The three parameters I_{inc} , d_{hs} and τ were used as independent fit parameters and were optimized using the procedure described previously.^[17–19]

For each sample, the value of the hard-sphere diameter, d_{hs} , was used to calculate the volume of the spherical scattering particles, V_p . This volume comprises both the volume of the inorganic constituents of the particle (the polar core) and the volume occupied by the TBP molecules (the lipophilic shell). By using the analytical data in Table 2, the volume of the shell was estimated by subtracting from V_p the volume occupied by the inorganic solutes. Finally, the average TBP aggregation number was calculated by dividing the volume of the shell by the molecular volume of TBP.

An example of the scattering data and calculated Baxter fit is presented for sample H-100 in Fig. 2. The observed scattering data, the calculated functions for $S(Q)$ and $P(Q)$, and the resulting calculation of $I(Q)$ as expressed in Eq. (1) are depicted. The calculated fit is quite good, with only slight deviation toward the lower values of Q . For $S(Q)$, there is a pronounced maximum near Q values of 0.5. Using Bragg's law, this maximum can be used to obtain the correlation distance between interacting micelles, $d_{\text{sep}} = 2\pi/Q_{\text{max}}$.

Baxter model fits for all of the investigated samples in both diluents are shown in Fig. 3. In general, the calculated fits are quite good. There are two small exceptions. For samples H-0 and H-50, the experimental data show a slight power curve trend at values of Q less than 0.015. None of the other eight curves exhibit this behavior, and the calculated fits do not capture this effect. It is suspected that these samples may have had a small solid contaminant.

The calculated Baxter fit parameters are given in Table 3. In both diluents, with the exception of the third and light phase, there is an increase in d_{hs} as nitric acid is replaced with plutonium nitrate. This swelling is also accompanied with an increase in n_{TBP} . Accordingly, as the $\text{Pu}(\text{NO}_3)_4$ concentration in the organic phase increases, there is an increase in $1/\tau$, which translates into a greater interaction potential. In *n*-dodecane, when $U(r)$ reaches the

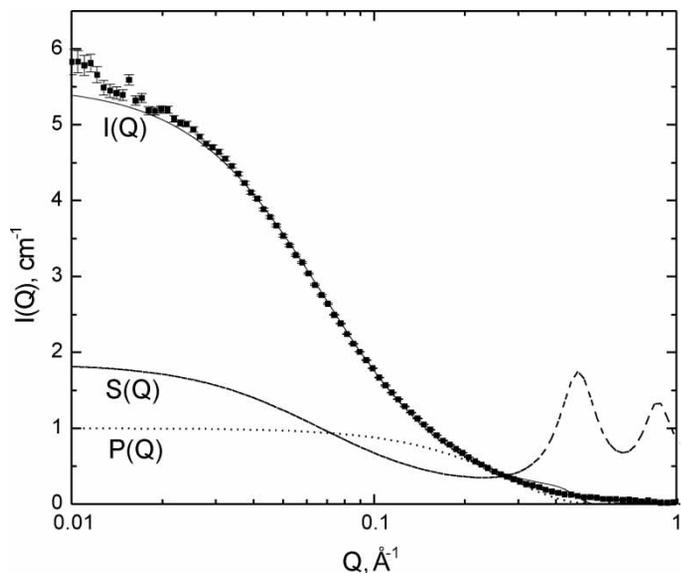


Figure 2. Scattering data (symbols) and calculated functions (lines) for sample H-100.

critical value of $-2.6 k_B T$, phase separation takes place and most of the solutes (TBP, $\text{Pu}(\text{NO}_3)_4$ and HNO_3) report in a separate and heavier organic phase.

To fit the SANS data for the third phase sample in *n*-dodecane, the same procedure outlined previously was followed.^[17–19] This sample, which has much higher concentrations of TBP, $\text{Pu}(\text{NO}_3)_4$ and HNO_3 than the other samples, was considered as a continuous phase made of the TBP-complexes of plutonium nitrate and nitric acid containing interspersed small amounts of *n*-dodecane. The Baxter model calculations for the third phase sample in

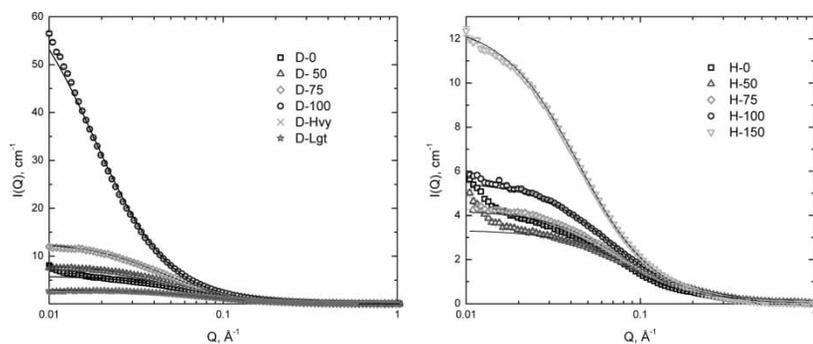


Figure 3. SANS data plots with Baxter model fits. The *n*-dodecane samples (D series) are on the left and HPT (H series) on the right.

Table 3. Results of Baxter fit parameters

Sample #	d_{hs} , Å	Error	d_{sep} , Å	n_{TBP}	Error	$1/\tau$	Error	$U(r)$, $k_B T$	Error
H-0	13.0	0.1	10.4	2.30	0.47	11.4	0.6	-2.25	0.07
H-50	15.6	0.1	12.7	3.53	0.07	8.8	0.3	-1.99	0.05
H-75	15.6	0.1	12.7	3.47	0.08	9.8	0.4	-2.10	0.06
H-100	16.1	0.1	13.3	3.77	0.09	10.5	0.5	-2.17	0.07
H-150	17.2	0.1	14.0	4.57	0.14	12.7	0.8	-2.36	0.09
H-Mix	14.1	0.1	11.5	2.56	0.06	13.3	0.8	-2.41	0.09
D-0	15.2	0.1	12.7	3.23	0.07	10.9	0.5	-2.21	0.07
D-50	16.4	0.1	13.3	4.01	0.09	11.4	0.7	-2.25	0.09
D-75	17.6	0.1	14.7	4.89	0.10	12.3	0.7	-2.33	0.08
D-100	17.5	0.1	14.4	4.84	0.09	16.0	1.2	-2.59	0.11
D-Hvy	14.8	0.7	12.3	4.55 ^a	0.60	7.9	0.1	-1.88	0.02
D-Lgt	16.4	0.2	14.0	3.60	0.09	8.5	0.0	-1.96	0.01

^aThis is not a TBP aggregation number; it indicates the number of *n*-dodecane molecules contained in diluent pockets interspersed in the third phase.

Table 3, performed by using the *n*-dodecane volume fraction obtained from the analytical data in Table 2, provided an aggregation number of 4.5. This value no longer represents a TBP aggregation number; rather it represents the number of dodecane molecules contained in pockets (or layers if the system is bicontinuous) interspersed in the third phase.

There are some obvious differences observed between the two diluents. In general, all of the parameters are minimized in the HPT systems. The micelles do not swell as much, nor do they accumulate as many TBP molecules. The critical $U(r)$ value of $-2.6 k_B T$ is never reached in the HPT system. Since the compositions in each matched system are equivalent, it can be concluded that the observed differences in the aggregate behavior can be strictly related to the nature of the HPT diluent. The bulkier molecules of this highly branched diluent prevent the swollen reverse micelles from reaching the level of intermicellar attraction energy required for phase separation.

For comparison purposes, the most similar published system is that of Th(IV) in 20% TBP/*n*-octane.^[18,19] This work showed consistent critical $U(r)$ of approximately $-2.10 k_B T$ over four different nitric acid conditions. Although comparisons between different diluents are not straightforward, the higher $U(r)$ values observed in the present work is likely due to differences in the TBP concentration and properties of the metal-extractant bonding. Though no quantitative explanation has been put forth, it is clear from the available data that characteristics of the metal play an important role in third phase formation.^[3] However, the slight increase in aggregation numbers for increasing the TBP concentration from 20 to 30 volume percent is consistent with expectations for non-aqueous micellar behavior.^[32] The values observed here are also in agreement with findings for simple nitric acid extraction under similar conditions.^[16]

The mixed valence sample (H-mix) exhibits several interesting features. For this sample, which contained 46 percent PuO_2^{2+} , the micelle diameter at LOC is substantially smaller than any of the pure Pu(IV) loaded samples, and is only about 1 Å larger than the H-0 sample. A similar pattern is observed for the aggregation numbers. In terms of energies, the absolute $U(r)$ value for the LOC condition in this system ($-2.41 k_B T$) is somewhat lower than for the LOC condition in the *n*-dodecane system, but the error ranges do overlap.

The most intriguing result obtained for the mixed valence sample is that the presence of Pu(VI) promotes third phase formation, which was observed even in HPT, and at a much lower total Pu LOC than the Pu(IV) LOC in *n*-dodecane (0.18 vs. 0.25). This result was unexpected, based on the similarity of behavior between Pu(VI) and U(VI), since it has been previously shown that U(VI) does not exhibit a strong tendency toward third phase formation when extracted by TBP in *n*-dodecane.^[11,17] The effectiveness of Pu(VI) in promoting third phase formation in TBP systems has been potentially linked to the trinitrato complex of Pu(VI), $\text{PuO}_2(\text{NO}_3)_3^-$.^[2] It has been reported that this complex has a significantly higher stability than the

corresponding U(VI) complex, and, therefore, starts to form at relatively low HNO_3 concentrations ($>4\text{ M}$).^[34,35]

The consequences of the large $\text{PuO}_2(\text{NO}_3)_3^-$ anion on third phase formation can be easily understood by considering that, when extracted by TBP in the form of the $\text{HPuO}_2(\text{NO}_3)_3$ acid, it should behave in a way similar to other acids of very large and little hydrated anions, such as HClO_4 . It is well known that HClO_4 , among other mineral acids, is the most effective in inducing phase splitting in TBP-alkane systems.^[36,37] A complete investigation should be performed on the Pu(VI)-TBP-alkane diluent system at various aqueous acidities to further determine whether Pu(VI) trinitrate complex is present in the organic phase and its role in third phase formation.

CONCLUSIONS

Third phase formation in the extraction of plutonium nitrate by TBP in *n*-dodecane and the HPT branched diluent was studied as a function of metal loading using the SANS technique. As anticipated, compositional data showed similar extraction behavior between the two diluents. Attempts to interpret the SANS data with a particle growth model led to unrealistically high aggregation numbers at the LOC condition. This result implies, as has been shown for other metals, that Pu third phase formation is not the result of progressive, extensive aggregation of TBP molecules. A particle interaction model using the Baxter sticky spheres model provided more consistent results.

According to this model, TBP in *n*-dodecane, in contact with aqueous phases containing nitric acid and plutonium nitrate, forms small reverse micelles containing three to five TBP molecules. These micelles swell when polar solutes such as nitric acid and metal nitrate are incorporated into their polar core. The swollen micelles interact through van der Waals forces between their polar cores. The separation of most of the solute particles in a new phase is energetically favorable when the energy of attraction between the particles in solution becomes substantially larger ($-2.6 k_B T$, for 30% TBP) than the average thermal energy ($k_B T$). Upon phase splitting, most of the solutes in the original organic phase (TBP, water, HNO_3 and metal nitrate) collect in a separate phase containing interspersed layers of *n*-alkane.

Our SANS data and the Baxter model provided an explanation of the different behavior of *n*-dodecane and HPT in terms of mechanism and energetics of third phase formation. When the reverse micelles are separated by molecules of a highly branched diluent such as a HPT, the critical attraction energy of $-2.6 k_B T$ is not reached, even at Pu(IV) loadings of 150 percent of the LOC for *n*-dodecane.

A single sample study of the effect of Pu(VI) on third phase formation confirmed that the presence of PuO_2^{2+} ions in the system strongly promotes phase splitting, causing the intermicellar attraction energy to reach the critical value at much lower total plutonium concentrations than for pure

Pu(IV). The negative effect of Pu(VI) on the ease of phase splitting can possibly be attributed to the formation, under the experimental conditions of this work (7 M HNO₃ in the aqueous phase), of significant amounts of the plutonyl trinitrato complex species.

ACKNOWLEDGEMENTS

The authors wish to thank Bill Brown for his assistance in the design and fabrication of the SANS sample cassette and Denis Wozniak for his assistance performing the SANS measurements. In addition, the first three authors wish to thank Duke Cogema Stone & Webster and the Professional Development Program of the Defense Nuclear Facilities Safety Board for their funding and support.

The parts of this work performed at the Chemistry Division and at the IPNS Division of ANL were funded by the U. S. Department of Energy, Office of Basic Energy Science, Division of Chemical Science (R.C.) and Division of Material Science (P.T.) under contract No. W-31-109-ENG-38.

REFERENCES

1. Lanham, W.G.; Runion, T.C. *Purex Process for Plutonium and Uranium Recovery*; USAEC Report ORNL-479, Oak Ridge National Laboratory: Oak Ridge, TN, 1949.
2. Plaue, J.; Gelis, A.; Czerwinski, K. Plutonium third phase formation in the 30% TBP/HNO₃/hydrogenated polypropylene tetramer. *Solvent Extr. Ion Exch.*, preceding paper.
3. Vasudeva Rao, P.R.; Kolarik, Z. A review of third phase formation in extraction of actinides by neutral organophosphorus extractants. *Solvent Extr. Ion Exch.* **1996**, *14*, 955–993.
4. Kolarik, Z. The formation of a third phase in the extraction of Pu(IV), U(IV), and Th(IV) nitrates with tributyl phosphate in alkane diluents. In *Proceedings of the International Solvent Extraction Conference ISEC 77*; Lucas, B.H., Ritcey, G.M., Smith, H.W., eds., CIM Special Volume 21, The Canadian Institute of Mining and Metallurgy: Montreal, 1979; 178–182.
5. Mason, C.; Thompson, R.; Tolchard, A.C. Third phase formation in the extraction of Plutonium(IV) and Uranium(VI) nitrates with tri-*n*-butyl phosphate (TBP) in odourless kerosene (OK) at different diluent ratios, temperature, and acidities. In *Extr. '87 Recovery High Value Mater. I. Chem. E. Symposium Series* **1987**, *103*, 75–85.
6. Horner, D.E. Formation of the third phase and the effect of temperature on the distribution of plutonium and uranium in extractions by tri-*n*-butyl phosphate, Report ORNL-4724, Oak Ridge National Laboratory: Oak Ridge, TN, 1971; 16–21.
7. Mills, A.L.; Logan, W.R. Third phase formation between some actinide nitrates and 20% tri-*n*-butyl phosphate/odourless kerosene. In *Solvent Extraction Chemistry*; Dyrssen, D., Liljenzin, J.O., Rydberg, J., eds.; Amsterdam: North-Holland, 1967, 322–334.

8. Srinivasan, T.G.; Ahmed, M.K.; Shakila, A.M.; Dhamodaran, R.; Vasudeva Rao, P.R.; Mathews, C.K. Third phase formation in the extraction of plutonium by tri-*n*-butyl phosphate. *Radiochimica Acta* **1986**, *40*, 151–154.
9. Osseo-Asare, K. Aggregation, reversed micelles and microemulsions in liquid-liquid extraction: The tri-*n*-butylphosphate-diluent-water-electrolyte system. *Adv. Colloid Interface Sci.* **1991**, *37*, 123–173.
10. Osseo-Asare, K. Microemulsions and third phase formation. In *ISEC 2002, Proceedings of the International Solvent Extraction Conference*; Sole, K.C., Cole, P.M., Preston, J.S., Robinson, D.J., eds., S. African Inst. Mining and Metallurgy: Marshalltown, South Africa, 2002; 118–124.
11. Chiarizia, R.; Jensen, M.P.; Borkowski, M.; Ferraro, J.R.; Thiyagarajan, P.; Littrell, K.C. SANS study of third phase formation in the U(VI), HNO₃/TBP, *n*-dodecane system. *Sep. Sci. Technol.* **2003**, *38*, 3313–3331.
12. Borkowski, M.; Chiarizia, R.; Jensen, M.P.; Ferraro, J.R., Thiyagarajan, P.; Littrell, K.C. SANS study of third phase formation in the Th(IV), HNO₃/TBP, *n*-octane system. *Sep. Sci. Technol.* **2003**, *38*, 3333–3351.
13. Erlinger, C.; Gazeau, D.; Zemb, T.; Madic, C.; Lefrançois, L.; Hebrant, M.; Tondre, C. Effect of nitric acid extraction on phase behavior, microstructure and interactions between primary aggregates in the system dimethyldibutyltetradecylmalonamide (DMDBTDMMA)/*n*-dodecane/water: A phase analysis and small-angle X-ray scattering (SAXS) characterisation study. *Solvent Extr. Ion Exch.* **1998**, *16*, 707–738.
14. Erlinger, C.; Belloni, L.; Zemb, Th.; Madic, C. Attractive interactions between reverse aggregates and phase separation in concentrated malonamide extractant solutions. *Langmuir* **1999**, *15*, 2290–2300.
15. Baxter, R.J. Percus-yevick equation for hard spheres with surface adhesion. *J. Chem. Phys.* **1968**, *49*, 2770–2774.
16. Nave, S.; Mandin, C.; Martinet, L.; Berthon, L.; Testard, F.; Madic, C.; Zemb, Th. Supramolecular organization of tri-*n*-butyl phosphate in organic diluent on approaching third phase transition. *Phys. Chem. Chem. Phys.* **2004**, *6*, 799–808.
17. Chiarizia, R.; Nash, K.L.; Jensen, M.P.; Thiyagarajan, P.; Littrell, K.C. Application of the Baxter model for hard-spheres with surface adhesion to SANS data for the U(VI)-HNO₃/TBP, *n*-dodecane system. *Langmuir* **2003**, *19*, 9592–9599.
18. Chiarizia, R.; Thiyagarajan, P.; Jensen, M.P.; Borkowski, M.; Littrell, K.C. Third phase formation in TBP solvent extraction systems as a result of interaction between reverse micelles. In *Proceedings of Hydrometallurgy 2003*; Young, C.A., Alfantazi, A.M., Anderson, C.G., Dreisinger, D.B., Harris, B., James, A., eds.; Leaching and Solution Purification, TMS (The Minerals, Metals and Materials Society): Warrendale, PA, 2003; Vol. 1, 917–928.
19. Chiarizia, R.; Jensen, M.P.; Borkowski, M.; Thiyagarajan, P.; Littrell, K.C. Interpretation of third phase formation in the Th(IV)-HNO₃, TBP-*n*-octane system with Baxter's "sticky spheres" model. *Solvent Extr. Ion Exch.* **2004**, *22*, 325–351.
20. Vasudeva Rao, P.R.; Dhamodaran, R.; Srinivasan, T.G.; Mathews, C.K. The effect of diluent on third phase formation in thorium nitrate-TBP system: Some novel empirical correlations. *Solvent Extr. Ion Exch.* **1993**, *11*, 645–662.
21. Maillard, C.; Adnet, J.M. Plutonium(IV) peroxide formation in nitric medium and kinetics of Pu(VI) reduction by hydrogen peroxide. *Radiochimica Acta* **2001**, *89*, 485–490.

22. Cleveland, J.M. *The Chemistry of Plutonium*; American Nuclear Society: La Grange Park, IL, 1979.
23. Irving, H.; Edgington, D.N. The extraction of some metal chlorides into tri-*n*-butyl phosphate. *J. Inorg. Nucl. Chem.* **1959**, *10*, 306–318.
24. Hesford, E.; McKay, H.A.C. The extraction of mineral acids by tri-*n*-butyl phosphate (TBP). *J. Inorg. Nucl. Chem.* **1960**, *13*, 156–164.
25. Thiyagarajan, P.; Epperson, J.E.; Crawford, R.K.; Carpenter, J.M.; Klippert, T.E.; Wozniak, D.G. The time-of-flight small-angle neutron diffractometer (SAD) at IPNS, Argonne National Laboratory. *J. Appl. Cryst.* **1997**, *30*, 280–293.
26. Thiyagarajan, P.; Urban, V.; Littrell, K.C.; Wozniak, D.G.; Belch, H.; Vitt, R.; Toeller, J.; Leach, D.J.; Haumann, J.R.; Ostrowski, G.E.; Donley, L.I.; Hammonds, J.P.; Carpenter, J.M.; Crawford, R.K. The performance of the small-angle diffractometer SAND at IPNS. In *ICANS XIV, Proc. 14th Meeting on the International Collaboration on Advanced Neutron Sources*. Starved Rock Lodge, Utica, Illinois, June 14–19, 1998; Carpenter, J.M., Tobin, C., eds.; National Technical Information Service: Springfield, VA, 1998; Vol. 2, 864–878.
27. Guinier, A.; Fournet, G. *Small Angle Scattering of X-Rays*; John Wiley and Sons: New York, NY, 1955.
28. Menon, S.V.G.; Kelkar, V.K.; Manohar, C. Application of Baxter's model to the theory of cloud points of nonionic surfactant solutions. *Phys. Rev. A.* **1991**, *43*, 1.
29. Staritzky. *Anal. Chem.* **1956**, *28*, 2021–2022.
30. Healy, T.V.; McKay, H.A.C. The extraction of nitrates by tri-*n*-butyl phosphate. Part 2: The nature of the TBP phase. *Trans Faraday Soc* **1956**, *52*, 633.
31. Borkowski, M.; Ferraro, J.R.; Chiarizia, R.; McAlister, D.R. FT-IR study of third phase formation in the U(VI) or Th(IV)/HNO₃, TBP/alkane systems. *Solvent Extr. Ion Exch.* **2002**, *20*, 313–330.
32. Ruckenstein, E.; Nagarajan, R. Aggregation of amphiphiles in nonaqueous media. *J. Phys. Chem.* **1980**, *84*, 1349–1358.
33. Pedersen, J.S. Analysis of small-angle scattering data from colloids and polymer solutions: Modeling and least-squares fitting. *Adv. Colloid Interface Sci.* **1997**, *70*, 171–210.
34. Krevinskaia, M.Ye.; Nikol'skii, V.D.; Pozharskii, B.G. *Radiokhimiya* **1959**, *1* (5), 554–561.
35. Vdovenko, V.M.; Lipovskii, A.A.; Kuzina, M.G. Spectrophotometric investigation of the formation of plutonyl nitrate complexes in aqueous solutions and extraction of Pu(VI) by dibutyl ether. *Radiokhimiya* **1960**, *2* (3), 307–311.
36. Kertes, A.S. The chemistry of the formation and elimination of a third phase in organophosphorus and amine extraction systems. In *Solvent Extraction Chemistry of Metals*; McKay, H.A.C., Healy, T.V., Jenkins, I.L., Naylor, A., eds.; MacMillan: London, UK, 1965, 377–400.
37. Indikov, E.M.; Ionov, V.I.; Solovkin, A.S.; Teterin, E.G.; Shesterikov, N.N. Separation into layers in the HClO₄-H₂O-tri-*n*-butyl phosphate–diluent system. *Russian J. Inorg. Chem.* **1965**, *10*, 1396–1397.