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SANS Study of Third Phase Formation in the Th(IV)-HNO_3/TBP-*n*-Octane System[#]

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ABSTRACT

Formation of a third organic phase at high metal loading in the extraction of tetravalent actinides by TBP in aliphatic diluents has been investigated mostly from the standpoint of the composition of the organic phase species before and after phase splitting. Very little is known of the structure and morphology of the organic phase species. In this work, a study of third phase formation upon either dissolution of $Th(NO_3)_4$ in 20% TBP in *n*-octane or $Th(NO_3)_4$ extraction from 1 M HNO_3 by 20%

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TBP in *n*-octane is reported. Chemical analyses have shown that, under the conditions of this work, Th(IV) exists in the organic phase mainly as the trisolvate $Th(NO_3)_4 \cdot (TBP)_3$. The third phase species also contains a small amount of HNO_3, presumably hydrogen-bonded to the trisolvate complex. Small-angle neutron scattering measurements on TBP solutions loaded with only HNO_3 or with increasing amounts of Th(IV) revealed the presence, before phase splitting, of large ellipsoidal aggregates with the parallel and perpendicular axes having lengths up to about 230 and 24 Å, respectively. Although the formation of these aggregates is observed in all cases, that is, when only HNO_3, only $Th(NO_3)_4$, or both HNO_3 and $Th(NO_3)_4$ are extracted by the TBP solution, the size of the aggregates is largest in the latter case. Formation of these aggregates is probably the main reason for phase splitting.

Key Words: Third phase; Th(VI); TBP.

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INTRODUCTION

Third (or heavy) organic phases, formed in the extraction of high amounts of metal species from aqueous phases containing mineral acids by extractants dissolved in nonpolar diluents, are highly structured phases that can be regarded as liquid crystals having a lamellar stucture.[1,2]Very little structural information, however, is available on the species that are present in the organic phase immediately before separation into a light and a heavy layer.

It has been recently recognized that in the solvent extraction of metal species by a variety of extractants in nonpolar diluents, the phenomenon of third phase formation is preceded, in general, by extensive aggregation of the metal-extractant complexes in the organic phase. This was reported for the first time, to our knowledge, in the extraction of $Pr(NO_3)_3$ by octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) in various diluents.[3,4] In this study, small-angle neutron scattering (SANS) measurements revealed the presence in solution of polymeric species having an elongated shape with a diameter up to 40 Å and a length as high as 500 Å. The investigators hypothesized that the formation of these large particles might be an intermediate stage between a single organic phase containing only monomers and the separation of a third phase.

Similar observations have been reported in recent works on HNO_3 extraction by N,N′-dimethyl-N,N′-dibutyl-2-tetradecylmalonamide (DMDB-TDMA) in *n*-dodecane.[5–7]Also in this case, small-angle x-ray scattering measurements revealed the onset of extensive aggregation of the organic phase species when phase splitting was approached. In one of these works,[6]

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the investigators successfully attempted the theoretical prediction of third phase formation through the Flory–Huggins theory of polymer solutions. This approach was based on the analogy between the clouding phenomena occurring in aqueous solutions of nonionic surfactants and the DMDBTDMA system, in which aggregate interactions seemed to be responsible for third phase formation.

In other SANS investigations of metal extraction by dialkyl-substituted alkylenediphosphonic acids in toluene, some of the present authors observed the formation of large cylindrical aggregates upon loading the organic phase with progressively higher concentrations of certain metal ions, such as Fe(III) and Th(IV).[8–10]Attempts to further increase the metal concentration in the organic phase eventually led to the separation of a semisolid third phase. The appearance of this new phase might be interpreted as the final step of an extensive aggregation process involving the organic phase species. In these studies, it was also observed that the aggregates formed by the Th(IV)-diphosphonic acid complexes were much larger than those brought about by other cations, and that the tendency of these aggregates to grow increased substantially as the point of phase separation was closely approached.

The extraction systems just mentioned involve bifunctional extractants. In these systems, large polymeric species in the presence of high-metal concentrations are expected, as metal ions can act as a bridges by binding to functional groups of different extractant molecules, thus leading to formation of large polynuclear species. However, formation of aggregates in the organic phase before third phase formation has also been observed with monofunctional extractants. In fact, in an attempt to verify that the formation of large aggregates in the organic phase before phase splitting is a general feature shared by most, if not all, solvent extraction systems, we have revisited the U(VI)-HNO_3/tri-*n*-butylphosphate (TBP)-*n*-dodecane system from the standpoint of third phase formation.[11] SANS measurements on TBP solutions loaded with only HNO_3 or with increasing amounts of $UO_2(NO_3)_2$ revealed the presence, before and after phase splitting, of ellipsoidal aggregates with the parallel and perpendicular axes having lengths up to about 64 and 15 Å, respectively.

The objective of this work is to report on the morphology of the species present in the organic phase before third phase formation in the extraction of $Th(NO_3)_4$ by alkane solutions of TBP. This study complements our previous work on $UO_2(NO_3)_2$ extraction by TBP.[11] We thought it would be interesting to investigate the Th(IV) system because: (1) the extraction of Th(IV) and other tetravalent actinides by TBP under conditions suitable for third phase formation has been the subject of several investigations (the most important physicochemical results are summarized in two excellent reviews[12,13]); (2) in

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analogy with the behavior of dialkyl-substituted alkylenediphosphonic acids, it was expected that the Th(IV)-TBP organic phase complexes would form much larger aggregates than those observed for U(VI).

EXPERIMENTAL

Materials

In the present work, the same materials were used as in our previous investigation.[11] *n*-Octane and deuterated octane (d_{18}, 98 atom % D, in the following indicated as D-octane) were obtained from Aldrich Chem. Co. (Milwaukee, WI, USA). In this study, D-octane was preferred to D-dodecane as the diluent to reduce the cost associated with the preparation of a large number of samples for SANS measurements. $Th(NO_3)_4{\cdot}4H_2O$ was obtained from Fisher Scientific Co. (Pittsburgh, PA, USA). and used as received.

Sample Preparation and Characterization

Four series of samples were prepared for the SANS measurements. 20% (v/v) TBP (0.73 M) in D-octane, not contacted with any aqueous phase, was the only sample of the first series.

The samples of series 2 (a through c) were prepared by dissolving increasing amounts of solid $Th(NO_3)_4{\cdot}4H_2O$ in the 20% TBP solution in D-octane. These samples did not contain HNO_3, but only the Th(IV) nitrate salt. Sample 2c has the highest concentration of $Th(NO_3)_4$ achievable in the organic phase (LOC, limiting organic concentration) without phase splitting. Any attempt to introduce more $Th(NO_3)_4$ in the system is followed by the splitting of the solution into a heavy (sample 2d, with a density of 1.246 g/mL) and a light organic phase (sample 2e). The behavior of $Th(NO_3)_4$ is thus quite different from that of $UO_2(NO_3)_2$. With the latter salt, it is possible to saturate the TBP solution without phase separation. The different behavior of the Th(IV) and U(VI) nitrate salts confirms the well-known fact that tetravalent actinides are much more effective than hexavalent actinides in promoting third phase formation.[14]

Samples 3 (a through f) were prepared by equilibrating, at 23 ± 1°C and at a phase ratio of 1 the 20% TBP solution with aqueous phases containing progressively higher HNO_3 concentrations (1, 2.5, 5.0, 7.5, 11.0, and 16.0 M, respectively) and no Th(IV) salt. With *n*-dodecane as the diluent, phase splitting is observed when TBP extracts nitric acid from concentrated aqueous HNO_3.[14]

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However, no third phase formation was observed in the preparation of the samples of series 3, in agreement with previous results showing that shorter alkyl chains in the diluent depress the tendency to third phase formation.[12]

The samples of series 4 (a through f) contained varying concentrations of both HNO_3 and Th(IV). They were prepared by contacting a small volume of the TBP solution with an equal volume of 1 M HNO_3 solutions containing progressively increasing concentrations of $Th(NO_3)_4$. When contacting the 20% TBP organic phase with an aqueous solution that was 1.11 M in $Th(NO_3)_4$ and 1 M in HNO_3, a third phase was obtained having a volume of about 17% of the original organic phase volume, and a density of 1.158 g/mL (sample 4e). Sample 4f was the light organic phase in equilibrium with the third phase sample. Sample 4d had the Th(IV) limiting organic concentration (LOC). This sample was obtained by first causing formation of the third phase and then adding very small amounts of lean organic phase and/or water until the third phase disappeared, as indicated by the absence of turbidity in the organic phase.

After centrifugation and phase separation, aliquots of the various phases were analyzed. The HNO_3 concentration in the aqueous phases was determined by potentiometric titration to pH ~ 6 with standard base after appropriate dilution and after making the solution 0.2 M in $(NH_4)_2C_2O_4$ to mask the metal. The aqueous Th(IV) concentration was determined by ICP-AES. The organic HNO_3 and Th(IV) were first stripped by contacting two times an aliquot of the organic phases diluted five fold with octane, with an equal volume of water and then with a larger and known volume of a 0.1 M $(NH_4)_2C_2O_4$. HNO_3 and Th(IV) in the stripping solution were then determined as discussed previously.

In all the samples where no third phase was generated, the equilibrium TBP concentration was assumed to be equal to the initial one, that is, 0.73 M, neglecting small changes of the organic phase volume upon dissolution or extraction of $Th(NO_3)_4$ and/or HNO_3. The TBP concentration in the heavy and light organic phases resulting from phase splitting were determined following a published procedure.[15] According to this procedure, if a TBP solution in aliphatic diluents is contacted with aqueous 10 M $HClO_4$, the TBP reports quantitatively to the heavy organic phase that is generated. The TBP concentration in the original solution can then be estimated with a good degree of approximation (± 10%) from the volume of the third phase. The 2d, 2e, 4e, and 4f samples were first diluted with a known volume of *n*-octane and then contacted with 10 M $HClO_4$ in thin calibrated test tubes after HNO_3 and Th(IV) stripping. In each case, the volume of the $TBP{\cdot}HClO_4$ containing third phase was converted into TBP concentration by using an ad hoc calibration curve of third phase volume vs TBP concentration.

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SANS Measurements

The SANS measurements were performed at the time-of-flight, small-angle neutron diffractometer (SAND) at the Intense Pulsed Neutron Source of Argonne National Laboratory.[16,17] The main characteristics of the SAND diffractometer have been described in the preceding paper.[11] For each sample, the data were collected as scattered intensity, I(Q) (cm^{-1}) vs momentum transfer [$\mathrm{Q} = (4\pi/\lambda)\sin(\theta)\,(\mathrm{\AA}^{-1})$], where θ is half the scattering angle and λ is the wavelength of the probing neutrons.

The SANS data were also analyzed using nonlinear, least-squares fits to the following form factor for an ellipsoid of rotation[18]:

$$\mathrm{P}(\mathrm{Q},a,b) = \int_0^{\pi/2} \frac{3[\sin(\mathrm{Qr}(a,b,\alpha)) - \mathrm{Qr}(a,b,\alpha)\cos(\mathrm{Qr}(a,b,\alpha))]}{(\mathrm{Qr}(a,b,\alpha))^3}\sin\alpha\, \mathrm{d}\alpha \tag{1}$$

including a multiplicative scale factor for the intensity at $\mathrm{Q} = 0$ and a constant background term to account for incoherent scattering from hydrogen. Here, α is an orientation angle used to integrate over all possible orientations of the particles relative to the incident beam, α is the length of the semiaxes pendicular to the axis of rotation, b is the length of the semiaxis parallel to the axis of rotation, and

$$\mathrm{r}(a,b,\alpha) = a\left(\sin^2\alpha + \frac{b}{a}\cos^2\alpha\right) \tag{2}$$

From the values of a and b, the radius of gyration, $\mathrm{R_g}$, of the particles was calculated through the relation $\mathrm{R_g} = \sqrt{((2a^2 + b^2)/5)}$. $\mathrm{R_g}$ is a measure of the spatial extension of the particle and is given by the root-mean-squared distances of all the atoms from the centroid of the scattering particle.

RESULTS AND DISCUSSION

Table 1 summarizes the analytical results for the samples investigated in this work. When solid $\mathrm{Th(NO_3)_4}$ is dissolved in 20% TBP in D-octane, the highest metal concentration achievable is 0.21 M (LOC condition). If $\mathrm{Th(NO_3)_4}$ is extracted from a 1 M $\mathrm{HNO_3}$ aqueous solution, the Th(IV) LOC concentration is lower, 0.18 M. This is the result of the competition between Th(IV) and $\mathrm{HNO_3}$ for the P═O groups of TBP. The competition is clearly visible in samples 4a through 4d, where an increase of metal concentration is accompanied by a decrease in $\mathrm{HNO_3}$ concentration.

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Table 1. Composition of samples for SANS measurements.

Sample	[TBP][a] M	[Th][b] M	[HNO$_3$][c] M	[Disolvate][d] M	[Trisolvate][e] M	[HNO$_3$·TBP] M	[TBP] free M
1	0.73	0	0	0	0	0	0.73
2a	0.73	0.038	0	0	0.038	0	0.62
2b	0.73	0.16	0	0	0.16	0	0.26
2c (LOC)	0.73	0.20_5	0	0	0.20_5	0	0.11_5
2d (third ph)	2.17	0.74	0	0	0.74	0	0
2e (light ph)	0.20	0.076	0	0.028	0.048	0	0
3a	0.73	0	0.17	0	0	0.17	0.56
3b	0.73	0	0.36	0	0	0.36	0.37
3c	0.73	0	0.61	0	0	0.61	0.12
3d	0.73	0	0.72	0	0	0.72	0.01
3e	0.73	0	0.84	0	0	0.73	0
3f	0.73	0	1.22	0	0	0.73	0
4a	0.73	0.021	0.11_5	0	0.021	0.11_5	0.55
4b	0.73	0.13	0.096	0	0.13	0.096	0.24
4c	0.73	0.16	0.090	0	0.16	0.090	0.16
4d (LOC)	0.73	0.18	0.079	0	0.18	0.079	0.11
4e (third ph.)	1.9	0.60	0.12_5	0	0.60	0	0
4f (light ph.)	0.44	0.12	0.059	0	0.12	0.059	0

[a] Estimated accuracy ± 5%, except for samples 2d, 2e, 4e, and 4f (± 10%).

[b] Estimated accuracy ± 5%.

[c] Estimated accuracy ± 10%.

[d] $Th(NO_3)_4{\cdot}(TBP)_2$.

[e] $Th(NO_3)_4{\cdot}(TBP)_3$.

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The table also reports the concentrations of the disolvate $Th(NO_3)_4\cdot(TBP)_2$, the trisolvate $Th(NO_3)_4\cdot(TBP)_3$, the $HNO_3\cdot TBP$ species, and the free TBP in the samples. These concentrations have been calculated from the TBP, Th(IV), and HNO_3 analytical concentrations by using the following metal and extractant mass-balance equations:

$$[Th] = [Th(NO_3)_4\cdot(TBP)_2] + [Th(NO_3)_4\cdot(TBP)_3] \tag{3}$$

$$[TBP] = 2\,[Th(NO_3)_4\cdot(TBP)_2] + 3\,[Th(NO_3)_4\cdot(TBP)_3] + [HNO_3\cdot TBP] + [TBP]_{free} \tag{4}$$

In these equations, thorium nitrate is assumed to exist in the TBP organic phase as disolvate and trisolvate species, in agreement with previous work indications,[12]and nitric acid is assumed to exist as the $HNO_3\cdot TBP$ species. TBP is known to extract HNO_3 from aqueous solutions forming species having the composition $(HNO_3)_i\cdot TBP$ with i equal to 1 through 4.[19]The data for the 3e and 3f samples in Table 1 clearly indicate that $(HNO_3)_i\cdot TBP$ species with $i > 1$ are formed when the TBP solution is contacted with 11 and 16 M aqueous HNO_3, respectively. However, as experimentally confirmed in our previous investigation,[11]for aqueous HNO_3 concentrations lower than $\sim 10\,M$, the approximation that HNO_3 exists in the organic phase predominantly, if not only, as the $HNO_3\cdot TBP$ species can be safely held.

When the Th(IV), HNO_3, and TBP analytical results are such that the presence of free TBP can be excluded, eqs. (3) and (4) can be solved for the two unknowns, the disolvate and trisolvate concentrations. On the other hand, when the initial TBP concentration is in excess of the concentrations of HNO_3 and metal (expressed as the trisolvate), the concentration of the disolvate can be neglected. In this case, eqs. (3) and (4) allow the calculation of the concentrations of the trisolvate and of free TBP. For the third phase samples, in analogy with the U(VI) case,[11] it is assumed that HNO_3 is part of the third phase Th(IV) complex species. The $[HNO_3\cdot TBP]$ term therefore does not appear in eq. (4) for these samples. Also, no free TBP is assumed to exist in the third phase solutions.

Based on the results of these calculations, a few considerations can be made on the composition of the samples in Table 1. In the samples of series 2, no HNO_3 is present and all the TBP is available for Th(IV) to form a trisolvate. The trisolvate is the preferred complex as long as there is free TBP. In the light phase sample, the TBP concentration is much lower and the extractant distributes between a disolvate and a trisolvate species.

In the samples of series 4, because the HNO_3 concentration is low, there is always enough TBP for the trisolvate to form. In the third (4e) and light phase

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(4f) samples, the TBP concentration is sufficiently high to form only the trisolvate, practically without free TBP.

Finally, it is interesting to observe that in the third phase sample (4e), the ratio of Th(IV) to HNO_3 concentration is much higher than 1. This is in contrast with the U(VI) system, for which a unit ratio of U(VI) to HNO_3 in the third phase was reported.[11]This difference between the Th(IV) and the U(VI) third phases undoubtely arises from the vastly different experimental conditions used for sample preparation [1 M aqueous HNO_3 for Th(IV) vs 10 M for U(VI)]. Preliminary measurements have indicated that if Th(IV) third phase samples are prepared by extracting the metal from concentrations of aqueous HNO_3 higher than 1 M, ratios of metal to acid concentration much closer and even lower than 1 are obtained. It seems, therefore, that the composition of the third phase species is not constant, but depends on the aqueous acidity. This phenomenon is relatively difficult to discern in the U(VI) system, simply because it is not possible to prepare a U(VI)-TBP third phase at aqueous HNO_3 concentrations lower than ~10 M.

Figure 1 shows the SANS data for the samples of the series 1 and 2. These data clearly illustrate the very pronounced increase in scattering intensity

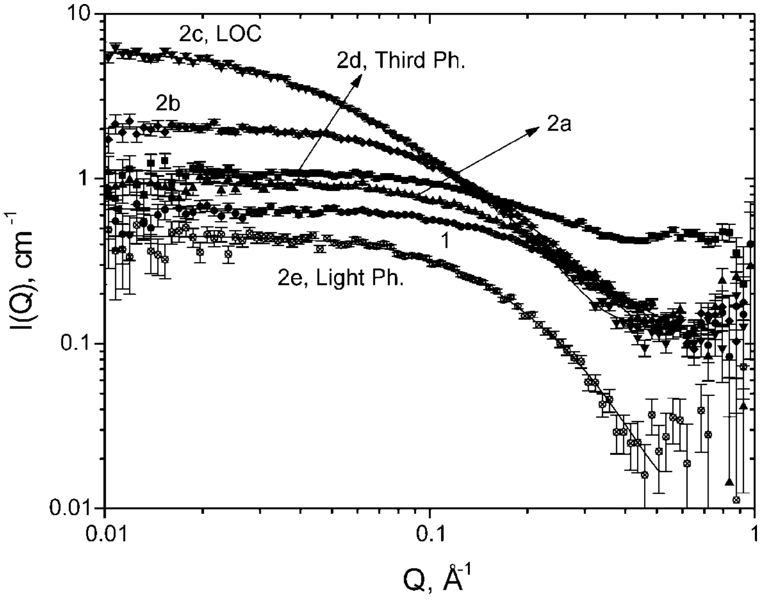

Figure 1. SANS data for samples of series 1 and 2. For the composition of the samples, see Table 1. The continuous lines represent the ellipsoid of rotation fit of the data.

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observed in the low Q region, when increasing amounts of solid $Th(NO_3)_4$ are dissolved in 20% TBP up to the LOC conditions (from data set 1 to data set 2c). After phase splitting, a much lower scattering intensity is exhibited by the light phase (sample 2e), while the scattering profile for the heavy phase (sample 2d), a concentrated solution of TBP and Th(IV), is quite different from that for the other samples.

Figure 2 shows the SANS data for selected samples of series 3. The data for sample 1 (TBP alone) are included for comparison. The data in Fig. 2 indicate that introduction of a small amount of HNO_3 in the TBP solution (sample 3a) causes an increase of the scattering intensity at low Q. However, this intensity remains essentially constant with an increase of the HNO_3 concentration, until a stoichiometric excess of HNO_3 relative to TBP is present in the organic phase (sample 3e), and increases substantially only when the HNO_3 to TBP concentration ratio is much higher than one, as in sample 3f.

Figure 3 collects the SANS data for the samples of series 4, together with sample 3a (no metal) for comparison. The scattering intensity for samples 3a, 4a, and 4b is practically the same, indicating that small amounts of $Th(NO_3)_4$

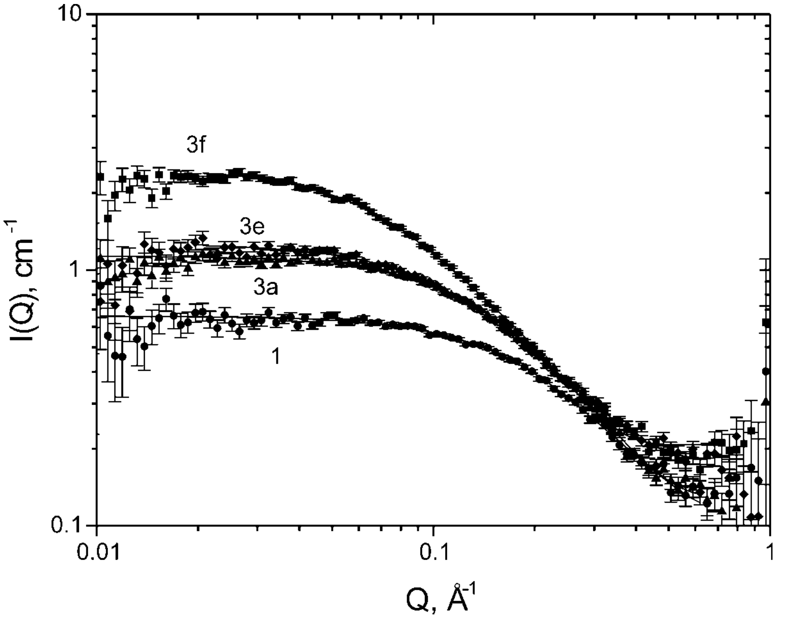

Figure 2. SANS data for samples 1, 3a, 3e, and 3f. For the composition of the samples, see Table 1. The continuous lines represent the ellipsoid of rotation fit of the data.

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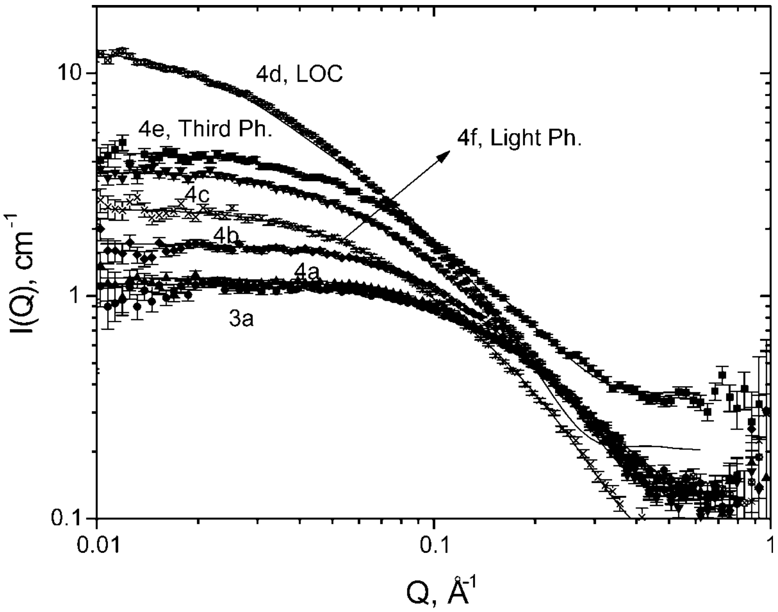

Figure 3. SANS data for sample 3a and for samples of series 4. For the composition of the samples, see Table 1. The continuous lines represent the ellipsoid of rotation fit of the data.

extracted together with HNO_3 from a 1 M aqueous HNO_3 solution, have little or no effect on scattering. On the other hand, when the metal concentration approaches the LOC conditions (samples 4c and 4d), a very pronounced increase in scattering intensity is observed. After phase splitting, similar to the data in Fig. 1, the light phase exhibits a reduced scattering intensity (sample 4f), while the heavy phase (sample 4e) originates a quite different scattering profile.

Figures 1, 2, and 3 also show the fit of the data with an ellipsoid of rotation form factor. The fit is generally good, except for the LOC solution of series 4. For each data set, Table 2 reports the perpendicular (a) and parallel (b) semiaxes, the gyration radius calculated from the values of the semiaxes, and I(0), the scattering intensity at $Q = 0$.

The values of the semiaxes and of R_g in Table 2 clearly indicate that by dissolving $Th(NO_3)_4$ or by extracting $Th(NO_3)_4$ and HNO_3 in 20% TBP, large aggregates are generated in solution, whose growth with increasing metal concentration that takes place mostly along the b axis. The largest particles are

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Table 2. Ellipsoid of rotation fit of SANS data.

Sample	*a*, perpendicular semiaxis, Å	*b*, parallel semiaxis, Å	R_g Å	I(0) cm^{-1}	$n_{w,exp}$	$n_{w,calc}$
1	4.7 ± 0.6	15.2 ± 0.4	7.4 ± 0.4	0.55 ± 0.02	1.6 ± 0.1	1.6
2a	4.5 ± 0.9	19.3 ± 0.3	9.1 ± 0.4	0.87 ± 0.01	2.5 ± 0.2	2.8
2b	7.0 ± 0.2	29.3 ± 0.3	13.8 ± 0.3	1.98 ± 0.02	5.5 ± 0.3	5.0
2c (LOC)	9.5 ± 0.1	73.8 ± 0.8	33.5 ± 0.7	5.87 ± 0.05	16 ± 1	17.5
2d (third ph)	6.8 ± 0.4	19.1 ± 0.5	9.6 ± 0.5	0.71 ± 0.01	—	—
2e (light ph)	6.4 ± 0.5	21.7 ± 0.6	10.5 ± 0.6	0.44 ± 0.01	4.5 ± 0.3	5.3
3a	5.9 ± 0.2	20.7 ± 0.2	10.0 ± 0.2	1.01 ± 0.01	2.8 ± 0.2	2.9
3b	6.1 ± 0.2	23.5 ± 0.3	11.2 ± 0.3	1.19 ± 0.01	3.3 ± 0.2	3.5
3c	6.2 ± 0.3	23.9 ± 0.4	11.4 ± 0.3	1.06 ± 0.01	3.0 ± 0.2	2.9
3d	5.6 ± 0.2	24.1 ± 0.3	11.3 ± 0.2	1.03 ± 0.01	2.9 ± 0.2	3.0
3e	6.5 ± 0.2	25.2 ± 0.4	12.0 ± 0.3	1.09 ± 0.01	3.1 ± 0.2	3.0
3f	8.5 ± 0.1	39.4 ± 0.5	18.4 ± 0.4	2.30 ± 0.02	6.4 ± 0.4	6.0
4a	6.1 ± 0.2	21.2 ± 0.2	10.2 ± 0.2	1.09 ± 0.01	3.1 ± 0.2	2.9
4b	7.0 ± 0.1	27.2 ± 0.2	12.9 ± 0.2	1.61 ± 0.01	4.5 ± 0.3	4.4
4c	8.3 ± 0.1	45.7 ± 0.3	21.1 ± 0.3	3.53 ± 0.02	9.9 ± 0.6	9.7
4d (LOC)	12.1 ± 0.1	114 ± 1	51.4 ± 0.9	13.2 ± 0.1	37 ± 2	36
4e (third ph.)	9.6 ± 0.1	46.6 ± 0.5	21.7 ± 0.4	4.11 ± 0.03	—	—
4f (light ph.)	8.1 ± 0.1	44.3 ± 0.5	20.5 ± 0.4	2.42 ± 0.02	11 ± 1	11

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formed in the LOC solutions or series 2 and 4, with the *b* axis reaching the lengths of ~148 and 228 Å, respectively.

Following the same approach reported previously,[11] the scattering entities in the samples of Table 2 can be described as TBP aggregates. Since the SANS data are available on an absolute scale, the I(0) values can be used to determine the molecular weight of the extractant aggregates and, hence, the aggregation number of TBP in the aggregates, through eq. (5), which holds for $Q = 0$:

$$I(0) = N_p(\rho_p - \rho_s)^2 V_p^2 \tag{5}$$

where N_p is the number of scattering particles per volume, V_p is the particle volume, and ρ_p and ρ_s are the scattering length densities of the extractant and solvent respectively.

After rearranging and introducing molar quantities in eq. (5), one obtains eq. (6), from which the weight average aggregation number of TBP, n_w, can be calculated for each sample:

$$n_w = \frac{M_w}{MW_{TBP}} = \frac{6.022 \times 10^{26}\, d_{TBP}^2 I(0)}{[TBP]_{total}\,(\rho_p - \rho_s)^2 MW_{TBP}^2} \tag{6}$$

In eq. (6), M_w is the weight average molecular weight of the extractant aggregates, MW_{TBP} and d_{TBP} are the molecular weight (266.32) and the density (0.973 g/mL) of the extractant, and $[TBP]_{total}$ is the total extractant concentration in the organic phase. The scattering length densities of TBP ($\rho_p = 1.566 \times 10^9\,cm^2$) and of D-octane ($\rho_s = 6.426 \times 10^{10}\,cm^2$) were calculated from the sum of the scattering length densities of the individual atoms. As the scattering contrast between solute and solvent is essentially determined by the different neutron scattering properties of the H and D atoms, only the highly hydrogenous molecule of TBP was considered in the calculation of ρ_p.

Table 2 reports the TBP aggregation number obtained by using eq. (6) for all samples, except the third phase. For the latter samples, a different approach was followed (vide infra). Uncertainties in the n_w values were derived from the uncertainty in I(0) and the assumption of 2% uncertainty in d_{TBP} and 5% uncertainty in $[TBP]_{total}$ (for samples 2e and 4f, the uncertainty in $[TBP]_{total}$ was about 10%).

In Fig. 4a, the n_w values are plotted as a function of the metal concentration in the samples of series 2 and 4. In Fig. 4b similar data are shown for the U(VI) system described previously.[11]For the Th(IV)-TBP system, the curves in Fig. 4a exhibit a much steeper increase of n_w for metal concentrations approaching the LOC condition than for the U(VI) case. These

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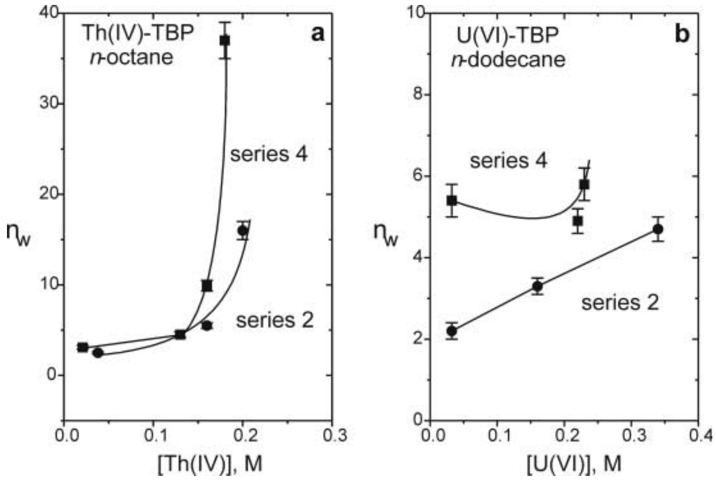

Figure 4. TBP aggregation number, n_w, as a function of metal concentration in the organic phase: a) data from the present work; b) data from Chiarizia et al.[11]

results confirm the tendency of Th(IV) to promote formation of larger aggregates than other cations, in analogy to our previous observation with dialkyl-substituted alkylenediphosphonic acids.[9,10]

The experimental $n_{w,exp}$ values in Table 2 can be reproduced by making hypotheses on the species in solution, and then obtaining calculated $n_{w,calc}$ values from mass-balance considerations and the following expression for the weight average aggregation number[20]:

$$n_w = \frac{\sum_n n^2 [(TBP)_n]}{\sum_n n[(TBP)_n]} \tag{7}$$

where $[(TBP)_n]$ is the organic phase concentration of each n-mer of TBP with or without HNO_3 and/or Th(IV). In the calculations, it has been assumed that free, unbound TBP exists either as a monomer or as a dimer with a dimerization constant of 2.6.[21]The validity of this approach was confirmed by the excellent agreement of calculated and experimental n_w values for sample 1, where only TBP is present in solution.

For the samples of series 2, calculated n_w values that agree with the experimental ones are obtained by assuming that the $Th(NO_3)_4{\cdot}(TBP)_3$ trisolvate (as well as the disolvate in the light phase sample) exists as dimers (seen in the SANS data as TBP hexamers and tetramers, respectively). For

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sample 2c, however, representing the LOC conditions, a hexameric trisolvate (for a total of 18 molecules of TBP) needs to be assumed. According to this model, the steep increase in the TBP aggregation number observed prior to third phase formation (see Fig. 4a) corresponds to the self-assembly of six trisolvate molecules in a large, ellipsoidal aggregate with axes of 19 and 148 Å, respectively.

For the samples of the series 3, containing only HNO$_3$, the hypothesis that HNO$_3$·TBP exists in solution as tetramers (samples 3a and 3b) or trimers (samples 3c, 3d and 3e) leads to calculated n_w values that match the experimental values well. For sample 3f, where each TBP molecule is bound to more than one HNO$_3$, the $n_{w,exp}$ can be reproduced by assuming that the $(HNO_3)_i$·TBP complexes are hexameric.

The samples of series 4 contain both the $Th(NO_3)_4$· $(TBP)_3$ trisolvate and the HNO$_3$·TBP species, besides monomeric and dimeric TBP molecules. The HNO$_3$·TBP should be tetrameric, as indicated by the results of sample 3a for the extraction of HNO$_3$ from 1 M aqueous HNO$_3$. To reproduce the experimental n_w values, it is necessary to hypothesize that the trisolvate exists as a dimer in samples 4a and 4b, and as a tetramer in samples 4c and 4f. To reproduce the experimental n_w value for the LOC sample, one must assume the existence of very large aggregates of the trisolvate (a 13-mer, for a total of 39 TBP molecules) together with tetrameric HNO$_3$·TBP. As for the samples of series 2, the almost "explosive" increase of the TBP aggregation number just before phase splitting (see Fig. 4a) can then be rationalized as the self-assembly of 13 molecules of $Th(NO_3)_4·(TBP)_3$ in a huge ellipsoidal aggregate with axes as long as 24 and 228 Å, respectively. From a TBP aggregation standpoint, it seems, therefore, legitimate to interpret third phase formation as the result of a very pronounced aggregation process leading to particles that when the LOC condition is approached, may be too large for remaining in solution and may thermodynamically be more stable if separated in a third phase.

For the interpretation of the SANS data of the third phase samples, the same approach outlined previously[11] was attempted. According to this appproach, the third phase is considered as a solution of D-octane in a diluent made of the $Th(NO_3)_4·(TBP)_3$ trisolvate (with some HNO$_3$ in the case of sample 4e). For these samples, the scattering data should reveal the presence of pockets of D-octane in a matrix of hydrogeneous TBP.

From the analytical data in Table 1 and the densities of the third phase samples, the D-octane concentrations in the third phase were estimated to be 2.26 and 2.69 M for samples 2d and 4e, respectively. The scattering length density of $Th(NO_3)_4·(TBP)_3$ ($9.761 \times 10^9\,cm^2$) was calculated by including the contribution of all its atoms. This value was used, together with

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the scattering length density of D-octane, in a properly modified version of eq. (6), to calculate the average number of D-octane molecules contained in pockets of D-octane in the third phase samples.

The results were about one and six D-octane molecules for samples 2d and 4e, respectively. The first value seems unrealistic because the radius of gyration of one *n*-octane molecule, calculated as shown by Chiarizia et al.[11]for *n*-dodecane, is only 3.6 Å and, therefore, much lower than the value of 9.6 Å provided by the SANS data for sample 2d. The second value, however, is more representative. In fact, six contiguous molecules of *n*-octane describe a cylinder about 74 Å long, with a radius of gyration that is 21.4 Å, in perfect agreement with the value of 21.7 Å obtained from the fit of the data for sample 4e.

CONCLUSION

When $Th(NO_3)_4$ is introduced into a 20% TBP solution in *n*-octane, organic phase splitting into a heavy and a light layer is readily achieved both when solid $Th(NO_3)_4$ is dissolved in the solution, and when the metal is extracted from dilute aqueous nitric acid. This behavior is quite in contrast with that of U(VI), for which no phase splitting is observed by dissolution in 20% TBP of solid $UO_2(NO_3)_2$ or by U(VI) extraction from aqueous $HNO_3 \leq 10\,M$.

Under the experimental conditions of this work, chemical analyses have indicated that Th(IV) exists in the TBP phase predominantly as the trisolvate $Th(NO_3)_4 \cdot (TBP)_3$. This also applies to the metal species in the heavy and light phases resulting from phase splitting. In the third phase obtained by extracting $Th(NO_3)_4$ from 1 M HNO_3, the third phase species also contains a small amount of HNO_3 at a Th(IV) to HNO_3 concentration ratio of about 5.

Small-angle neutron scattering measurements on D-octane solutions containing only TBP, or TBP loaded with increasing amounts of HNO_3 and/or Th(IV), provided information on size and shape of the particles in solution.

When HNO_3 is extracted by a 20% TBP solution in *n*-octane in the absence of metal ions, the SANS data indicate the formation of small ellipsoidal aggregates, each containing three to four $HNO_3 \cdot TBP$ molecules. Larger aggregates are observed if the TBP solutions is contacted with 16 M HNO_3.

When $Th(NO_3)_4$ is dissolved in the TBP solution, or when $Th(NO_3)_4$ is extracted from 1 M aqueous HNO_3, small aggregates are initially formed, containing six TBP molecules (dimeric trisolvate). However, as the Th(IV) concentration in the organic phase is increased, the size of the aggregates

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increases dramatically, especially for metal concentrations immediately preceding third phase formation, as it is the case for samples containing the metal limiting organic concentration (LOC). In the case of Th(IV) extraction from 1 M HNO_3, for example, the ellipsoidal aggregates have axes that are about 24 and 228 Å long, respectively.

The aggregates in the light phase resulting from phase splitting are somewhat smaller than those observed in the LOC samples. The third phase can be described as a continuous and probably highly structured $Th(NO_3)_4 \cdot (TBP)_3 \cdot (HNO_3)_x$ phase, where the value of the *x* coefficient depends on the aqueous HNO_3 concentration. The third phase has interdispersed pockets of diluent, each containing about six molecules of D-octane (at least in the case of the third phase obtained through solvent extraction).

In the U(VI)-TBP system investigated previously, much smaller aggregates than those of the present work were detected in solution prior to phase splitting.[11]It was concluded, therefore, that the main reason for third phase formation was the presence of a molecule of HNO_3 in the third phase species having the $UO_2(NO_3)_2 \cdot (TBP)_2 \cdot HNO_3$ composition. It was hypothesized that the introduction of a large amount of HNO_3 in the polar core of the reverse micelle-like TBP aggregates made the aggregates too polar for being compatible with an alkane diluent.

A similar explanation can still apply for the Th(IV)-TBP system investigated in this work. The polarity increase of the TBP aggregates can be provided in this case by the high charge of the Th(IV) cation. However, an alternative explanation can be given for third phase formation in the Th(IV)-TBP system. In this case, this phenomenon can be reasonably attributed to the presence in solution of very large aggregates where the TBP molecules are structured in the coordination sphere of the Th(IV) cation. When these aggregates become exceedingly large, as observed for example in the LOC samples investigated in this work, the Th(IV)-TBP species separate in a different and thermodynamically more stable phase, from which most of the diluent has been expelled.

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REFERENCES

1. Zilberman, B.Ya.; Fedorov, Yu. S.; Borovikov, E.A.; Afonin, M.A.; Korolev, V.V. Extraction Chemistry of Uranyl Nitrate and Nitric acid in High Concentrating Systesm. J. Radioanal. Nucl. Chem. **1991**, *150* (2), 363–367.
2. Fu, X.; Hu, Z.; Wang, D.; Liu, H.; Hu, X. Progress in the Study of Three-Phase Extraction System - The Formation, Microstructure and Application of the Third Phase. Chem. J. Internet **2000**, *2* (3), 18–25.
3. Thiyagarajan, P.; Diamond, H.; Horwitz, E.P. Small-Angle Neutron Scattering Studies of the Aggregation of Pr (NO_3) 3-CMPO and $PrCl_3$ - CMPO Complexes in Organic Solvents. J. Appl. Cryst. **1988**, *21*, 848–852.
4. Diamond, H.; Thiyagarajan, P.; Horwitz, E.P. Small-Angle Neutron Scattering Studies of Praseodymium - CMPO Polymerization. Solvent Extr. Ion Exch. **1990**, *8* (3), 503–513.
5. Erlinger, C.; Gazeau, D.; Zemb, T.; Madic, C.; Lefrançois, L.; Hébrant, M.; Tondre, C. Effect of Nitric Acid Extraction on PhaseBehavior, Microstructure and Interactions Between Primary Aggregates in the System Dimethyldibutyltetradecylmalonamide (DMDBTDMA) / n-Dodecane / Water: A Phase Analysis and Small-Angle X-Ray Scattering (SAXS) Characterisation Study. Solvent Extr. Ion Exch. **1998**, *16* (3), 707–738.
6. Lefrançois, L.; Belnet, F.; Noel, D.; Tondre, C. An Attempt to Theoretically Predict Third-Phase Formation in the Dimethyldibutyltetradecylmalonamide (DMDBTDMA) / Dodecane / Water / Nitric Acid Extraction System. Sep. Sci. Technol. **1999**, *34* (5), 755–770.
7. Lefrançois, L.; Delpuech, J.J.; Hébrant, M.; Chrisment, J.; Tondre, C. Aggregation and Protonation Phenomena in Third Phase Formation: An NMR Study of the Quaternay Malonamide / Dodecane / Nitric Acid / Water System. J. Phys. Chem. **2001**, *105*, 2551–2564.
8. Chiarizia, R.; Urban, V.; Thiyagarajan, P.; Herlinger, A.W. Aggregation of P, P′-Di (2-ethylhexyl) Methanediphosphonic Acid and its Fe(III) Complexes. Solvent Extr. Ion Exch. **1998**, *16* (5), 1257–1278.
9. Chiarizia, R.; Urban, V.; Thiyagarajan, P.; Herlinger, A.W. Aggregation of Complexes Formed in the Extraction of Selected Metal Cations by P,

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P′-Di (2 ethylhexyl) Methanediphosphonic Acid. Solvent Extr. Ion Exch. **1999**, *17* (1), 113–132.

10. Chiarizia, R.; Urban, V.; Thiyagarajan, P.; Herlinger, A.W. SANS Study of Aggregation of Complexes Formed in the Extraction of Selected Metal Cations by P, P′-Di (2-ethylhexyl) Ethane- and Butane-Diphosphonic Acids. Solvent Extr. Ion Exch. **1999**, *17* (5), 1171–1194.
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)-HNO_3/TBP-n-Dodecane System, Sep. Sci. Technol., preceding paper.
12. 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* (6), 955–993.
13. 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*; McMillan: London, 1965, pp. 377–399.
14. Marcus, Y.; Kertes, A.S. *Ion Exchange and Solvent Extraction of Metal Complexes*; Wiley Interscience: New York, 1969.
15. Shilin, I.V.; Indikov, E.M.; Zhdanov, Yu.F.; Makarov, D.G. Method for Determination of Tributylphosphate in Tributylphosphate-Kerosene Mixtures. USSR Patent 114, 186, 1958, (in Russsian).
16. 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.
17. Crawford, R.K.; Thiyagarajan, P.; Epperson, J.E.; Trouw, F.R.; Kleb, R.; Wozniak, D.G.; Leach, D.J. *The new small angle diffractometer SAND at IPNS*, in *Proc. 13th International Collaboration on Advanced Neutron Sources*, Villingen, Switzerland, Oct 11–14, 1995, *PSDI-Proc* 95-02, (1997).
18. Guinier, A. La Diffraction des Rayons X aux Très Petits Angles: Application à l'Etude de Phènomènes Ultramicroscopiques. Ann. Phys. **1939**, *12*, 161–237.
19. Schaekers, J.M. Extraction of Inorganic Acids. In *Science and Technology of Tributyl Phosphate*; Schulz, W.W., Navratil, J.D., Kertes, A.S., Eds.; CRC Press: Boca Raton, Fl, 1991; Vol. IV, 71–204.
20. Young, R.J.; Lovell, P.A. *Introduction to Polymers*, 2nd Ed.; Chapman-Hall: London, 1991, 11–14.
21. Vandegrift, G.F. *Diluents for TBP Extraction Systems, in Science and Technology of Tributyl Phosphate*; Schulz, W.W., Navratil, J.D., Kertes, A.S., Eds.; CRC Press: Boca Raton, Fl, 1984; Vol. I; 69–136.