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**NEW INSIGHTS IN THIRD PHASE FORMATION IN THE U(VI)-HNO₃,
TBP-ALKANE SYSTEM**

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NEW INSIGHTS IN THIRD PHASE FORMATION IN THE U(VI)-HNO₃, TBP-ALKANE SYSTEM

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In this work, the system U(VI)-HNO₃-tributylphosphate (TBP)-*n*-dodecane has been revisited with the objective of gaining coordination chemistry and structural information on the species that are formed in the organic phase before and after third phase formation. Chemical analyses, spectroscopic and EXAFS data indicate that U(VI) is extracted as the UO₂(NO₃)₂•2TBP adduct, while the third phase species has the composition UO₂(NO₃)₂•2TBP•HNO₃. Small-angle neutron scattering (SANS) data reveal the presence in the organic phase, both before and after phase splitting, of ellipsoidal aggregates whose formation seems to depend more on the extraction of HNO₃ than that of U(VI).

INTRODUCTION

The phenomenon of third phase formation in solvent extraction is well known and has been investigated in a number of studies. Excellent reviews, one of which is quite recent, have summarized the most important aspects of this phenomenon [1,2]. The main focus in previous works has been on the conditions under which third phase formation is observed and avoided, and on the composition of the species present in the heavy organic phase. Very little information is available on structural aspects of third phase formation.

A recent work has reported that, in the case of HNO₃ extraction by a diamide extractant in *n*-dodecane, small-angle X-ray scattering measurements revealed the onset of extensive aggregation of the organic phase species when phase splitting was approached [3]. Similar observations have been reported by some of the present authors in small-angle neutron scattering studies (SANS) of metal extraction by dialkyl-substituted alkylenediphosphonic acids [4]. Large cylindrical aggregates form in toluene solutions of the extractants when they are loaded with progressively higher concentrations of certain metal ions such as Fe(III) and Th(IV). The aggregation eventually leads to the separation of a gelatinous material that can be considered a particular case of third phase formation.

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)-HNO₃-tributylphosphate (TBP)-*n*-dodecane system from the standpoint of third phase formation. We chose this system because, in spite of its technological importance, very few detailed studies are available on third phase formation when U(VI) is extracted by alkane solutions of TBP [5-7]. The objective of this work was to gain information on coordination chemistry and morphology of the species present in the organic phase before and after third phase formation.

SAMPLE PREPARATION AND CHARACTERIZATION

n-Dodecane solutions containing 20% (v/v) TBP (0.73 M) and varying concentrations of HNO₃ and U(VI) were prepared by contacting at 23 ± 1 °C a small volume of the TBP solution, preequilibrated twice with 10 M HNO₃ (phase ratio = 1), with an equal volume of 10 M HNO₃ solutions containing progressively increasing concentrations of UO₂(NO₃)₂ (from 0.040 to 0.66 M). When contacting the 20% TBP organic phase with an aqueous solution that was 0.66 M in UO₂(NO₃)₂ and 10.5 M in HNO₃, a third phase was obtained having a volume of about 13% of the original organic phase volume, and a density of 1.26 g/mL. The solutions containing the U(VI) limiting organic concentration (LOC), that is, the highest metal concentration in the organic phase that could be achieved under the selected experimental conditions without phase splitting, 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. The samples for the SANS measurements were prepared by following an identical procedure, with the exception that the diluent was *d*₂₆-deuterated dodecane.

After centrifugation and phase separation, aliquots of the various phases were analyzed. The aqueous phase HNO₃ concentrations were determined by titration to pH ~6 with standard base after appropriate dilution and after making the solution 0.2 M in (NH₄)₂C₂O₄. The aqueous U(VI) concentration was determined by ICP-AES. The organic HNO₃ and U(VI) were first stripped by contacting an aliquot of the organic phases diluted 10-fold with dodecane with a larger and known volume of 0.1 M (NH₄)₂C₂O₄. HNO₃ and U(VI) in the stripping solution were then determined as above. The TBP concentration in the heavy and light organic phases resulting from phase splitting were determined, after HNO₃ and U(VI) stripping, from the distribution ratio (D) of ²³³U between the organic phase and 3 M HNO₃ by using an *ad hoc* calibration curve of D_U vs. TBP concentration.

Table 1 summarizes the composition of the organic phases investigated in this work. The table also reports the concentration of TBP bound to U(VI) (assuming that the U(VI) exists as UO₂(NO₃)₂•2TBP in the organic phase), the concentration of the excess TBP, (that is, the TBP not bound to U(VI)), and the ratio of the HNO₃ to the excess TBP.

TBP is known to form complexes with HNO₃ having the composition TBP•(HNO₃)_n, with *n* equal to 1 through 4 [8]. Under our experimental conditions (equilibrium aqueous phase 10 M in HNO₃), the data in Table 1 indicate that HNO₃ exists in the organic phase predominantly as the 1:1 HNO₃:TBP complex. Also, as more and more U(VI) is extracted from 10 M HNO₃, the data in Table 1 show that U(VI) displaces the acid from the phosphoryl group of TBP, forming the well-known UO₂(NO₃)₂•2TBP adduct [9], while the excess TBP remains in the form of TBP•HNO₃. Finally, the data in Table 1 indicate that the third phase is highly concentrated in TBP and U(VI). Karl Fisher titrations of the third phase samples provided a water concentration of 0.4 M. Based on the results shown in Table 1, the composition of the third phase species can be expressed as UO₂(NO₃)₂•2TBP•HNO₃ (neglecting water), in agreement with previous findings [6].

Table 1. Composition of the U(VI)-TBP samples investigated

Sample	[TBP] mol/L	[U] mol/L	[HNO ₃] mol/L	[TBP] _{bound to U} mol/L	[TBP] _{excess} mol/L	[HNO ₃]/ [TBP] _{excess}
1	0.73	-	-	-	-	-
2	0.73	-	0.74	-	-	-
3	0.73	0.032	0.72	0.064	0.67	1.1
4	0.73	0.23	0.27	0.47	0.26	1.0
5	0.73	0.26	0.22	0.52	0.21	1.0
6 (LOC)	0.73	0.26	0.19	0.52	0.20	0.95
7 (Third Ph.)	2.1	1.02	0.92	2.04	~ 0	-
8 (Light Ph.)	0.51	0.18	0.19	0.35	0.16	1.2

RESULTS AND DISCUSSION

Infrared Spectroscopy

IR spectra of the samples in Table 1 were collected using a Nicolet Nexus 870 FTIR Spectrometer equipped with a HATR Attenuated Total Reflectance accessory containing a diamond resolution element. The results will be treated in more detail elsewhere [10]. However, several important features of the IR spectra that give insight into the nature of the third phase are summarized here. Overall, the shifts of the P=O stretching vibration upon U(VI) extraction by TBP ($\sim 100 \text{ cm}^{-1}$) provide clear evidence that the P=O oxygen is strongly coordinated to U(VI). Also, the magnitude of the frequency separation between the asymmetric and symmetric stretching vibrations of the NO₂ group of the nitrate ion ($\sim 250 \text{ cm}^{-1}$) indicates a bidentate coordination of the nitrates in the organic complex [11].

A marker band for molecular HNO₃ (1672 cm^{-1} [12]) is present in the spectra of samples 2 through 8. This band exhibits two peaks indicating that two forms of HNO₃ occur in these solutions: the lower energy vibration (1648 cm^{-1}) can be attributed to strongly hydrogen-bonded acid, while the higher energy one (1671 cm^{-1}) is associated with unbonded or weakly bonded acid. Sample 7 (third phase) exhibits a much stronger 1671 cm^{-1} band than the other samples, thus providing support to the conclusion that in $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP} \cdot \text{HNO}_3$, the third phase species, the HNO₃ molecule is not in the primary coordination sphere of the uranyl ion, in agreement with previous results [5]. Other studies, however, concluded that the trinitrato complex, $\text{HUO}_2(\text{NO}_3)_3 \cdot 2\text{TBP}$, exists in the third phase [6,7].

Visible Spectroscopy

Spectra of the organic phases (Figure 1) were obtained using a Cary-14 spectrophotometer and quartz cells of various pathlengths. Before phase splitting (Samples 3-6), the shape, energy, and intensity of each of the absorption bands is invariant and in complete agreement with literature reports of the spectrum of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ [13]. After phase splitting, the light phase (Sample 8) displays the same spectrum as the pre-splitting samples (represented in Figure 1 by Sample 6). However, the spectrum of the third phase (Sample 7) is distinctly different from the rest, indicating that the coordination of U(VI) is unique in the heavy phase. The intensity differs for most of the heavy phase absorption bands, the shape and energy of each peak change, and a weak new band appears at 494 nm. Taken together, this indicates that the U(VI) complex in the third phase has a lower symmetry [14,15] than $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$. This could be accounted for by any number of complexes, not only the trinitrato complex $\text{HUO}_2(\text{NO}_3)_3 \cdot 2\text{TBP}$, as previously postulated based on the modest resemblance of the spectra of the third phase and $\text{UO}_2(\text{NO}_3)_3^-$ [6,7]. The abrupt change in the spectrum on phase splitting suggests that in this system, third phase formation is *not* driven by progressive assembly of discrete molecules of the extracted complex into large aggregates that are insoluble in the original organic solvent.

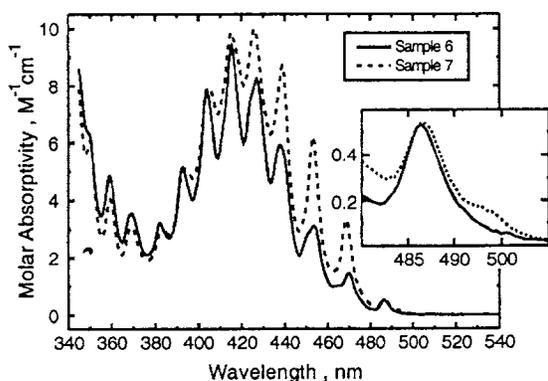


Figure 1. Visible Absorption spectra of the Limiting Organic Concentration (LOC) and third phase samples.

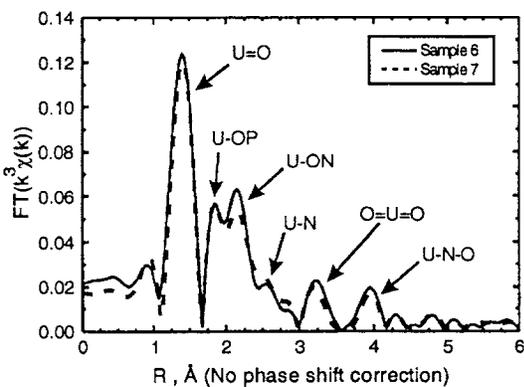


Figure 2. Fourier transformation of k^3 weighted uranium L_3 edge EXAFS for the LOC and third phase samples.

EXAFS Measurements

Extended X-ray absorption fine structure (EXAFS) measurements of the organic phases were made on the BESSRC-CAT bending magnet beamline of the Advanced Photon Source at the uranium L_3 edge. The data were fit using the program EXAFSPAK [16] to the theoretical phase and amplitude functions generated by FEFF 7.02 [17].

The results show similar patterns to those observed in each of the other experiments. The third phase is distinctly different from each of the other samples, which are identical to each other regardless of U(VI) loading or TBP concentration. Figure 2 shows the radial distribution of the shells of atoms about the U(VI) center (without phase shift correction). The EXAFS of the samples before phase splitting (Samples 4-6) and the light phase after splitting (Sample 8) are indistinguishable. The two “-yl” oxygen atoms are observed at $1.765 \pm 0.005 \text{ \AA}$ in all of the samples. Two TBP oxygen atoms at $2.35 \pm 0.02 \text{ \AA}$ and 4 oxygen atoms from bidentate nitrate groups at $2.50 \pm 0.01 \text{ \AA}$ can be partially resolved in the equatorial coordination sphere. These results agree well with previous work [18, 19].

None of the uranium-oxygen bond distances change significantly upon formation of the third phase. In addition, the number of inner sphere TBP oxygen atoms (2) observed in the third phase (Sample 7) is exactly the same seen for the other samples. The primary difference in the U(VI) inner coordination sphere of the heavy phase is a significant decrease (from 4.0 to 3.5) in the average number of nitrate oxygen atoms (when the Debye-Waller factor, σ^2 , for the equatorial oxygen atoms is held constant). This decrease in the number of coordinated nitrate oxygen atoms with no change in the number of coordinated TBP groups is entirely inconsistent with the formation of even small amounts of $\text{UO}_2(\text{NO}_3)_3^-$ in the heavy phase, given the bicoordinate nature of the nitrate groups demonstrated by the IR data. The additional equivalent of NO_3^- present in the third phase cannot be present in the U(VI) inner coordination sphere.

All of our results are consistent with some of the bidentate nitrate ligands of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ becoming monodentate with respect to a single U(VI) in order to bridge two uranyl centers or possibly to form a strong hydrogen bond with the water or nitric acid present in the heavy phase. Such behavior would lower the symmetry of the complex, accounting for the change in the UV-visible spectrum for the heavy phase without requiring the presence of an inner sphere trinitrato complex. Nevertheless, the changes in the U(VI) inner coordination sphere that induce, or are a result of, third phase formation in the uranyl/nitrate/TBP system are subtle.

SANS Measurements

SANS measurements on samples similar to those in Table 1, but prepared in deuterated *n*-dodecane, were made using the small-angle neutron diffractometer SAND at the Argonne National Laboratory Intense Pulsed Neutron Source (IPNS) as previously described [4]. Figure 3 shows the neutron scattering data for selected samples together with their fit to an elliptical form factor. Table 2 reports the values of the perpendicular (*a*) and parallel (*b*) semiaxis resulting from the elliptical form factor fit for all samples investigated, together with the gyration radius (R_g) of the scattering entities present in solution.

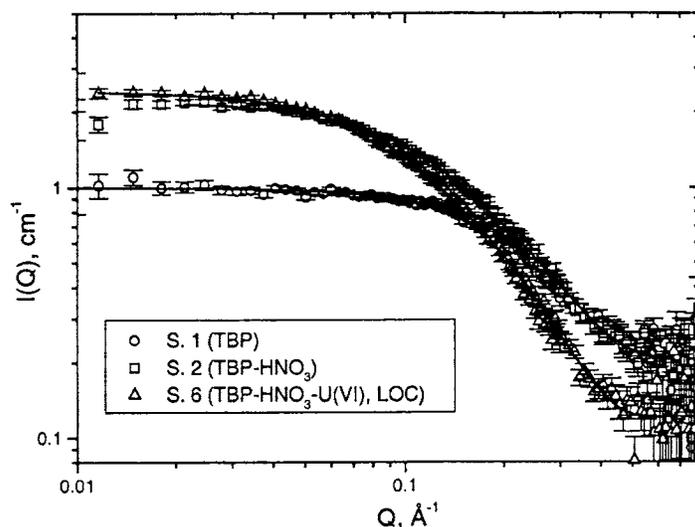


Figure 3. SANS data and fit to elliptical form factor for samples 1, 2 and 6.

Table 2. Elliptical form factor fit for U(VI)-TBP samples

Sample no.	<i>a</i> Å	<i>b</i> Å	R_g Å
1	7.0 ± 0.4	12.2 ± 0.6	7.0 ± 0.5
2	6.7 ± 0.2	25.9 ± 0.3	12.3 ± 0.3
3	6.7 ± 0.1	27.1 ± 0.2	12.8 ± 0.2
4	7.4 ± 0.1	28.8 ± 0.3	13.7 ± 0.3
6 (LOC)	7.5 ± 0.1	32.1 ± 0.3	15.1 ± 0.3
8 (Light Ph.)	7.1 ± 0.2	25.2 ± 0.3	12.1 ± 0.3

From the data in Table 2 it appears that growth of the solute particles along the parallel axis occurs when HNO_3 is extracted by TBP. When extracted U(VI) progressively replaces HNO_3 in the aggregates, only modest further growth takes place. The largest aggregates exist, as expected, in sample 6 (LOC), with the parallel axis *b* equal to approximately 3 times that for the TBP species in sample 1. Somewhat smaller aggregates exist in the light phase after phase splitting. The third phase sample presents a more complex scattering profile. Because the third phase is a highly concentrated sample, interpretation of the SANS data requires a different approach. Attempts to this effect are in progress.

CONCLUSIONS

Chemical analyses, spectroscopic and EXAFS evidence indicate that, under the experimental conditions of this work, U(VI) is extracted by 20 % TBP in *n*-dodecane as

$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$, while the third phase species has the composition, $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP} \cdot \text{HNO}_3$ where both of the TBP oxygen atoms are in the inner coordination sphere. Aggregation of the organic phase species occurs upon HNO_3 extraction in the absence of metal. Coextraction of U(VI) promotes only modest additional growth. Based on these results, it seems reasonable to conclude that formation of a third phase in this system is probably not caused by extensive solute aggregation. More likely, a dramatic change in solution leading to phase splitting takes place when one molecule of HNO_3 becomes part of the U(VI)-adduct. At this point, the solute probably becomes too polar for existing in the alkane diluent and collects in a separate phase.

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