Acid-Switched Eu(III) Coordination Inside Reverse Aggregates: Insights into a Synergistic Liquid-Liquid Extraction System

Abstract

Determining the structure of complex solutions bearing metal ions is challenging, but crucial for developing important technologies such as liquid-liquid extraction for metal refining and separation purposes. Herein, the structure of an organic Eu(III) solution consisting a binary mixture of lipophilic ligands di-2-ethylhexyl phosphoric acid (HDEHP) and tetraoctyl diglycolamide (TODGA) in dodecane is studied using synchrotron small angle X-ray scattering (SAXS) and X-ray absorption fine structure spectroscopy (EXAFS). This system is of technological importance in f-element separation for nuclear fuel cycle applications, where extraction is controlled by varying nitric acid concentration. Extraction is promoted at low and high concentration, but is retarded at intermediate concentration, leading to a U-shaped function; the structural origins of which we investigate. At the nanoscale, the solution is apparently comprised of reverse micelles with polar cores of approximately 1 nm in size, and these remain virtually unchanged as acid concentration is varied. Inside the polar cores, the coordination environment of Eu(III) switches from a 9-coordinate $\text{Eu}(\text{TODGA})_3]^{3+}$ motif at high acid, to a 6-coordinate HDEHP-dominated complex resembling $\text{Eu}(\text{HDEHP}.\text{DEHP})_3$ at low acid. The results show that extraction is controlled within the coordination sphere, where it is promoted under conditions that favor coordination of either one of the two organic ligands, but is retarded under conditions that encourage mixed complexes. Our results link solution structure with ion transport properties in a technologically-important liquid-liquid ion extraction system.

Uncovering the structure and interactions around ions in solution is key to understanding solvation.¹ Most systems of natural or technologic importance that hinge on ion chemistry operate in the solution state, where the inherent dynamics facilitate transformations, such as protein folding around Fe(III), to liquid-liquid ion transport for industrial metal refining.² Fundamental to these applications is the coordination structure of metal ions inside the wider nanoscale solution structure, and how this relates to conditions (e.g. pH) and ion transport / solvation. It is crucial, therefore, to conduct studies that probe solution structure directly, despite the dynamics and rotational averaging inherent to solutions that makes experimental structural studies extremely challenging.

The present study is concerned with the structure of a metalloamphiphile-alkane solution. Metal ions are dissolved as lipophilic complexes by binding to the amphiphile headgroups; a phenomenon that underpins liquid-liquid ion separations for nuclear fuel reprocessing as well as metal refining processes. In these systems, metal ions are transported from an aqueous phase and into the hydrocarbon solution as they interact with the coordinating amphiphilic species (known as “extractants”) within the oil. The organic solution is notoriously prone to micellization, where the self-assembly of extractant amphiphiles into aggregates provides a nanoscale solvation environment encapsulating the target ion.³ The competitive solvation of ions between the immiscible aqueous and organic solutions dictates the performance of the process. Recent

This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>).

research has shown that ion solvation in the organic phase is influenced by both the nanoscale structure of the reverse micelle, as well as the local coordination interactions between the lipophilic donors and metal center.⁴ Therefore, in order to understand the structural origins of liquid-liquid extraction behaviors, it is important to investigate the solution at both the supramolecular and molecular scales.

Synchrotron small angle X-ray scattering (SAXS) and X-ray absorption fine structure spectroscopy (EXAFS) techniques are employed herein to simultaneously probe the supramolecular structure and coordination environment inside a Eu(III) liquid-liquid extraction organic phase. The subject system involves the extraction of Eu(III) from nitric acid into n-dodecane oil using a binary mixture of an acidic and a neutral extractant. The extractants in question are di-2-ethylhexyl phosphoric acid (HDEHP) and tetraoctyl diglycolamide (TODGA) (shown in Figure 1a,b). When dissolved in a water-immiscible hydrocarbon oil, these extractants are used in a process to separate f-block elements from aqueous solutions via liquid-liquid extraction for next-generation nuclear fuel recycling.⁵ This process was designed to operate at 0.05 M TODGA and 0.75 M HDEHP concentrations, and f-element extraction can be controlled by varying the concentration of nitric acid in the aqueous phase. Binary mixtures of extractants are often used in liquid-liquid ion separation processes because they can behave synergistically and yield useful extractive properties.⁶ However, such complex solution mixtures can yield complex extractive properties, particularly with regard to acidity (see Figure 1c and the discussion below).

It is important to understand the fundamental structural origins of metal ion extraction behaviors in order to better predict and control the process. Muller et.al. have shown recently that acid-induced changes in synergistic properties of binary extractant mixtures may be related to changes in ion complexation.⁷ Rey et.al. have shown that synergism is also related to changes in the nanoscale reverse micelle structure.⁸ Therefore, to understand the acid dependence observed in the present HDEHP-TODGA-Eu(III) system, both the coordination and supramolecular solution structures must be investigated. Using synchrotron X-ray techniques, I thus address the fundamental question: *how are coordination and micellar solution structures related to acid-induced changes in Eu(III) extraction behaviors in the TODGA-HDEHP liquid-liquid extraction system?* My findings give new insight into the effects of acid on synergistic liquid-liquid extraction in particular, as well as structured rare earth organic solutions, in general.

This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>).

Figure 1: Depictions showing the molecular structures of (a) neutral extractant TODGA and (b) acidic extractant HDEHP. (c) The extraction dependence of Eu(III) relative to acid concentration. Distribution coefficient (D) is the concentration ratio of Eu in the organic phase over Eu in the aqueous phase against nitric acid concentration in the aqueous phase. Organic phase was 0.05 M TODGA + 0.75 M HDEHP in dodecane.

Experimental

Solvent extraction: > 99% purity TODGA was purchased from Technocomm (Scotland). All other reagents were of > 99% purity and purchased from Sigma Aldrich (Milwaukee). 1 mL volumes of the organic phase were vortexing in capped plastic test tubes at 23 °C with an equal volume of 10 mM europium nitrate in nitric acid (0.1 to 3 M). Initial experiments showed that a 30 min vortexing time was sufficient to reach equilibrium. Aliquots of the aqueous phases were withdrawn for analysis after centrifugation and phase separation. The metal concentration in the aqueous phase before and after extraction was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

XAS data collection and analysis: EXAFS data collection and analysis were performed using the same general method as reported in our previous publication.⁹ Eu L3-edge spectra were collected in fluorescence mode at beamline 12-BM-B at the Advanced Photon Source (APS) at Argonne National Laboratory. A multi-element Ge detector (Canberra) was used to collect the fluorescence signal. The incident X-ray energy was calibrated against the inflection point energy of a Eu oxide foil. The solutions were injected into 1 mm Kapton capillaries for data acquisition. Three 1 hr scans were averaged for each solution. Analyses of the $k^3\chi(k)$ EXAFS were performed using EXAFSPAK and curve-fitting using theoretical phase and amplitude functions calculated with FEFF8.01.

SAXS data collection: SAXS data were collected at the APS beam-line 12-ID-C. Samples were contained in 1.5 mm diameter quartz capillary tubes (Charles Supper Co., 20-QZ) with incident photon energy of 19.0 keV. 2D scattering profiles were acquired in 0.1 second exposure times with a MAR-CCD-165 detector (MAR USA). The scattering vector, Q , was calibrated using a silver behenate standard and the 2D scattering images were corrected for spatial distortion and detector sensitivity before radial averaging to produce plots $I(Q)$ versus Q . The GIFT method¹⁰ was used to obtain real space functions from the scattering data as described previously.¹¹ Briefly, GIFT interprets the globular particle system, $I(q) = nP(q)S(q)$, in which n is the number of particles per unit volume, $P(q)$ is the average form factor (corresponding to the shape and size of the scattering particles) and $S(q)$ is the average structure factor (scattering produced from inter-particle interactions). $P(q)$ is the Fourier transformation of its real space counterpart, $p(r)$. Thus, the real space functions are obtained by removing $S(Q)$ and conducting the inverse Fourier transform on the remaining $P(Q)$ function. The selection of the appropriate structure factor model is key to the calculation and the Percus–Yevick (PY) closure relation was used. This has been shown previously to closely approximate the interaction effects of micelles.¹²

Results and Discussion

Four liquid-liquid extraction experiments were performed by mixing a 0.05 M TODGA + 0.75 M HDEHP in dodecane organic solutions with nitric acid aqueous phases (0.1 to 3 M HNO_3) containing Eu(III) (10 mM). These conditions mirror those used in the f-element separation process, and show the characteristic U-shaped acid dependence of Eu(III) extraction observed in previous studies (see Figure 2).⁵ This dependence is exactly the same as found previously by Gelis et.al. with the same HDEHP-TODGA-dodecane mixture.⁵ SAXS and Eu L3-edge EXAFS measurements were then collected from all four solutions to probe simultaneously the supramolecular solution structure as well as the coordination environment around Eu(III).

We turn our attention first to the SAXS data that correspond to the nanoscale morphologies of the aggregate structures in the organic solutions. SAXS works on the principle that X-rays are sensitive to variations in electron density within a material, and are scattered. The scattering pattern yields information on the shape and size of the scattering region, which is the part of the material that has a different electron density contrast from the surrounding medium. In this case, SAXS is sensitive to the morphology of the regions made up from the minority P, N and O atoms on the extractant headgroups, nitrate and water, as well as the electron-rich Eu(III) ions. The aliphatic extractant tail-groups have approximately the same electron density profile as the surrounding aliphatic solvent (dodecane) and are not, therefore, expected to contribute to the coherent small angle scattering signal.

The background-subtracted SAXS data are shown in Figure 2. The shapes of the SAXS curves are typical for particle scattering, as would be expected for a solution of reverse micellar aggregates where the polar extractant headgroups form nanoscale clusters containing acid, water and extracted ions inside a continuous aliphatic medium. Very little difference is noted between the four data sets with all curves approaching a flat line at $Q < 0.2 \text{ \AA}^{-1}$. Slopes in the low- Q region give qualitative indication of particle morphology; e.g. a slope of -1 suggests rod-shaped aggregates and a slope of 0 suggests spherical aggregates.¹³ These SAXS data suggest, therefore, that the aggregates have approximately spherical (globular) character. The slightly higher scattering intensity observed in the low- Q region of the SAXS curve for 3 M acid concentration might suggest larger aggregates are formed at high acid concentrations. However, remarkably little difference is observed between the SAXS curves from the lower acid concentrations systems, suggesting that acidity has a negligible impact on nanoscale aggregation.

The generalized indirect Fourier transform (GIFT) method¹⁰ was applied to the SAXS data to give a more quantitative insight into aggregate shape and size as a function of acid concentration. This method allows for the generation of real-space functions that correspond to the scattering particle morphology by deconvoluting the interfering effects of inter-particle scattering (known as ‘structure factor’), and are shown in Figure 2b. For all acid concentrations, the GIFT functions show very similar asymmetric bell-shapes, with a tail that extends up to around 20-25 $\text{\AA}$. This supports the qualitative conclusions drawn from the flat low- Q trend in the SAXS data (Figure 2a). The diameter of the polar reverse micelle core (made up from the electron-rich Eu, P, O and N atoms) can be obtained from the position of the second inflection point of the PDDF,¹⁴ which was calculated to be at 8.8 $\text{\AA}$ for all acid concentrations. The

maximum linear extent of the scattering aggregates (i.e. the maximum dimension of the polydisperse globular reverse micelle cores) is indicated from the maximum extend of the PDDF, which is around 20 Å for the lower acid concentrations and 25 Å for the 3 M nitric acid extraction.

The general picture that emerges from the SAXS data analysis is that the solution is aggregated into small reverse micelles that have polar cores just under 1 nm in average diameter, and that acid concentration has very little impact on these species. This is surprising as changing nitric acid concentration has been shown to have a pronounced impact on the nanoscale structure of TODGA-alkane phases in several previous studies,¹⁵ and would may be expected to alter HDEHP aggregation. It appears, therefore, that the variation in Eu(III) extraction as nitric acid concentration is varied is not related to a change in nanoscale aggregate structure.

Figure 2: (a) Background subtracted SAXS data and (b) GIFT-generated real space functions corresponding to 0.05 M TODGA, 0.75 M HDEHP in dodecane after mixing with various concentrations of nitric acid bearing 10 mM Eu(III). (c) a depiction of the average morphology of the scattering cores of the reverse aggregates.

Next we turn our attention to the Eu L3-edge EXAFS data taken from the same organic solution. The $k^3\chi(k)$ EXAFS are presented in ESI2, and these all show sinusoidal-like behavior, especially in the region ($2 \leq k \leq 9 \text{ Å}^{-1}$) in which there are four strong peaks and valleys. For k values higher than 9 Å^{-1} , the response flattens out, suggesting a significant spectral congestion due to numerous scattering paths associated with the coordinating molecules, as noted in other organic solutions.^{4, 9, 16} Like in the SAXS data, real-space functions can be generated using a Fourier transform, yielding a physical portrayal of the immediate coordination environment around the Eu(III) ion. All four Fourier transformed (FT) EXAFS (Figure 3) show an intense peak at around $1.904 + \Delta \text{ Å}$, which does not move significantly in position with changing acid concentration. Significant changes are seen, however, in the minor features between 2.5 and $4 + \Delta \text{ Å}$, suggesting that acid may be having an impact on the outer-coordination sphere. In the following, the acid-induced changes in the minor FT-EXAFS features are discussed by looking at the data in pairs.

Figure 3: Comparison of the FT-EXAFS data for the four nitric acid concentrations. The intensities of all the peaks have been normalized to the intensity at 0.1 M nitric acid concentration to allow for ease of comparison. FT magnitude is an arbitrary unit and should not be used to infer relative changes in coordination number. The Δ term indicates that the Fourier Transform did not involve a phase shift correction and the positions of the peaks do not correlate to the positions of the back-scattering atoms.

In Figure 4, the FT-EXAFS data for the organic phase generated from the 3 M nitric acid extraction is shown in red. Aside from the major peak, there are two sharp oscillations above and below $3+\Delta$ Å, followed by broad features at 3.5 to $4.5 +\Delta$ Å. The positions and intensities of these peaks are similar to EXAFS data from a $[\text{Eu}(\text{TODGA})_3]^{3+}$ complex in methanol that was recently diagnosed by Antonio.¹⁷ The FT-EXAFS data from this previously-characterized complex is reproduced in Figure 4b in black, and the major and minor features overlap significantly with the data collected from the high acid extraction, strongly suggesting that the same inner-sphere $[\text{Eu}(\text{TODGA})_3]^{3+}$ species is formed. The data were then fit with the same three-shell O, C, C model used in the previous publication,¹⁷ and the fits of the $k^3\chi(k)$ EXAFS exhibit good correspondence with the experimental data (see ESI2). The metrics to this fit are presented in Table 1, showing bond distances that agree well with those previously reported for the $[\text{Eu}(\text{TODGA})_3]^{3+}$ complex. Both the qualitative comparison of the FT-EXAFS as well as the metrical parameters developed from the model suggest, therefore, that the dominant coordination structure at high acid concentration is the homoleptic $[\text{Eu}(\text{TODGA})_3]^{3+}$ complex. In this sense, it appears that HDEHP does not coordinate to the metal ion under these conditions, and instead TODGA saturates the coordination sphere. Although the homoleptic $[\text{Eu}(\text{TODGA})_3]^{3+}$ has been identified in polar organic solvents in the presence of non-coordinating anions (as in the aforementioned study),¹⁷ to my knowledge this is the first time it has been diagnosed in a very low dielectric constant oil (dodecane) in the presence of coordinating anions (nitrate and DEHP). At first glance, the prevalence of such a charge-dissociated rare earth species in the presence of coordinating anions in a low dielectric constant alkane oil is difficult to justify. However, although the bulk solvent is dodecane, at the nanoscale the complex is actually solvated inside the polar core of a reverse micelle, which may stabilize the dissociated ion pair and screen the powerful electrostatic interactions.

Figure 4: FT-EXAFS data comparing the 3 M nitric acid extraction in the current study with the previously-characterized homoleptic $[\text{Eu}(\text{TODGA})_3]^{3+}$ complex.¹⁷

We move now to discussing the EXAFS data taken from the solution formed after extraction from 0.1 M acid concentration (Figure 5). At this low acid concentration, aside from the major peak, the FT-EXAFS data shows a medium-sized peak at around $3.2 + \Delta \text{ \AA}$. Both the intensity of this and its position are reminiscent of phosphorous back scattering from coordinated HDEHP.¹⁸ At low acid concentrations, lanthanide(III) ions are often coordinated by three mono-deprotonated HDEHP.DEHP dimers, as shown in the sketch in Figure 5. EXAFS data have previously been collected from such solutions and fitted with a 2-shell O,P model to take into account both the inner-sphere coordinating O and the back scattering P.¹⁸ The black line in Figure 5 shows the FT-EXAFS from an organic solution made from extracting Eu(III) into 0.75 M HDEHP in dodecane at pH 2; conditions well known to form the $\text{Eu}(\text{HDEHP.DEHP})_3$ species. Comparing the two spectra, there are obvious similarities in terms of the relative heights of the major and minor peaks. However, the main peak for the mixed TODGA-HDEHP system is at a slightly longer distance than that of the known $\text{Eu}(\text{HDEHP.DEHP})_3$ complex, and the shorter peak attributed to P back scattering is broader. Despite these differences, the EXAFS spectrum for the low acid concentration extraction was fitted with an unconstrained two-shell O,P model and the fits to the $k^3\chi(k)$ EXAFS exhibit good correspondence with the experimental data (see Supporting Information). The metrics to this fit are presented in Table 1, showing an inner-sphere O coordination number of 6 ± 1 and an outer-sphere P coordination number of 8 ± 1 . The bond distance for the P shell agrees almost exactly with that quoted for the $\text{Eu}(\text{HDEHP.DEHP})_3$ species previously, but the bond length for the inner-sphere O is almost 0.1 Å longer.¹⁸ Although the complex possesses the 6 O coordinate and distinct P scattering that is characteristic of the well-known $\text{Eu}(\text{HDEHP.DEHP})_3$ species, the presence of TODGA is clearly making a difference to the inner-coordination sphere. The origins of this are not clear, but perhaps the H-bond acceptor groups on the diglycolamide interrupt the H-bonds between the inter-molecular HDEHP.DEHP dimer, changing the coordination structure. I note that the number of P atoms is higher than would be expected considering the molecular structure of HDEHP and may suggest that there may be other atoms contributing to this peak intensity aside from P or coordination number is perturbed because of the simplicity of the model used to interpret a complex and probably polydispersity complex. It is well-known that inner-sphere coordination numbers

refined using EXAFS tend to have large errors, and outer-sphere coordination numbers even more so (probably more than the ± 1 that was calculated in the fitting). Indeed, it is common to fix coordination numbers in EXAFS data modelling to resemble an assumed model in order to obtain physically reasonable results; I did not do this. Aside from the limitations in the EXAFS technique for providing reliable coordination numbers, the goodness of fit, the position of the atoms and the not-completely-absurd coordination number (considering the simplicity of the model) lends credence to the hypothesis that this peak comes primarily from P on HDEHP.

Figure 5: FT-EXAFS data comparing the 0.1 M nitric acid extraction in the mixed TODGA-HDEHP system (blue) with that of a solution containing the well-known $\text{Eu}(\text{HDEHP}.\text{DEHP})_3$ species (black).

The data shown in Figure 6 compares the intermediate acid FT-EXAFS signals with the end members. Comparing the FT-EXAFS from the 0.1 M acid extraction with the 0.3 M acid extraction (Figure 6a) shows that the incremental increase in acid concentration results in a slight decrease in the relative intensity of the peak attributed to the back scattering P at $3.32+\Delta$ Å. There is also the emergence of a second weaker oscillation at $2.86+\Delta$ Å. The two-shell O,P model that gave a good fit to the 0.1 M acid extraction does not provide statistically reasonable parameters for the EXAFS from the 0.3 M acid extraction, suggesting that the speciation is more complex. Instead, a one-shell O model was used to account for the major peak at $1.93+\Delta$ Å, providing good correspondence with the experimental data (see ESI2). The bond length and coordination number for this single O shell (Table 1) for the 0.3 M acid extraction are exactly the same as for the 0.1 acid extraction. This suggests that the increase in acid is primarily impacting the second coordination shell. In Figure 6b, the FT-EXAFS for the two intermediate extractions are compared. Going from 0.3 M to 1 M acid, the minor features between 2.5 and $3.5+\Delta$ Å change significantly, and the position of the major peak shifts slightly to longer distance. The dominant peak attributed to the backscattering P at $3.32+\Delta$ Å disappears at 1 M acid and is replaced by two minor oscillations at 3 and $3.4+\Delta$ Å. These minor oscillations in the 1 M acid extraction are at different positions to those identified for the $[\text{Eu}(\text{TODGA})_3]^{3+}$ complex in the 3 M extraction (Figure 6c). In the absence of a rational model with which to attempt to fit these minor oscillations, the 1 M extraction EXAFS data were also fit with an unconstrained one-shell O model, providing good correspondence with the experimental data (see ESI2). The metrics to this fit are presented in Table 1, showing an inner-sphere O coordination number of 7 ± 1 and a

bond distance of 2.410 Å; slightly longer than that of the 0.3 M extraction and less than that of the 3 M extraction.

Figure 6: FT-EXAFS data comparing pairs of data for the two low acid extraction (a), intermediate acid extractions (b) and high acid extractions (c).

Table 1: EXAFS data fitting parameters (see ESI2 for fits). Errors are reported in brackets in relation to the final significant figure.

[Acid] (M)	model	CN	r (Å)	σ^2 (Å ²)	$E(0)$ (eV)	chi ²
0.1	O,P	O=6(1), P=8(1)	O=2.395(4), P=3.87(1)	O=0.013(9), P=0.025(3)	3.0	0.2
0.3	O	O=6(1)	O=2.395(5)	O=0.0136(8)	3.6	0.3
1	O	O=7(1)	O=2.410(5)	O=0.014(1)	2.3	0.3
3	O,C,C	O=9, C=6, C=6	O=2.423(5), C=3.69(1), C=3.44(2)	O=0.015(5), C=0.007(2), C=0.010(2)	2.4	0.5

The EXAFS analysis shows that changing acid concentration has a pronounced impact on the coordination structures inside the organic solutions. At high acid concentration, the coordination complex appears to be dominated by only one of the extractants; i.e. TODGA. This is probably because high acidity disfavors deprotonation of the HDEHP, inhibiting coordination. Although HDEHP does not appear to play an active role in coordinating to the inner-sphere, it may be important in forming the nanoscale polar solvation environment inside the reverse micelle to stabilize the dissociated ionic species in the low dielectric constant medium. The roles of the two extractants are reversed at low acid concentrations, with HDEHP apparently dominating the coordination sphere, with TODGA possibly playing a role in the outer-sphere. The formation of either the pure TODGA or pure HDEHP inner-sphere complex at high or low acid favors extraction (see Figure 1c), whereas the intermediate acid concentrations disfavor extraction. It is not possible from the limited data to say whether the coordination complexes in the intermediate acid concentrations are either mixed species (i.e. where TODGA and HDEHP both coordinate to the inner-sphere) or a mixture of species (i.e. a mixture of pure TODGA or pure HDEHP).

This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>).

Conclusions

Synchrotron SAXS and EXAFS were used to interrogate the solution structure of an organic phase generated by liquid-liquid extraction of Eu(III) into a mixture of HDEHP and TODGA. Experiments were conducted to study in particular the role of acid on the supramolecular structure of the reverse aggregates as well as the molecular scale structure of the coordination complexes. Changing acid from low to high concentrations had negligible impact on the micellar structures, but caused a switching in coordination complexes from one dominated by HDEHP to one dominated by TODGA.

Acknowledgements

Work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division. The author thanks Dr. Mark “Mantonio” Antonio for kindly providing EXAFS data for the Eu(III)-TODGA system.

References

1. Havenith, M., Solvation Science: A New Interdisciplinary Field. *Angew. Chem., Int. Ed.* **2016**, 55 (4), 1218-1219.
2. Wilson, A. M.; Bailey, P. J.; Tasker, P. A.; Turkington, J. R.; Grant, R. A.; Love, J. B., Solvent extraction: the coordination chemistry behind extractive metallurgy. *Chem. Soc. Rev.* **2014**, 43, 123-134.
3. Zemb, T.; Bauer, C.; Bauduin, P.; Belloni, L.; Dejugnat, C.; Diat, O.; Dubois, V.; Dufreche, J.-F.; Dourdain, S.; Duvail, M.; Larpent, C.; Testard, F.; Pellet-Rostaing, S., Recycling metals by controlled transfer of ionic species between complex fluids. En route to "ienatics". *Colloid Polym. Sci.* **2015**, 293, 1-22.
4. Ellis, R. J.; Meridiano, Y.; Muller, J.; Berthon, L.; Guilbaud, P.; Zorz, N.; Antonio, M. R.; Demars, T.; Zemb, T., Complexation-induced supramolecular assembly drives metal-ion extraction. *Chem. - Eur. J.* **2014**, 20, 12685.
5. Gelis, A. V.; Lumetta, G. J., Actinide Lanthanide Separation Process-ALSEP. *Ind. Eng. Chem. Res.* **2014**, 53, 1624-1631.
6. Zangen, M., Some aspects of synergism in solvent extraction. II. Some di-, tri- and tetravalent metal ions. *J. Inorg. Nucl. Chem.* **1963**, 25, 1051-63.
7. Muller, J. M.; Berthon, C.; Couston, L.; Zorz, N.; Simonin, J.-P.; Berthon, L., Extraction of Lanthanides(III) by a Mixture of a Malonamide and a Dialkyl Phosphoric Acid. *Solvent Extr. Ion Exch.* **2016**, 34 (2), 141-160.
8. Rey, J.; Dourdain, S.; Berthon, L.; Jestin, J.; Pellet-Rostaing, S.; Zemb, T., Synergy in Extraction System Chemistry: Combining Configurational Entropy, Film Bending, and Perturbation of Complexation. *Langmuir* **2015**, 31 (25), 7006-7015.

This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>).

9. Ellis, R. J.; Meridiano, Y.; Chiarizia, R.; Berthon, L.; Muller, J.; Couston, L.; Antonio, M. R., Periodic behavior of lanthanide coordination within reverse micelles. *Chem.--Eur. J.* **2013**, *19*, 2663-75.
10. Fritz, G.; Glatter, O., Structure and interaction in dense colloidal systems: evaluation of scattering data by the generalized indirect Fourier transformation method. *J. Phys.: Condens. Matter* **2006**, *18*, S2403-S2419.
11. Ellis, R. J.; Audras, M.; Antonio, M. R., Mesoscopic Aspects of Phase Transitions in a Solvent Extraction System. *Langmuir* **2012**, *28*, 15498-15504.
12. Shrestha, L. K.; Shrestha, R. G.; Aramaki, K., Intrinsic parameters for the structure control of nonionic reverse micelles in styrene: SAXS and rheometry studies. *Langmuir* **2011**, *27*, 5862-5873.
13. Glatter, O., The inverse scattering problem in small-angle scattering. In *Neutrons, X-Rays and Light*, Lindner, P.; Zemb, T., Eds. Elsevier Science B.V.: Amsterdam, 2002; pp 73-102.
14. Glatter, O., The interpretation of real-space information from small-angle scattering experiments. *J. Appl. Crystallogr.* **1979**, *12*, 166-75.
15. (a) Jensen, M. P.; Yaita, T.; Chiarizia, R., Reverse-micelle formation in the partitioning of trivalent f-element cations by biphasic systems containing a tetraalkyldiglycolamide. *Langmuir* **2007**, *23* (9), 4765-4774; (b) Nave, S.; Modolo, G.; Madic, C.; Testard, F., Aggregation properties of N,N,N',N'-tetraoctyl-3-oxapentanediamide (TODGA) in n-dodecane. *Solvent Extr. Ion Exch.* **2004**, *22* (4), 527-551.
16. Ellis, R. J.; Antonio, M. R., Coordination Structures and Supramolecular Architectures in a Cerium(III)-Malonamide Solvent Extraction System. *Langmuir* **2012**, *28*, 5987-5998.
17. Antonio, M. R.; McAlister, D. R.; Horwitz, E. P., An europium(III) diglycolamide complex: insights into the coordination chemistry of lanthanides in solvent extraction. *Dalton Trans.* **2015**, *44*, 515-521.
18. Gannaz, B.; Antonio, M. R.; Chiarizia, R.; Hill, C.; Cote, G., Structural study of trivalent lanthanide and actinide complexes formed upon solvent extraction. *Dalton Trans.* **2006**, (38), 4553-4562.