

Microemulsions and Aggregation Formation in Extraction Processes for Used Nuclear Fuel: Thermodynamic and Structural Studies

Fuel Cycle Research and Development

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Microemulsions and Aggregation Formation in Extraction Processes
for Used Nuclear Fuel:
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University Of California Irvine
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Abstract

Advanced nuclear fuel cycles rely on successful chemical separation of various elements in the used fuel. Numerous solvent extraction (SX) processes have been developed for the recovery and purification of metal ions from this used material. However, the predictability of process operations has been challenged by the lack of a fundamental understanding of the chemical interactions in several of these separation systems. For example gaps in the thermodynamic description of the mechanism and the complexes formed will make predictions very challenging. Recent studies of certain extraction systems under development and a number of more established SX processes have suggested that aggregate formation in the organic phase results in a transformation of its selectivity and efficiency. Aggregation phenomena have consistently been interfering in SX process development, and have, over the years, become synonymous with an undesirable effect that must be prevented. This multiyear, multicollaborative research effort was carried out to study solvation and self-organization in non-aqueous solutions at conditions promoting aggregation phenomena. Our approach to this challenging topic was to investigate extraction systems comprising more than one extraction reagent where synergy of the metal ion could be observed. These systems were probed for the existence of stable microemulsions in the organic phase, and a number of high-end characterization tools were employed to elucidate the role of the aggregates in metal ion extraction. The ultimate goal was to find connections between synergy of metal ion extraction and reverse micellar formation. Our main accomplishment for this project was the expansion of the understanding of metal ion complexation in the extraction system combining tributyl phosphate (TBP) and dibutyl phosphoric acid (HDBP). We have found that for this system no direct correlation exists for the metal ion extraction and the formation of aggregates, meaning that the metal ion is not solubilized in a reverse micelle core. Rather we have found solid evidence that the metal ions are extracted and coordinated by the organic ligands as suggested by classic SX theories. However, we have challenged the existence of mixed complexes that have been suggested to exist in this particular extraction system. Most importantly we have generated a wealth of information and trained students on important lab techniques and strengthened the collaboration between the DOE national laboratories and US educational institution involved in this work.

Intro and Objectives

This 3-year project was a collaboration between University of California Irvine (UC Irvine), Idaho National Laboratory (INL) and Argonne National Laboratory (ANL). The project was led from UC Irvine under the direction of Prof. Mikael Nilsson. The leads at INL and ANL were Dr. Peter Zalupski and Dr. Mark Antonio, respectively. The project was initially delayed and started in December 2011 and was extended to a 4th year, ending in December 2015, through a no-cost extension.

Studies of solvent extraction systems using phosphoric acid reagents, as well as other reagents, have suggested that aggregate formation in the organic phase results in a transformation of its selectivity and efficiency. Aggregation phenomena have consistently interfered in extraction process development, and, over the years, became synonymous with an undesirable effect that must be prevented. In this project the overall objective was to study solvation and self-organization in non-aqueous solutions as the experimental conditions of the organic solution become increasingly disposed towards aggregation.

This project had the following specific objectives:

1. Investigate the important trends and relationships between the formation of water-in-oil microemulsions and the mechanisms of metal ion phase transfer.
2. Use 2-phase calorimetry to investigate thermodynamic signatures of progressive structural organization of the organic phase leading to third phase formation.
3. Use synchrotron radiation techniques, such as small angle X-ray scattering (SAXS) and X-ray absorption spectroscopy (XAS), to characterize and gain an improved understanding of the structure of reverse micelles, how and why they form and their role in metal extraction.
4. Compile the accumulated systems knowledge, perspectives and insights obtained from the coordinated experimental and theoretical efforts in a database to allow us to describe, understand and predict the mechanisms and formation of reverse micelles and stable water-in-oil microemulsions in liquid-liquid distribution systems.

Our approach to this project was to start by studying a well-established extraction system with a relatively simple extraction mechanism. It is well-known that tributyl phosphate (TBP, figure 1a) exhibit aggregate formation under certain conditions. There was also evidence that combining TBP and an acidic chelating agent, *e.g.* HDEHP or dibutyl phosphoric acid (HDBP, figure 1b), could result in synergistic extraction, often explained by an increased dehydration of the metal ion. By displacing the water in the inner coordination sphere with a functional group from a lipophilic extraction reagent the metal ion is more readily extracted. Of course this mechanism would likely result in a lower water content in the organic phase. Some of our early results that laid the foundation of this work were obtained using a combination of TBP and HDBP. This system indicated non-linear metal ion extraction and a synergy in water uptake, suggesting the existence of microemulsions. The existence of aggregates was also confirmed using small angle X-ray scattering (SAXS). This system became our starting point and benchmarked the methodologies for studying these systems. What we found, though, was that the wealth of information hidden in this seemingly simple system was more than enough to occupy one graduate student for his entire PhD and involved work from several other graduate and undergraduate students and spawned other ideas. As a result much of this report is focused on this system and only a moderate amount of data for other extraction systems was collected.

In the following text each objective will be addressed, what experiments we carried out and our findings. Each objective was addressed although—as will be shown in the report—the general trends and perspectives proved difficult as we found that studying aggregates in organic phase was a grander challenge than we had expected. Towards the end of the report we also outline outcomes and markers for success from this project.

Objective I: Investigate the relationship between water in oil microemulsions and mechanism of metal ion extraction.

As mentioned above, we started with TBP/HDBP extraction, looking at trends in metal ion extraction and water uptake. Water uptake can be a marker for formation of reverse micelle aggregates capable of solubilizing significant amount of water as well as mineral acids and other solutes. Extraction systems displaying interesting properties were later studied by X-ray techniques, outlined in Objective III.

Investigations on the TBP:HDBP synergistic extraction system

The synergistic extraction system of (TBP) and dibutyl phosphoric acid (HDBP), see Figure 1, occupied a large part of this project.

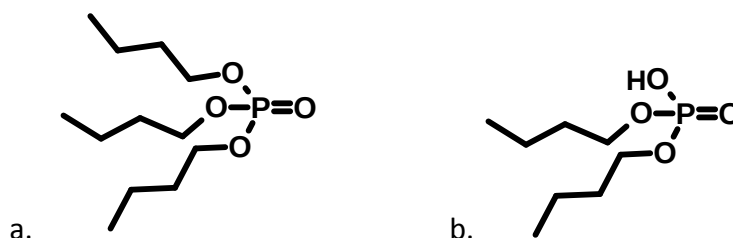


Figure 1. Chemical Structure of TBP (a) and HDBP (b).

Experimental

The experimental approach was similar for most of the experiments outlined in this section. The two reagents in figure 1 were combined in different molar ratios in *n*-dodecane and the extraction of various metal ions, including lanthanum, europium, dysprosium, lutetium and uranium, from acidic aqueous solutions has been tested. The metal concentration was, in most cases, varied between 10^{-4} M and 10^{-2} M while the total extraction reagent used was 1 M (TBP + HDBP). The nitric acid concentration in the aqueous phase was either 0.2 M HNO_3 or 2 M HNO_3 . We have also investigated the effect of adding 1.8 M NH_4NO_3 to the 0.2 M HNO_3 samples to match the ionic strength of the 2 M HNO_3 solution. At high metal concentration there was third phase formation (a heavy organic phase) or sometimes slight turbidity seen in the organic phase. In this report the distribution ratios shown below are the ratios between light organic and the aqueous phase. The distribution ratios for lutetium, dysprosium, lanthanum and uranium were measured by neutron activation analysis by irradiating both the organic and the aqueous phases in the 250kW UCI TRIGA reactor. Europium extraction was measured using tracer of $^{152/154}\text{Eu}$ produced in the UCI TRIGA reactor. Samples were counted on a high purity germanium (HPGe) detector. The organic phases were samples for water uptake and measured using a Karl Fisher titrator. Aliquots of the organic phase were washed with water, and acid and nitrate uptake were measured by potentiometric titration and ion chromatography, respectively. The aqueous phases were tested for acidity and nitrate concentration as well.

In addition to studying the distribution ratios of metal ions a number of experiments were carried out with the intent of analyzing the organic solutions using fluorescence spectroscopy. The idea was that significant changes in the environment around the extracted metal ion might be apparent using this technique. The experiments were carried out the same way as the extraction study and the collected organic phases were analyzed using a Fluoromax-4 spectrophotometer from HORIBA Scientific, Ltd. and quartz fluorescence cuvettes from Starna Cells, Inc. The measurements were carried out over a large excitation range of 240 nm to 500 nm at 5 nm increments with an emission range of 290 nm to 750 nm at 2 nm increments.

Furthermore, to investigate whether the additional uptake of water into the organic phase affects the coordination sphere of the metal ion we carried out time resolved fluorescence studies with europium and dysprosium, outlined in more detail below.

Extraction Results

In one of our first experiments we investigated the extraction of dysprosium. Figure 2 below shows the metal uptake as well as the water uptake. One of the important results in this experiment was that the addition of ammonium nitrate to balance the ionic strength did not alter the metal ion extraction or water uptake (shown in figure 3) to any significant degree. Figure 3 also shows the nitrate uptake, which was slightly elevated when ammonium nitrate was added. This is correlated with increased ionic strength. Based on these results our continued extraction studies omitted the addition of ammonium nitrate in order to simplify the chemistry of the systems.

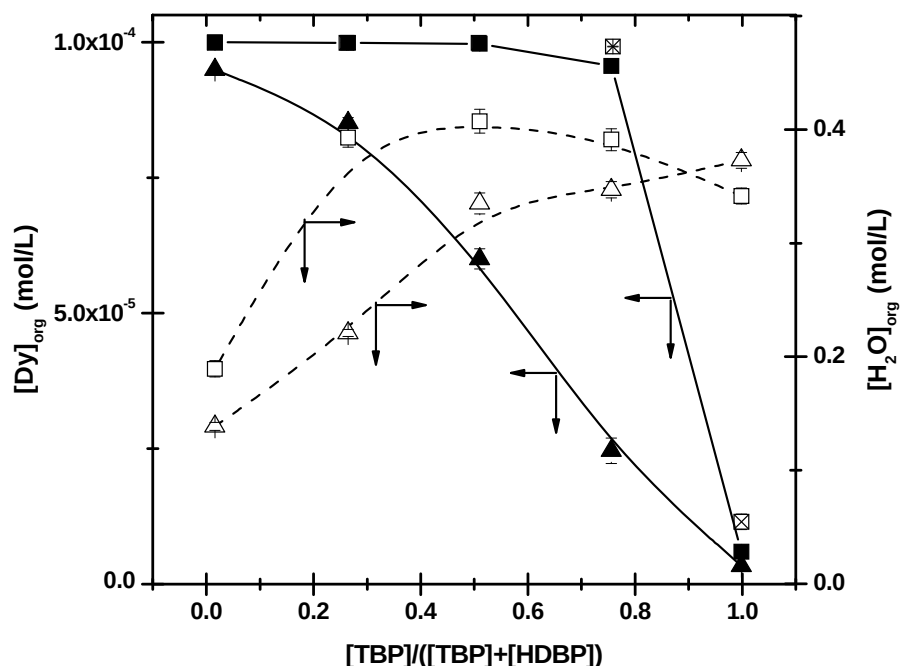


Figure 2. Concentration of dysprosium (closed and crossed out points) and water (open points) in the organic phase from contacting 2 M HNO_3 (triangles) or 0.2 M HNO_3 (squares) + 1.8 M NH_4NO_3 with organic phases containing varying ratios of TBP and HDBP at a constant, 1 M, total concentration of extracting reagent. Also shown are the concentrations of dysprosium in the organic phase for the experiment using 0.2 M HNO_3 without addition of NH_4NO_3 (crossed out squares). The error bars represent standard deviations from triplicate measurements. The lines in the figure do not represent best fits to the data but are there to guide the eye of the reader.

The extraction trends for this system show, as expected, that HDBP is a stronger extractant for lanthanides compared to TBP. The extraction at low acid shows a non-linear trend while increased acidity shows a more linear trend.

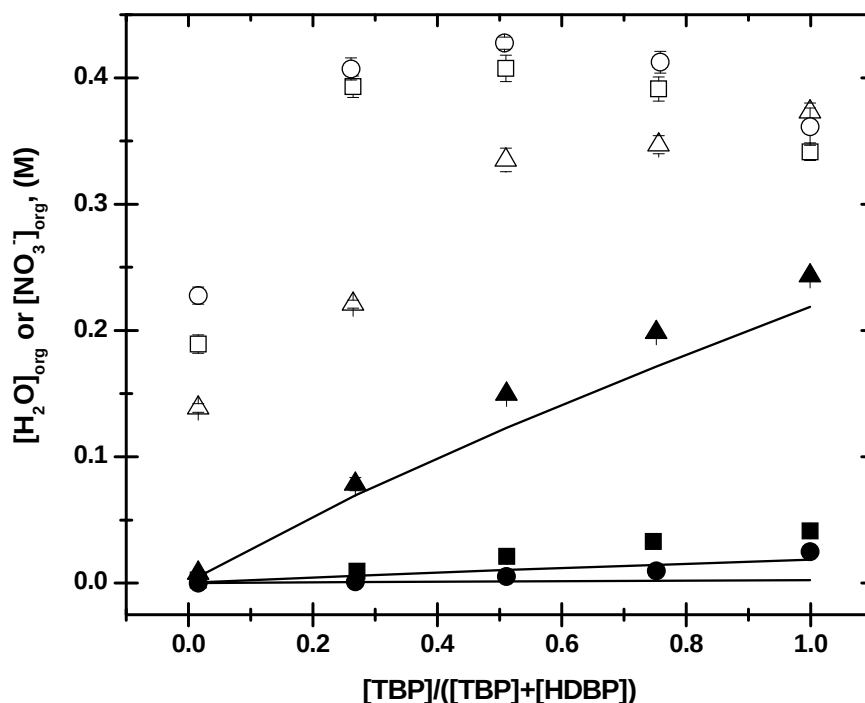


Figure 3. Concentration of nitrate (closed points) and water (open points) in the organic phase from experiments using 2 M HNO₃ (triangles) or 0.2 M HNO₃, with (squares) and without (circles) the addition of 1.8 M NH₄NO₃, contacted with organic phases containing varying ratios of TBP and HDBP at a constant, 1 M, total concentration of extracting reagent. The error bars represent standard deviations from triplicate measurements. The lines are theoretical nitric acid uptakes calculated for 2 M HNO₃, 0.2 M HNO₃ + 1.8 M NH₄NO₃ and 0.2 M HNO₃, respectively.

From the results in figure 3 there is a clear different for water and acid uptake between 0.2 M HNO₃ and 2M HNO₃ concentration in the aqueous phase. For the samples containing 0.2 M HNO₃ there is a maximum for the uptake of water when there is a mixture of HDBP and TBP. The 2 M HNO₃ does not show such a maximum although the trend of water uptake as a function of the molar ratio of extraction reagents is not linear. Adding 1.8 M ammonium nitrate to balance the ionic strength has a very small effect indicating that the ammonium nitrate is not extracted to any appreciable extent. The nitrate uptake is slightly higher when ammonium nitrate is added to reach 2 M total nitrate but the data in Figure 3 indicates that the nitrate uptake is much higher for the case of using 2 M nitric acid. The nitrate uptake do not show any synergistic effect and increases linearly with increasing TBP concentration indicating that HDBP do not interact with nitric acid. For more details of the analysis of this dataset we refer to Paper I (Anderson et al. Solvent Extr. Ion Exch. 2013).

The extraction data for lanthanum, dysprosium and lutetium at two different metal ion concentrations (10⁻⁴ and 10⁻³ M) are shown in figure 4 below. Higher metal ion concentrations (10⁻² M) were tested for lanthanum and dysprosium and showed identical trends in the distribution ratios. However, for dysprosium the onset of third phase formation was apparent at this concentration and for lutetium significant third phase was observed as such high metal concentration. Throughout this project we

observed that the extraction trends are very reproducible for this extraction system suggesting that the chemicals used remain stable and that any effect of impurities in the stock chemicals are negligible.

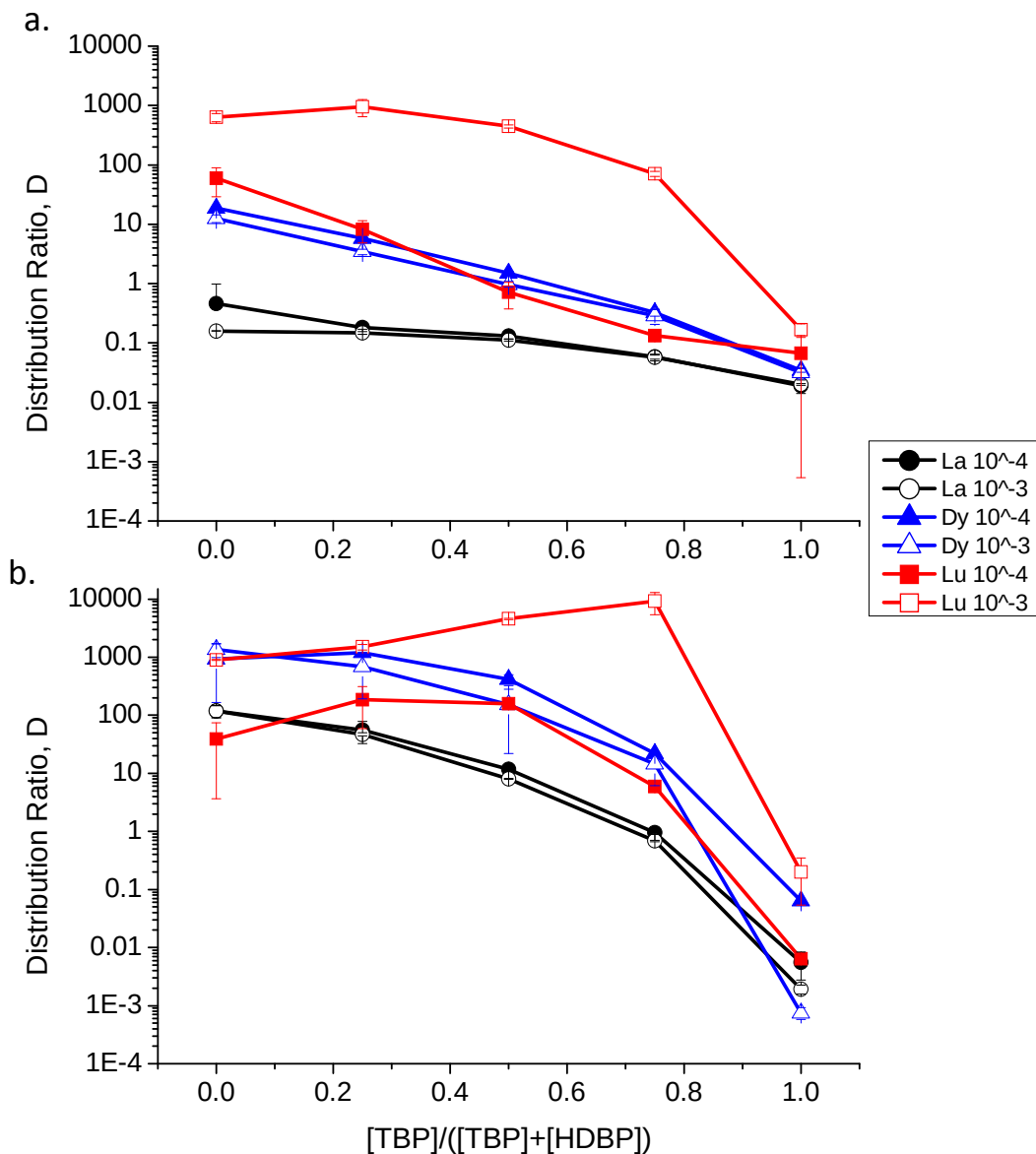


Figure 4: Distribution ratios for 10^{-4} M and 10^{-3} M Ln^{3+} at varying ratios of TBP:HDBP. Extraction from 2 M HNO_3 is shown top (a) and extraction from 0.2 M HNO_3 is shown bottom (b). The error bars represent the standard deviation of triplicate measurements.

For lanthanum and dysprosium the extraction trends show that low acid results in non-linear metal ion distribution while higher acid show a more linear trend, also there is no effect of increasing the metal ion

concentration. The results for lutetium, being the smallest ion in the lanthanide series and hence displaying the highest surface charge, are significantly different. At low acid a non-linear trend is observed however the concentration of metal ion appears to impact the distribution ratios. At higher acid concentration a non linear trend is observed when 10^{-3} M of metal ion was used. We observed in our X-ray scattering studies that lutetium is prone to formation of needle-like crystals in the organic phase at elevated metal ion concentrations. We were not able to observe these crystals with the naked eye, i.e., the phase appeared clear, although the existence of Bragg scattering led us to investigate the phases under a microscope, where the crystals were indeed visible (see figure 5). It is possible that the existence of these crystals in the organic phase affects the distribution ratios as we are no longer measuring a simple extraction equilibrium but rather metal ion complexation followed by precipitation of the metal ion complexes. This could have the effect of artificially decreasing the concentration of metal-ligand complexes dissolved in the organic phase, which govern the extraction equilibrium, resulting in further extraction and hence elevated distribution ratios.



Figure 5: Photograph of a 1.25×10^{-3} M Lu extraction into a 1:3 TBP:HDBP organic solution.

The water uptake for these systems is shown below. No effect is seen due to metal ion concentration or the type of metal ion. Furthermore, organic phases contacted with an aqueous phase where no metal ion was present also show similar water uptake (denoted as PEQ in figure 6). This suggests that aggregates forming in the organic phase where water is solubilized will form regardless of the presence of metal ions.

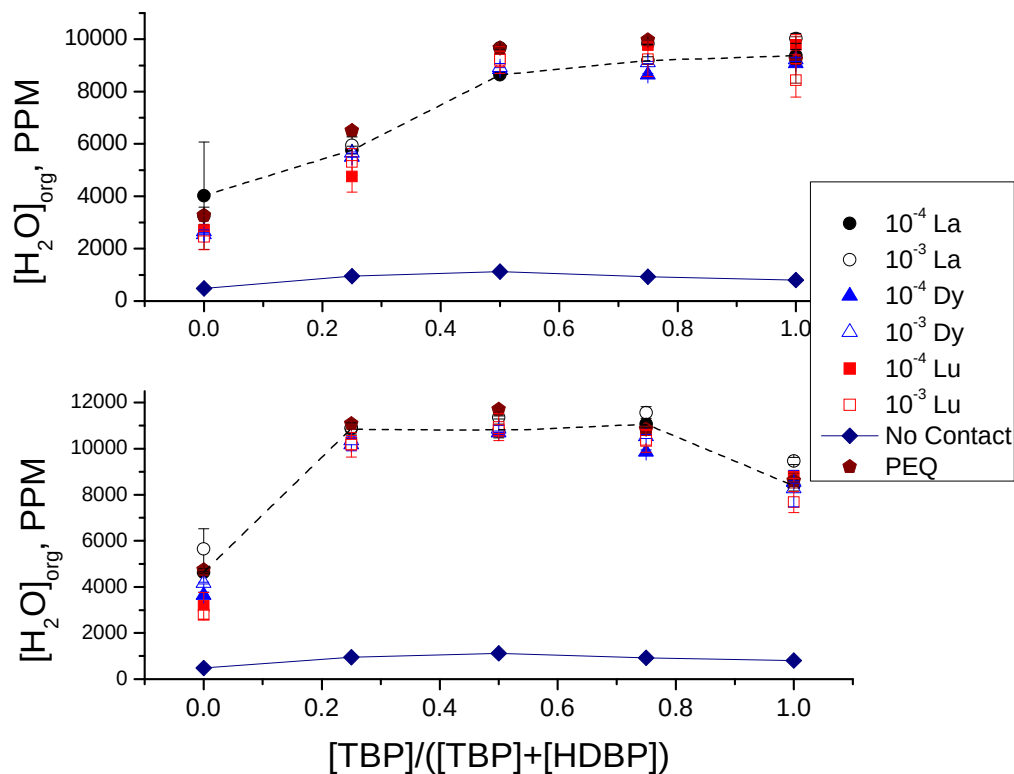


Figure 6: Water uptake into the organic phase for all metal ions investigated. Water uptake from 2 M HNO_3 is shown top and water uptake from 0.2 M HNO_3 is shown bottom. PEQ refers to pre-equilibrated organic phase without any metal ion present.

As mentioned earlier, extraction of europium and uranium was also investigated using the TBP/HDBP system. Shown in figure 7 below the metal ion extraction trends for europium are similar to dysprosium, while the extraction trends for uranyl exhibit stronger synergistic trends, most likely due to the stronger affinity of TBP to coordinate uranyl ion compared to trivalent lanthanides.

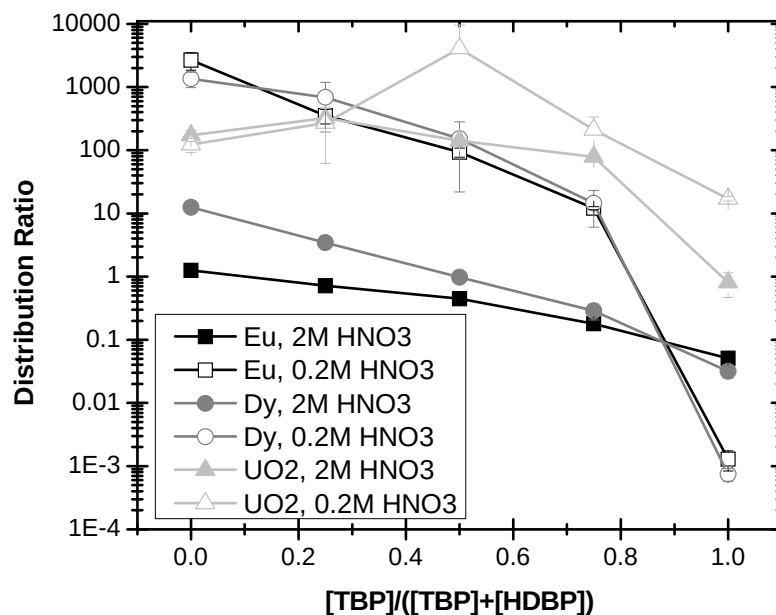


Figure 7: Distribution ratios for 10^{-3} M Eu^{3+} and Dy^{3+} and 10^{-4} M UO_2^{2+} at 2 and 0.2 M HNO_3 .

Fluorescence Studies

Dy, Eu and U (as uranyl, UO_2^{2+}) were chosen for their strong fluorescence signals. The fluorescence spectra of Dy complexes were collected using an excitation wavelength of 350 nm, the Eu complexes were collected using an excitation wavelength of 395 nm, and the uranium spectra were collected with an excitation wavelength of 275 nm. Figure 8 shows the reference spectra in aqueous solution and figures 9 and 10 show the spectra in the different organic phases.

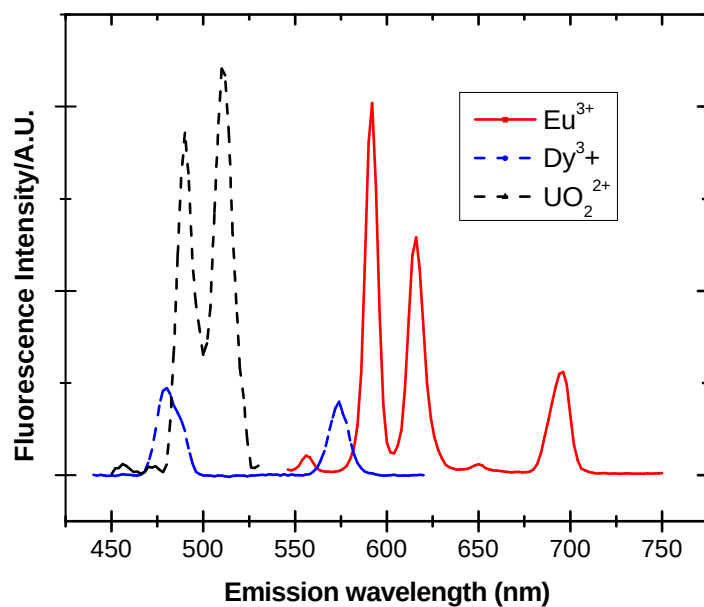


Figure 8: Fluorescence spectra of Eu, Dy, and UO_2^{2+} in 0.2 M HNO_3 .

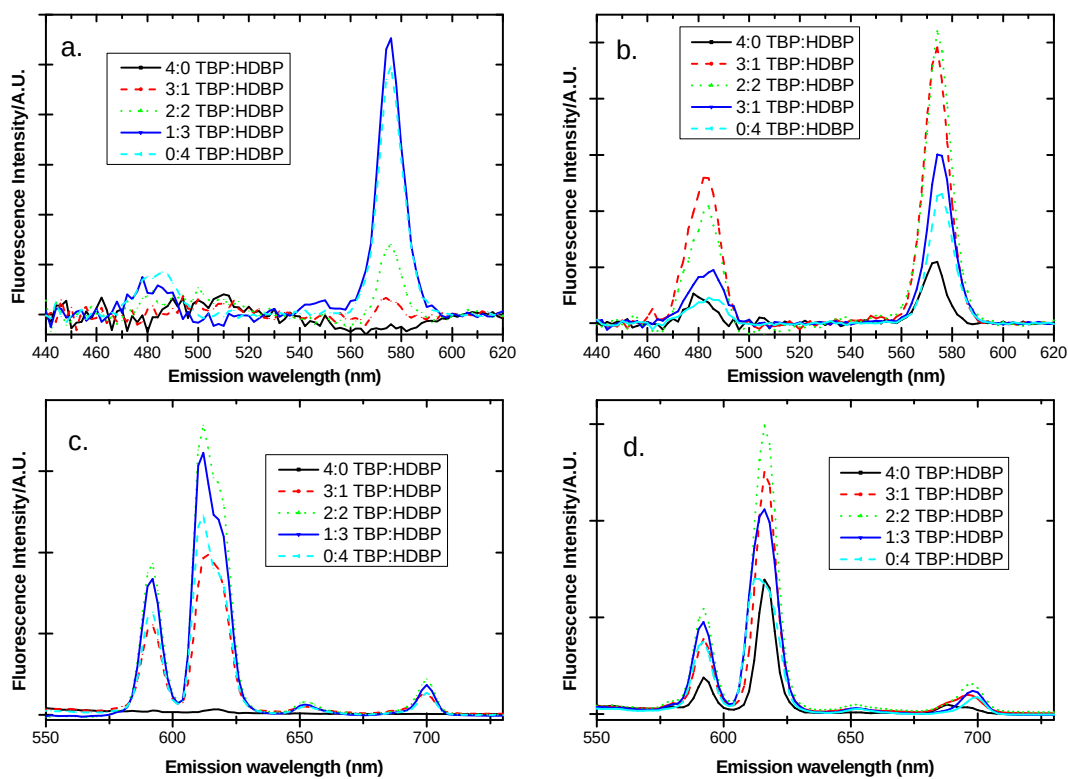


Figure 9: Fluorescence spectra for 10^{-3} M Dy at 0.2 M HNO_3 (a), 10^{-3} M Dy at 2 M HNO_3 (b), 10^{-3} M Eu at 0.2 M HNO_3 (c), and 10^{-3} M Eu at 2M HNO_3 (d).

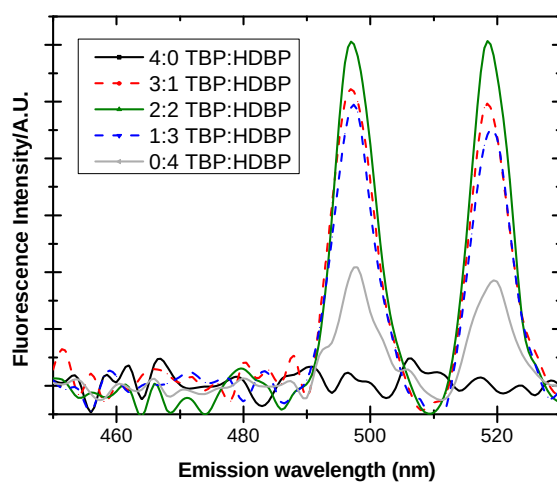


Figure 10: Fluorescence spectra for 10^{-4} M UO_2^{2+} in 0.2 M HNO_3 .

Looking at the fluorescence of dysprosium at low acid concentrations, Figure 9a, the fluorescence peak intensities at 576 nm show a maximum at a ratio of 25:75 TBP:HDBP in the organic phase. At high acid, Figure 9b, however, the highest intensity of fluorescence is seen for the 50:50 mixture of TBP:HDBP and a second peak at 482 nm is observed. This maximum intensity with a mixed organic system cannot be correlated to metal ion concentration in the organic phase. While previous results for Dy extraction have suggested a maximum extraction at a HDBP:TBP ratio of 75:25 the extraction of Dy at 100% HDBP is, within errors, equally high. Furthermore, the extraction at 2 M nitric acid indicate a more linear increasing trend with increasing HDBP ratio, which should result in a linear increase in intensity in the fluorescence spectra. It is possible that the inclusion of HDBP would result in quenching of the fluorescence emission of the metal ion causing the peak intensity to decrease at elevated HDBP:TBP ratios. Experiments to test for possible quenching effects in these systems were carried out by extracting Dy into organic solutions containing varying concentrations of HDBP, but high enough to yield close to 100% extraction for each experiment. Fluorescence measurements on these organic solutions showed that the differences in intensities are not due to quenching with increasing HDBP concentration. It is interesting to note that the maximum in intensity correlates with the maximum uptake of water reported in our previous studies. This does not confirm, however, whether the water is coordinated to the metal ion or present in reverse micelles separate from the metal-ligand complexes. In addition, it is observed that the peak shifts slightly to higher wavelengths as the concentration of HDBP increases. Figures 9c and 9d show the fluorescence spectra of europium at both acid concentrations and a similar trend as for dysprosium is observed. At low acid, there is a significant change in the shape of the largest peak at 612nm. This is likely due to a change in the complexes formed in the organic phase as HDBP is an efficient extractant at low acid and the mixture of TBP/HDBP may interact to enhance the extraction, as indicated in the distribution data for low acid. The trends seen in the lanthanide fluorescence data are also found for uranium, as shown in Figure 10, though at high acid concentrations, uranium fluorescence in the organic phase did not provide sufficient intensity to discern from the baseline due to absorption of nitric acid at the excitation wavelength of uranyl (~275nm).

Time Resolved Laser Induced Fluorescence Spectroscopy Studies

In order to see how many water molecules surround the metal ions in the TBP/HDBP complexes we chose to look in to Time Resolved Fluorescence Spectroscopy (TRFS) using both xenon lamps (for Eu) and a laser setup (for Dy). We were interested to determine if the number of water molecules would change when the ratio between TBP and HDBP was changed as this would be an indication of changes in the coordination environment, as was suggested by the Fluorescence data above.

We worked with the laser facility at UC Irvine to set up an experiment to carry out TRLIFS of organic samples containing Dy. In addition, experiments involving deuterated nitric acid and D₂O were carried out to allow us to make the necessary correlation between lifetime and hydration number of our complexes.

Time resolved fluorescence studies were also carried out on europium samples with the help of colleagues at Lawrence Berkeley National Laboratory (LBNL). Mikael Nilsson and Alex Braatz traveled to LBNL to participate in time resolved fluorescence experiments under the guidance of Dr. Linfeng Rao and Dr. Christina Leggett. The samples were analyzed on a Fluorolog 3 with a flash lamp set up for lifetime measurements. Figure 11 below show some of the raw data collected. It can be seen that when europium is extracted into an organic phase the life-time of the fluorescence increases, as expected, due to removal of water around the metal ion.

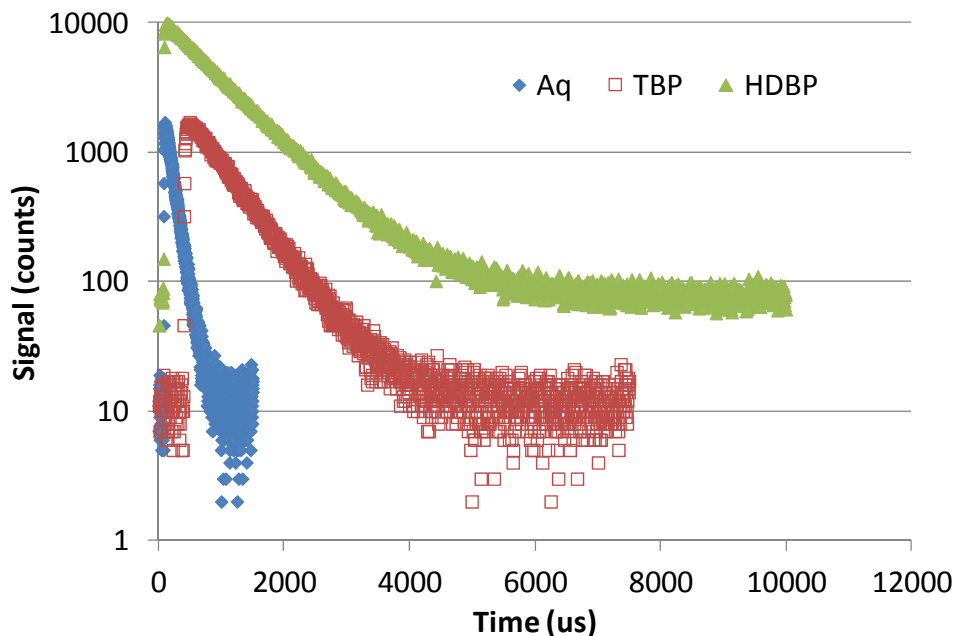


Figure 11. Time resolved laser fluorescence data for europium in aqueous solution (blue diamond), extracted into 1 M TBP from 2 M HNO_3 (red square) and extracted into 1 M HDBP from 2 M HNO_3 (green triangle).

For europium the correlation between decay constant and number of waters is well studied and can be expressed with the following equation:

$$N_{\text{H}_2\text{O}} = 1.05 \times 10^{-3} k_{\text{obs}}(\text{Eu}) - 0.44$$

where $k_{\text{obs}}(\text{Eu})$ is the decay constant determined experimentally from fitting the fluorescence signal decay with an exponential trend.

However, for dysprosium this trend was less well established and we decided to make our own correlation between decay constants and number of waters around a dysprosium ion. A set of experiments were carried out where dysprosium was complexed with different aqueous complexing agents with well-known geometry. Figure 12 shows the experimental luminescence decay constants versus hydration number for complexes of Dy with ethylene diamine tetraacetic acid (EDTA), diethylene triamine pentaacetic acid (DTPA), and nitrilo triacetic acid (NTA) as well as uncomplexed Dy in mildly acidic water (HNO_3 and H_2O) and uncomplexed Dy in mildly acidic deuterated water (DNO_3 and D_2O).

Utilizing the calibration curve from Figure 12, we were able to calculate a similar relation between number of waters and the decay constant for dysprosium excitation.

$$N_{\text{H}_2\text{O}} = 0.022 k_{\text{obs}}(\text{Dy}) - 0.76$$

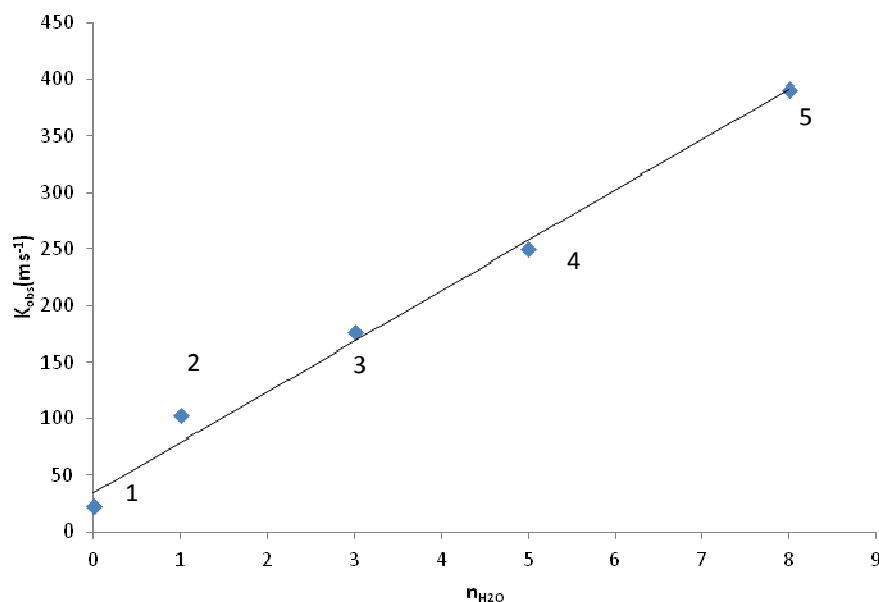


Figure 12: plot of $k_{\text{obs}}(\text{ms}^{-1})$ vs. $n_{\text{H}_2\text{O}}$ for Dy(III). The trend line shown is the relation shown in Eq. 3.9. The k_{obs} for Dy(III) in D_2O and H_2O as well as those for Dy(III)-polyamino polycarboxylate complexes. They are numbered as 1) D_2O , 2) DTPA, 3) EDTA, 4) NTA, and 5) H_2O .

Table 1 shows the calculated hydration numbers for the europium and dysprosium extractions. For europium we find that the hydration numbers are between 0 and 1 and for dysprosium they are lower, most likely 0 however some subtle differences are observed between the different systems. The hydration numbers are in line with complexes that are formed predominantly with monodeprotonated dimers of HDBP alone with the presence of some complexes formed with TBP that would include some water in the inner coordination sphere.

Table1: K_{obs} and hydration number for Dy^{3+} or Eu^{3+} from either 2 M HNO_3 or 0.2 M HNO_3 . Errors associated with these calculations are $\pm 0.5 N_{\text{H}_2\text{O}}$.

	Europium Extraction				Dysprosium Extraction			
	0.2 M HNO_3		2 M HNO_3		0.2 M HNO_3		2 M HNO_3	
Sample	$K_{\text{obs}}(\text{s}^{-1})$	$N_{\text{H}_2\text{O}}$	$K_{\text{obs}}(\text{s}^{-1})$	$N_{\text{H}_2\text{O}}$	$K_{\text{obs}}(\text{ms}^{-1})$	$N_{\text{H}_2\text{O}}$	$K_{\text{obs}}(\text{ms}^{-1})$	$N_{\text{H}_2\text{O}}$
4:0 TBP:HDBP			653.8	0.24			22.13	-0.27
3:1 TBP:HDBP	753.4	0.35	694.6	0.28	16.81	-0.39	23.61	-0.24
2:2 TBP:HDBP	754.8	0.35	823.4	0.42	24.72	-0.21	26.80	-0.17
1:3 TBP:HDBP	802.6	0.40	966.2	0.57	22.21	-0.27	25.18	-0.20
0:4 TBP:HDBP	884.2	0.48	1035.6	0.64	23.43	-0.24	26.71	-0.17

Discussion

The TBP/HDBP extraction system shows non-linear metal ion extraction at low acid concentration as well as non-linear water uptake. The extraction studies and the spectroscopy studies do not provide any evidence that the metal ion is present in a reverse micelle type aggregate. Overall, the lanthanides appear to be extracted in a similar way across the series though there are differences in the limit of metal ion that

can be solubilized in the organic phase. It appears that studying distribution ratios only will not provide an accurate picture of the extraction system. The system was further studied as part of objectives II and III and those results are outlined below.

Studies of other synergistic extraction systems

As mentioned above, the original plan for this project was to use TBP/HDBP as a benchmarking system to study other systems. Due to the level of detail we needed to understand the TBP/HDBP system less focus was put on investigating other systems. A number of extraction systems were tested using various combinations of extractants, see Figure 13, where metal ion extraction was studied to determine whether or not synergism was present in the system. Water uptake into the organic phase was also investigated as an indicator of reverse micellar aggregate formation. Combinations included some systems from literature reports showing synergy as well as combinations of extractants that were not reported in the open literature. No follow up studies were carried out using X-ray techniques, during the timeframe of this project, so the presence of aggregates could not be confirmed. Follow on studies of these systems will continue in our research group and when the results are presented partial credit will naturally be given to this research project.

For the following series of experiments, distribution ratio measurements were done with either neutron activation analysis (those experiments examining dysprosium) or radiotracer analysis (those experiments examining europium). Water uptake was measured using Karl Fischer titration. The experiments were carried out in a similar fashion as was detailed above.

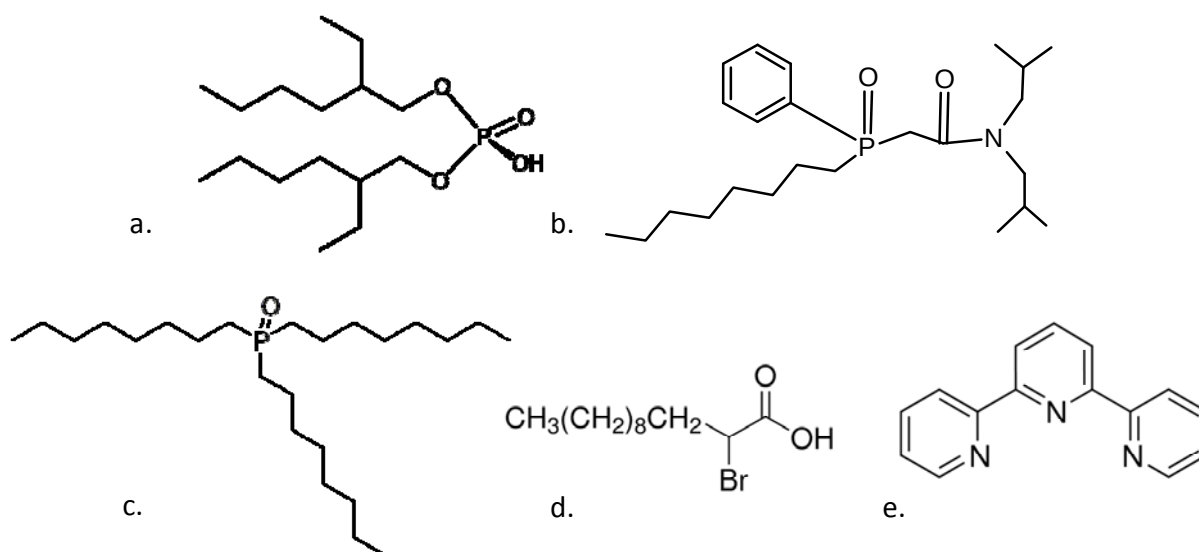


Figure 13. Chemical Structure of HDEHP (a), CMPO (b), Trioctyl phosphine oxide (TOPO), (c), Bromodecanoic acid (BDA) (d), 2,2':6',2''-terpyridine (Terpy) (e).

HDEHP and CMPO

Literature has shown that the combination of CMPO and HDEHP can be synergistic, given the correct conditions. These conditions typically involve more complex systems than those covered in this work and include competitive extraction of multiple metals, a buffered aqueous phase and holdback reagents in the aqueous phase. In our simplified system, Figure 14, comprising only a single metal extraction from an acidic medium, no synergism is observed.

For the same conditions, water uptake was also examined. Figure 15 shows these results. It is of note that the metal extraction and water uptake show opposite trends.

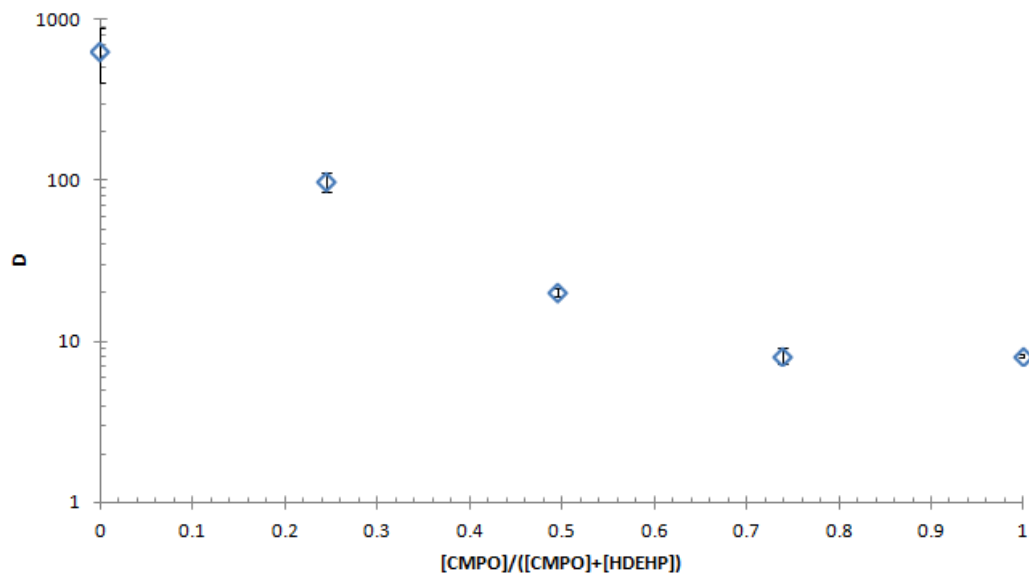


Figure 14: Distribution ratios for dysprosium extraction into n-dodecane using CMPO and HDEHP

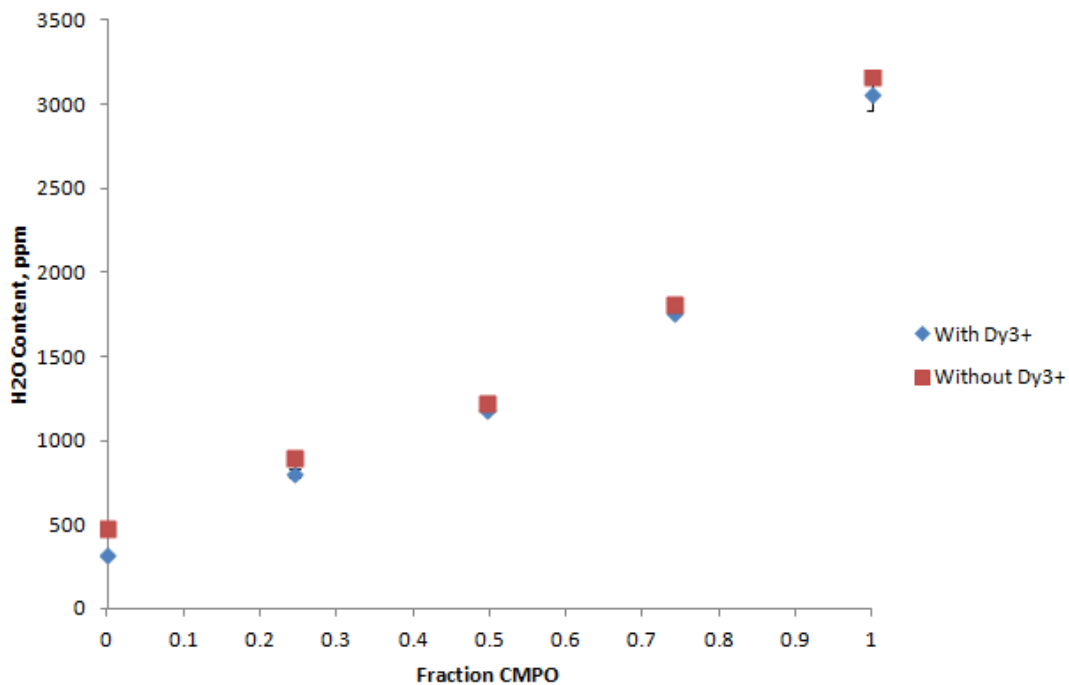


Figure 15: Water uptake for CMPO and HDEHP extraction of dysprosium

CMPO and TOPO

While no evidence exists in the open literature for the possible synergism between CMPO and TOPO, the difference between a chelating (CMPO) and a non-chelating (TOPO) extractant may offer an interesting interaction to be investigated.

Figures 16 and 17 depict the metal ion extraction and water uptake, respectively, at 0.2 M nitric acid concentration using 0.1 M TOPO and varying CMPO concentration. No synergism is observed in either metal extraction nor in water uptake, though there is a significant increase in water uptake as CMPO is added to the system.

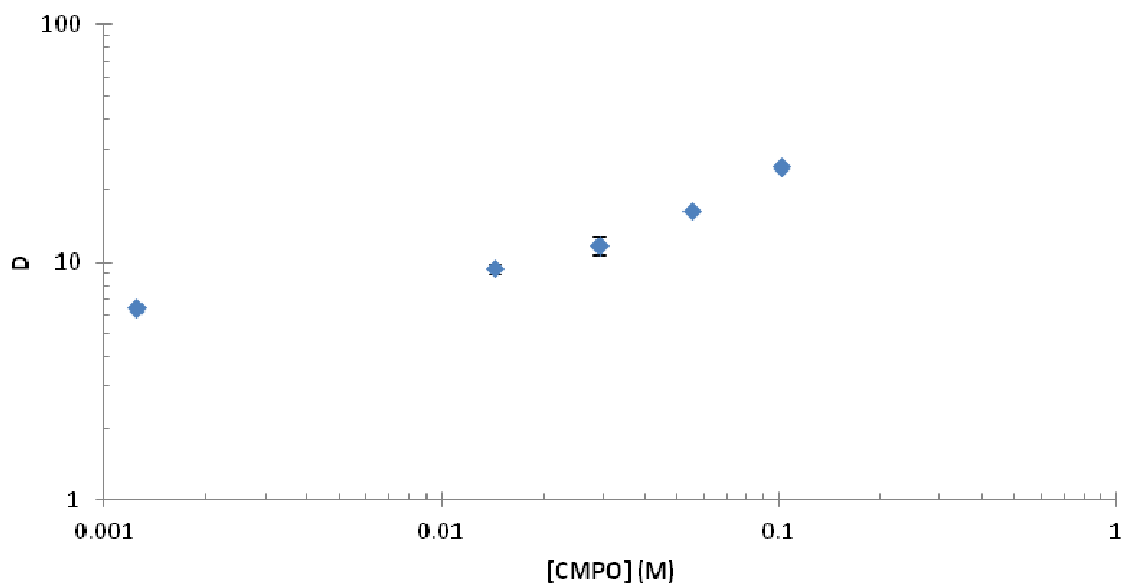


Figure 16: Europium extraction using 0.1 M TOPO and varying CMPO

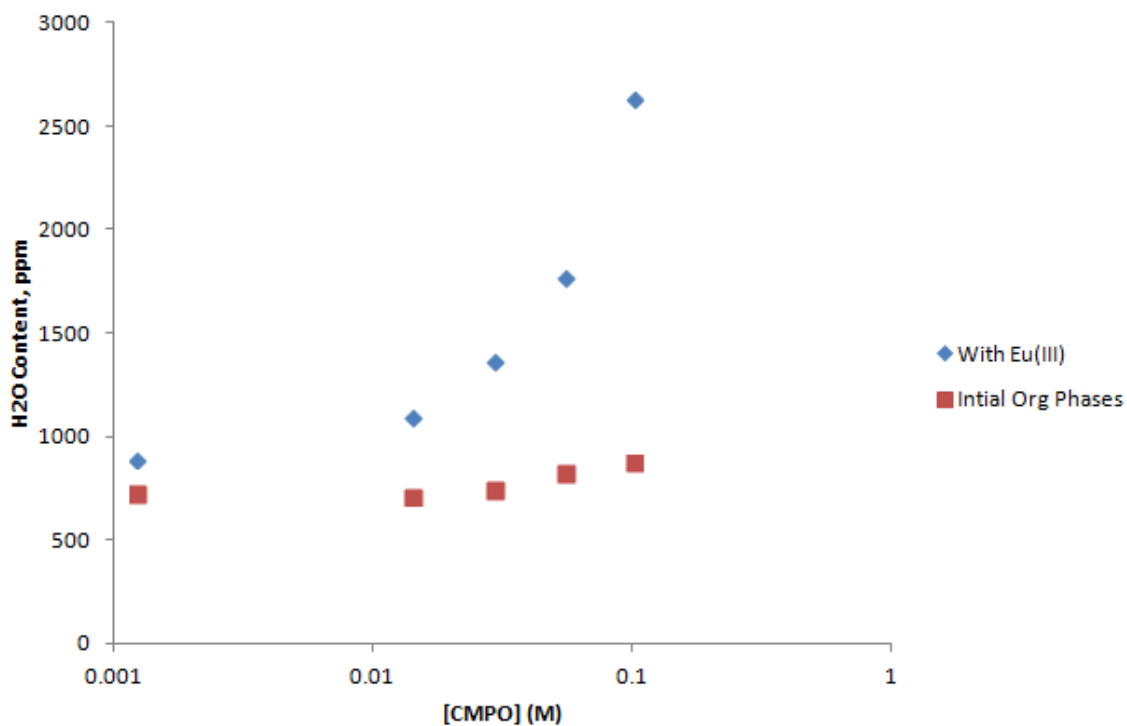


Figure 17: Water uptake for europium extraction with TOPO and CMPO

TOPO and HDBP

As we spent significant effort on the system comprising TBP and HDBP we decided to examine the effect of changing slightly the properties of one extractant in this system, we have exchanged TBP with TOPO. Results are shown in Figure 18 for metal extraction.

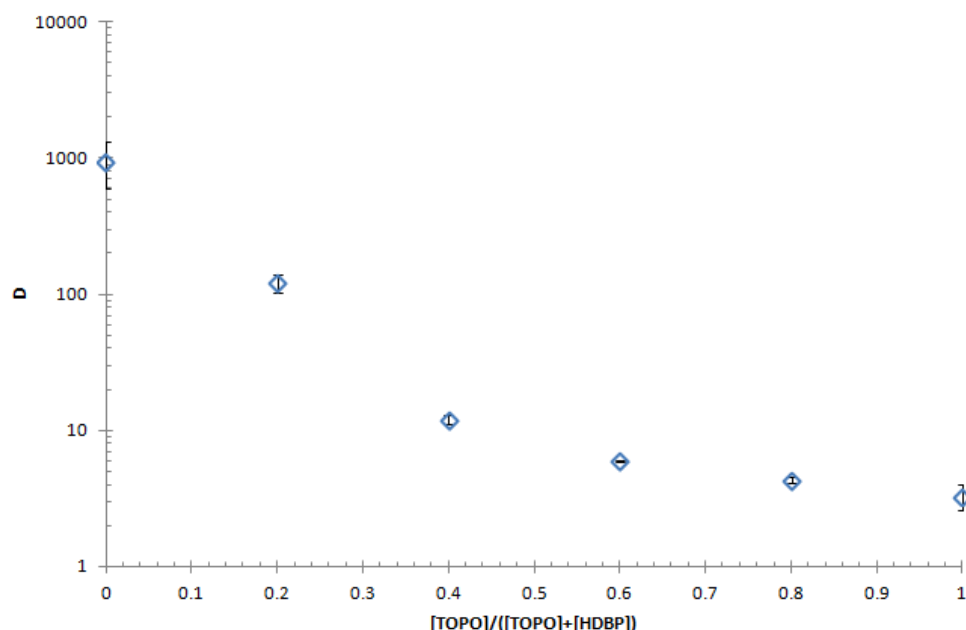


Figure 18: Distribution ratios for extraction of dysprosium with TOPO and HDBP

The behavior of this system is markedly different from that observed in the TBP/HDBP system. It is worth noting that shown here is 0.1 M total extractant concentration while previous results for TBP/HDBP were shown with 1 M total extractant concentration.

No significant water uptake was observed, suggesting the possible absence of large aggregates in the organic phase under these conditions.

TOPO and HDEHP

This system comprising HDEHP and TOPO could have similarities with the HDBP-TOPO system as HDEHP is also a monoacidic phosphoric acid reagent. As literature has suggested that this system is indeed synergistic (when extracting metal from hydrochloric acid) we tested this system further under varying organic and aqueous phase conditions. We were unable to observe any synergy and to reproduce the literature study. The extraction decreases as the concentration of TOPO increases while HDEHP is constant, Figure 19.

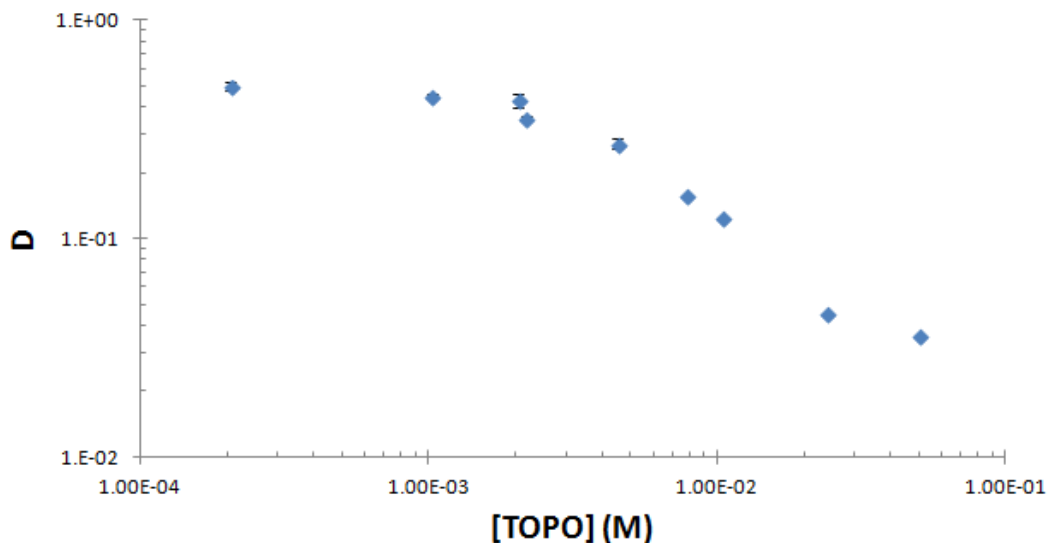


Figure 19: Dysprosium distribution ratios with 0.01 M HDEHP and varying TOPO from 0.01 M HCl

The water uptake follows an opposite trend, possibly suggesting a competition between water and metal uptake, Figure 20.

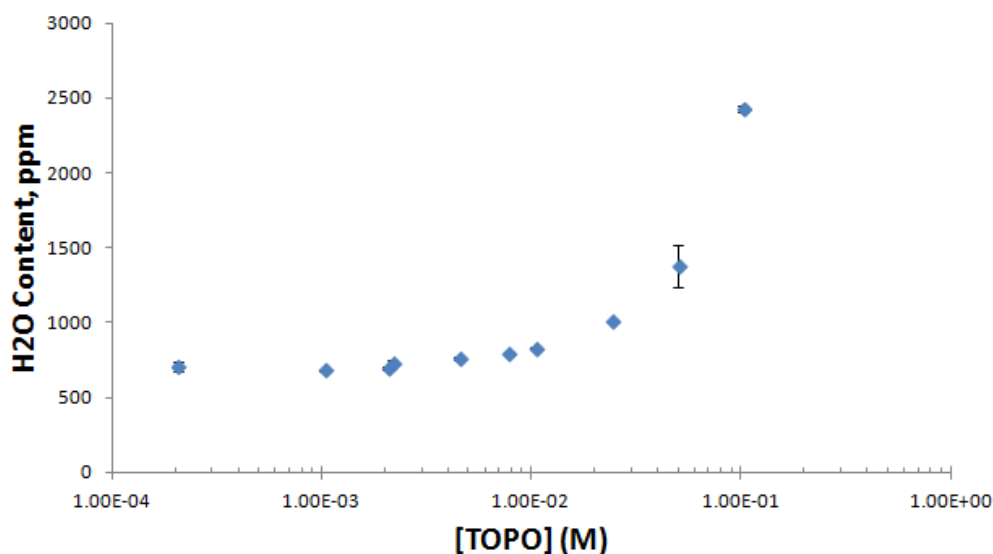


Figure 20: Water uptake data for the system shown in Figure 19

Attempts were made to adjust the concentrations of HDEHP and HCl further to 0.1 M HDEHP and 0.001 M HCl, though significant third phase was noted during contact with acidic aqueous phases both with and without metal ions. Distribution ratio measurements and water uptake measurements were therefore not possible to establish accurately.

2-bromodecanoic acid and 2,2':6',2''-terpyridine

The system combining 2-bromodecanoic acid (BDA) and 2,2':6',2''-terpyridine was also investigated. Synergism with Eu(III) has been noted in this system in the literature and we were able to reproduce these data for metal ion extraction as noted in Figure 21. Figure 22 shows the comparison of the organic phase water content between systems only differing in the presence of Terpy. It is clear that water uptake

during extraction is due to BDA and rapidly increases with increasing BDA concentration while metal ion extraction shows clear synergy when both Terpy and BDA are used.

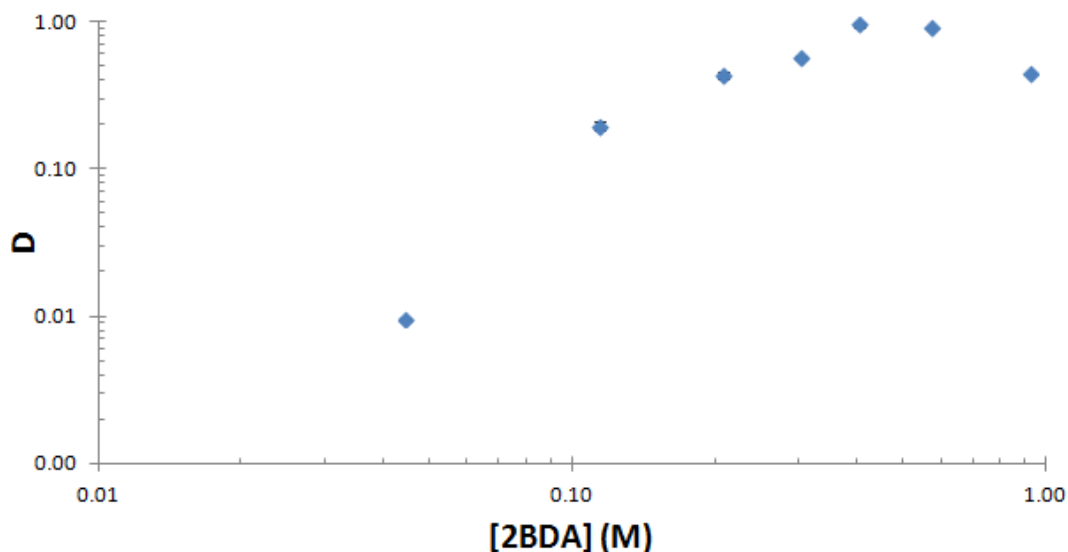


Figure 21: Extraction of europium using 0.02M terpyridine and varying 2-bromodecanoic acid from 0.01M nitric acid

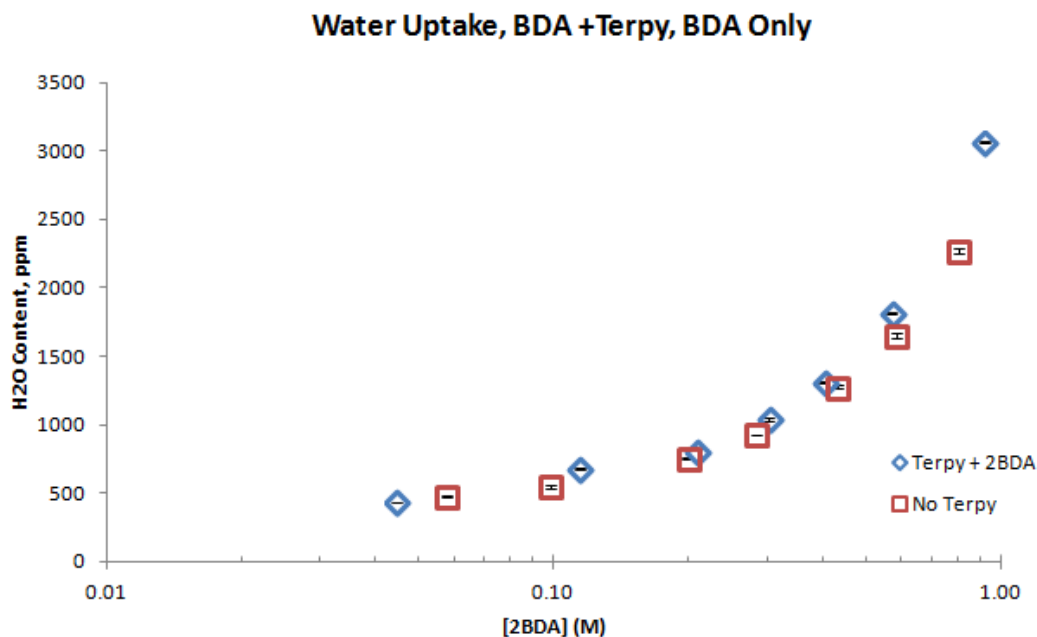


Figure 22: Comparison of 2-bromodecanoic acid organic phase water content with and without 2,2':6',2''-terpyridine

TBPO and HTTA

We also investigated the combination of HTTA and tributylphosphine oxide (TBPO). In this case we observed strong synergism in the distribution of metal ions, as shown in Figure 24.

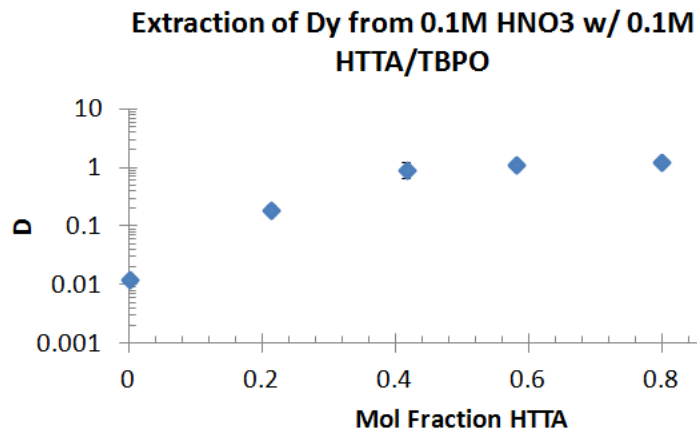


Figure 24: Dysprosium extraction from 0.1M HNO₃ + 0.9M NH₄NO₃ with 0.1 M total extractant.

This system is known to be synergistic and results shown above match well with those seen in previous works. Of interesting note is the water uptake data, shown in Figure 25. Synergism, which is seen in the metal ion uptake is also seen in the water uptake into the organic phase. The water contents, however, remain fairly low and such low water contents are unlikely to be indicative of reverse micelle formation, though this system might warrant further investigation.

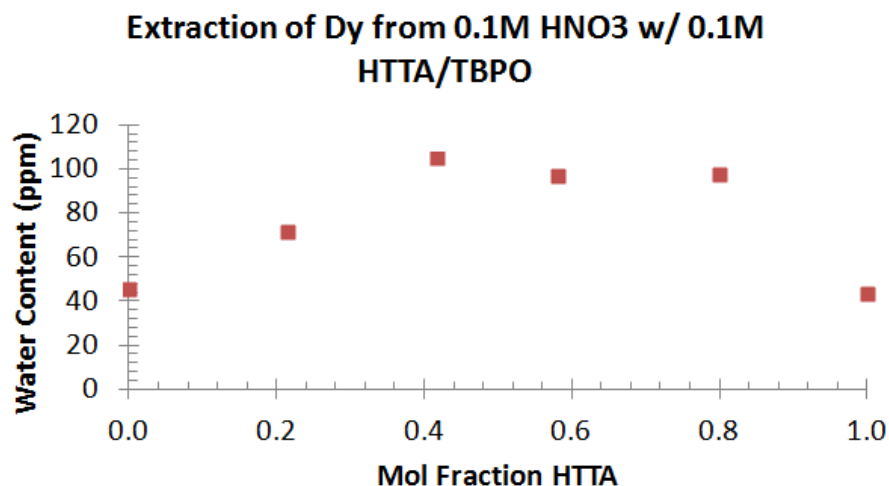


Figure 25: Organic phase water content for dysprosium extraction from 0.1M HNO₃+0.9M NH₄NO₃ with 0.1M total extractant

Measurements of the interfacial tension were also carried out on the HTTA:TBPO system as the measurement of this property has been used in the past to show the formation of aggregates in synergistic extraction systems. These measurements were carried out under conditions of constant extractant concentrations similar to the results shown in Figures 24 and 25. Results are shown in Figure 26.

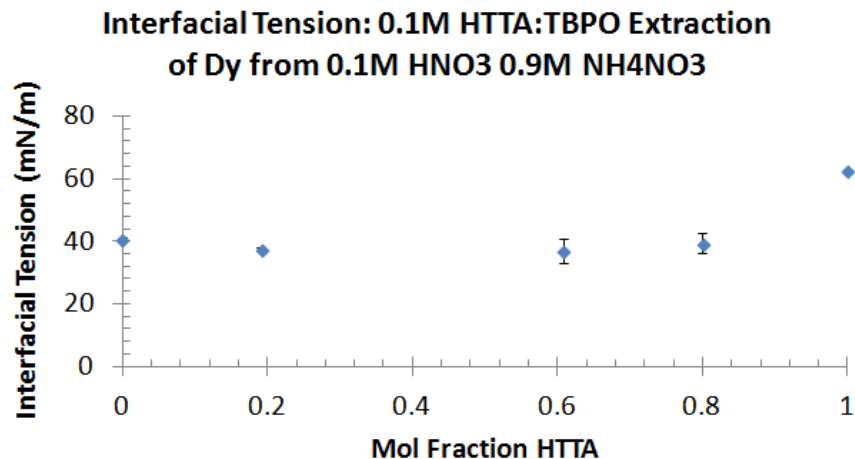


Figure 26: Interfacial tension values for extraction from 0.1M HNO₃ + 0.9M NH₄NO₃ with 0.1M total extractant

A significant decrease in interfacial tension is seen upon the addition of TBPO to the organic phase suggesting that perhaps TBPO is active at the interface in this system. A more typical measurement scheme for interfacial tension would be to hold one extractant concentration constant while gradually increasing the concentration of the other. These measurements were planned but were not carried out as we experienced problems with our tensiometer. We will pursue these studies as part of future work.

Discussion

Many of the combinations of extracting reagents that we investigated did not show any significant synergistic trends for water uptake or metal extraction. Only a couple of the systems displayed interesting trends. It may be worthwhile to continue to study these systems as part of a different project.

Objective II: Use 2-phase calorimetry to study microemulsion.

One of the objectives in this project was to utilize calorimetry to study our extraction systems. Two-phase calorimetry has the potential to offer a new dimension of thermochemical tracking of self-assembly in the organic phase resulting from the solute transfer across the liquid-liquid boundary. The effects of various components of the organic phase on the enthalpy of metal extraction can be studied in a dynamic mode using 2-phase calorimetry, allowing an investigation of an immediate thermochemical response of the solvating powers of the organic phase. Theoretically, two-phase calorimetric experiments will directly correlate the observed changes in the energetics of metal phase transfer with structural transformations in the organic phase. Progressive rearrangements may produce supramolecular organizations of solute molecules, which directly affect the kinetics and the thermodynamics of the transfer across the liquid-liquid interface.

The idea was to use Aerosol OT (AOT) as a benchmark aggregate forming molecule and for training purposes. AOT serves as the surfactant, n-dodecane is the non-polar solvent and water was added to form the core of the aggregates. The extension of this work was to investigate systems of TBP/HDBP as well as other combinations of extraction reagents using the same techniques.

A temperature study of the viscosity and its indication of the presence of reverse micelles was carried out for AOT in n-dodecane. The results, shown in Figure 27, show a sudden increase in viscosity when the AOT concentration is increased. Other works reported in the literature attribute this change in viscosity to the condition where the critical micelle concentration (cmc) is reached. The temperature of the solution does not appear to make a large impact of the viscosity trend, at least in the range of temperatures studied

here. The water content of each solution was such that the ratio of water to AOT was maintained at a constant value of 25 °C.

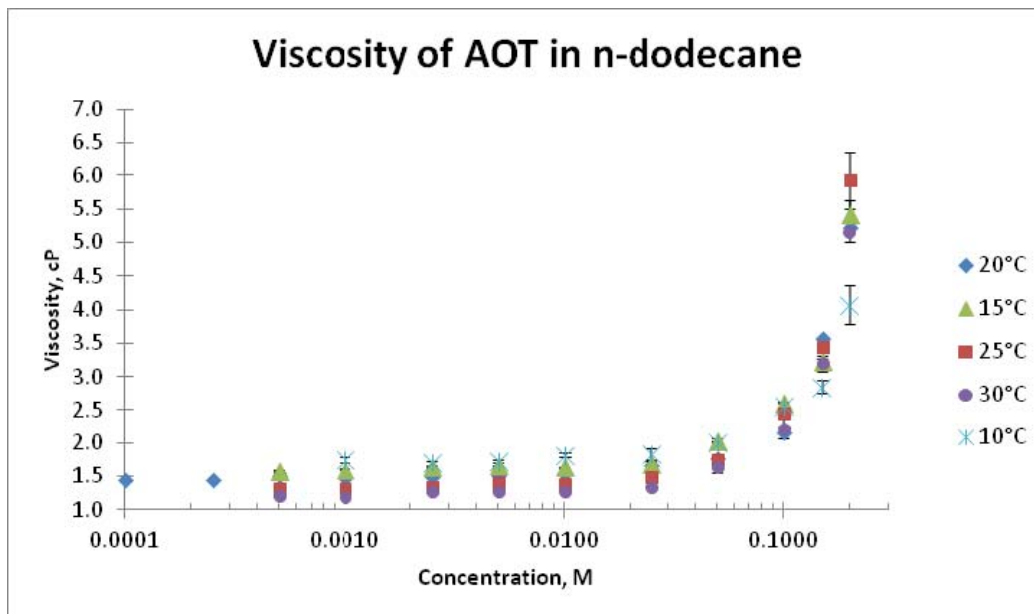


Figure 27. Temperature dependence of viscosity of solutions of AOT

These results suggest that aggregates are forming in this system and prompted us to investigate this system using microcalorimetry.

A graduate student, Andy Jackson, from UC Irvine travelled to Idaho National Laboratory (INL) to work with Dr. Peter Zalupski and carry out isothermal titration calorimetric measurements in systems of AOT in n-dodecane, as well as n-octane, and n-nonane. The instrument used was a TA Instruments NanoITC. Previous studies from the literature have reported evidence of a critical micelle concentration, CMC, in similar systems using calorimetry. However, our data show markedly different results from those previously reported as well as from a normal micellar system. Overall the calorimetry studies of reverse micelles suffered from poor reproducibility. A regular micelle system was studied to ensure the calorimeter was in good working condition. Figure 28 below depicts the typical behavior in a oil-in-water micellar system comprised of AOT and water, collected at INL. A dramatic shift in the heat signature, as shown in the figure below, suggest that the CMC was reached.

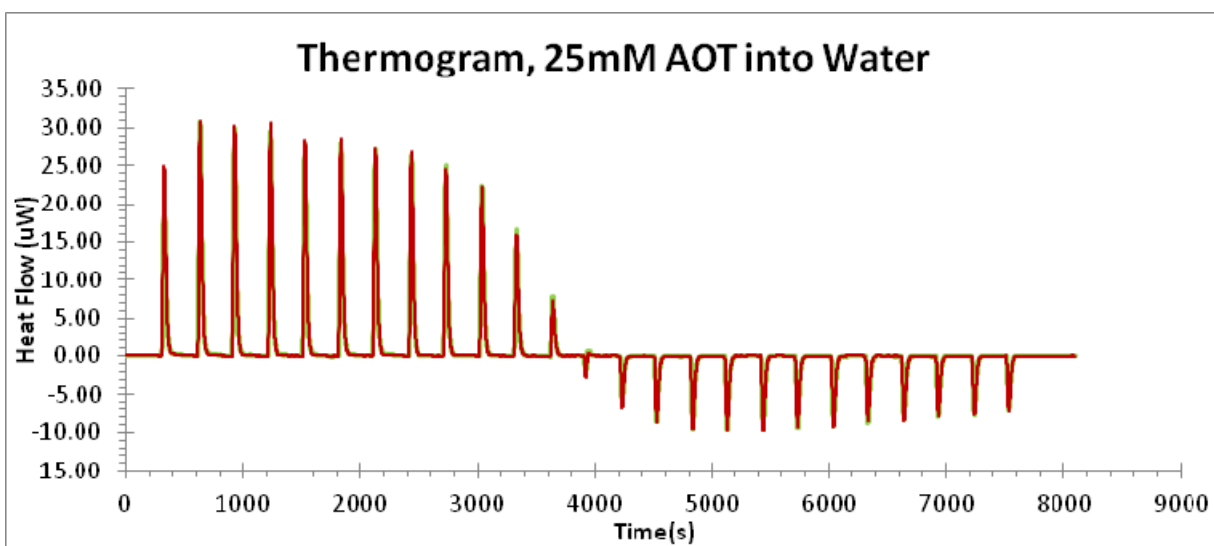


Figure 28: Oil-in-water micellar formation studied using isothermal titration calorimetry. Oil: AOT.

The peaks of a thermogram shown in figure 8 were integrated to give the curve shown in Figure 29. The inflection point of this curve corresponds to the location of the CMC. Once the CMC is known, the enthalpy of micellization can be estimated at the CMC.

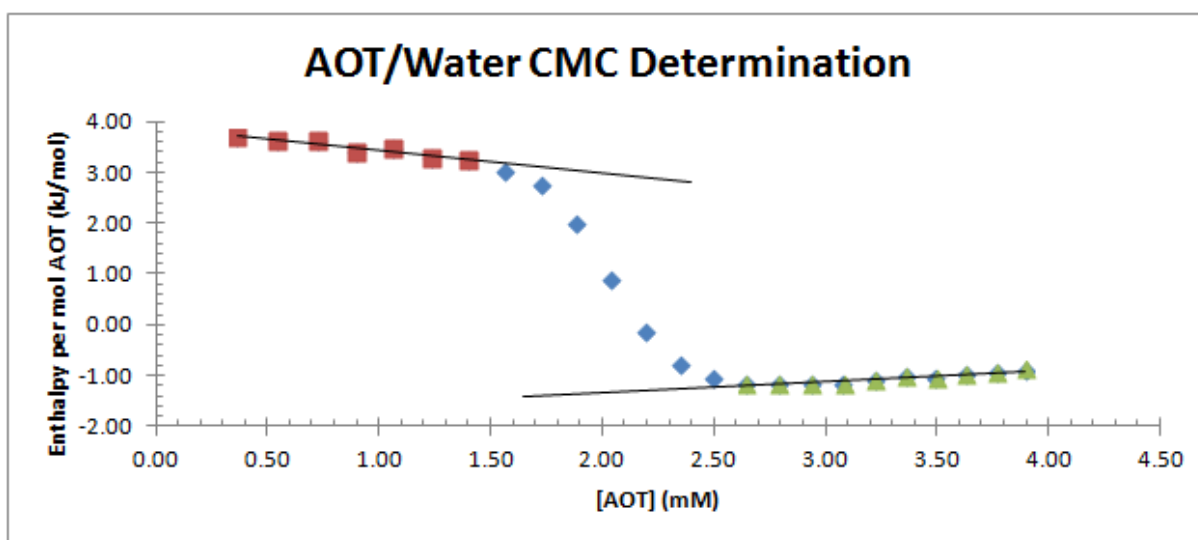


Figure 29. Enthalpy curve from analysis of the thermogram of the isothermal calorimetric measurement of AOT in water.

The CMC value obtained from the data shown above was found to be 2.02 mM which compares well to values found in the literature (2.56 mM by surface tension and 2.23 mM by calorimetry). Thus, the response of the calorimeter to a normal micelle was comparable to other studies and indicated that the instrument behaved as expected.

When isothermal calorimetric titrations on reversed systems (water-in-oil) were carried out no evidence of existence of a CMC was observed. Due to this, the heats of formation of aggregates in the organic phase were not possible to determine. Figure 30 depicts a representative sample of data from an organic system of AOT in n-dodecane collected during this reporting period. No shift in the heat signature was observed which may indicate that the CMC is less well defined for reverse micelles in organic solvents. It

is possible that aggregates forming in the organic phase appear gradually, starting with dimers, trimers and eventually grow into larger, and more structured, aggregates.

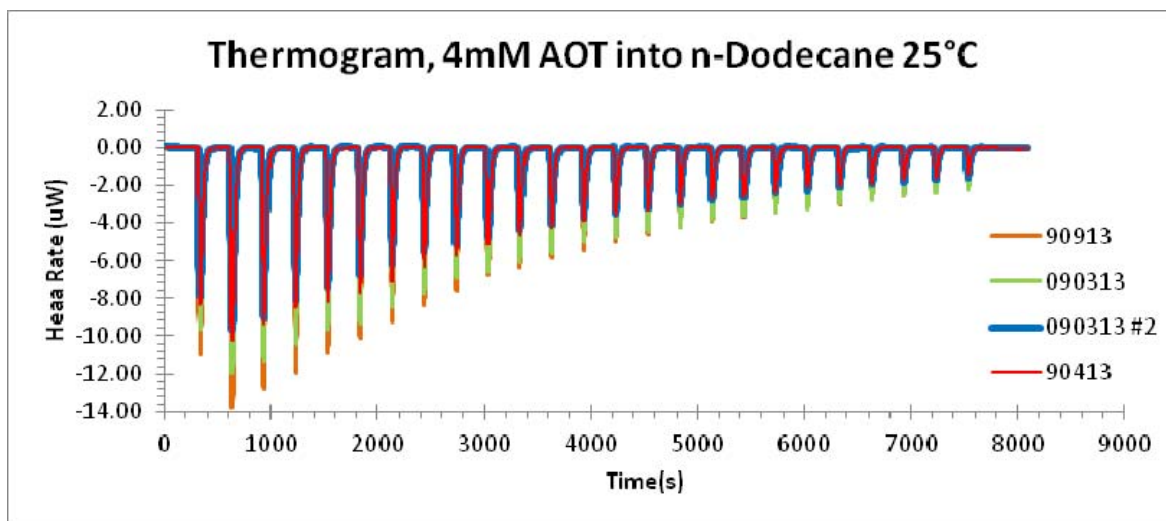


Figure 30: Sample AOT reverse micelle experiment using calorimetry. The legend indicated the dates of each experiment. 4 runs were made at three different days.

Clearly there are challenges for obtaining useful calorimetric results on reverse micelle formation in systems where we are fairly certain that aggregates are formed based on the results from the viscosity measurements. Due to these unforeseen results the microcalorimetry measurements of TBP/HDBP systems were cancelled until we were able to produce meaningful results on simpler systems.

A system of LIX 63 and HDNNS, shown to exhibit synergistic extraction of nickel as well as microemulsions, was studied using solution microcalorimetry. The results were more encouraging although it was not possible to complete the study and analyze the data as part of this project. The study will be completed outside this project and will be reported in future manuscripts, partial credit will be acknowledged to this project.

In order to investigate the heats of extraction in systems combining TBP and HDBP we decided to forego calorimetry and focused on slope analysis. A set of extractions of Dy(III) using combinations of TBP and HDBP in dodecane was carried out at different temperatures to estimate heats of extraction using the Van't Hoff equation. Extractions were carried out at 5 different TBP/HDBP ratios between 10 and 40 °C. The dysprosium extraction was analyzed by neutron activation analysis, a typical results from the extraction at 20 °C is shown in Figure 31b below. The results agree well with other extractions performed previously on this system.

The results of temperature dependent extractions for all temperatures are shown in Figure 31a. Only the dataset for 1 M TBP and 0.75 M TBP + 0.25 M HDBP are shown for clarity. The extraction trends for increasing HDBP resulted in similar slopes as the 3:1 TBP:HDBP system. All data shown are for extraction of dysprosium from 0.2 M HNO₃ by 1 M total extractant. As can be seen, the extraction is favored by low temperature when TBP is used but by high temperature when HDBP was added. This sudden shift in the extraction enthalpy from pure TBP to systems containing any addition of HDBP suggests a different extraction mechanism between the two systems. These results suggest that there are no mixed complexes of TBP/HDBP as one might observe via a more gradual change in the enthalpy of extraction as the ratio of the extractants is varied.

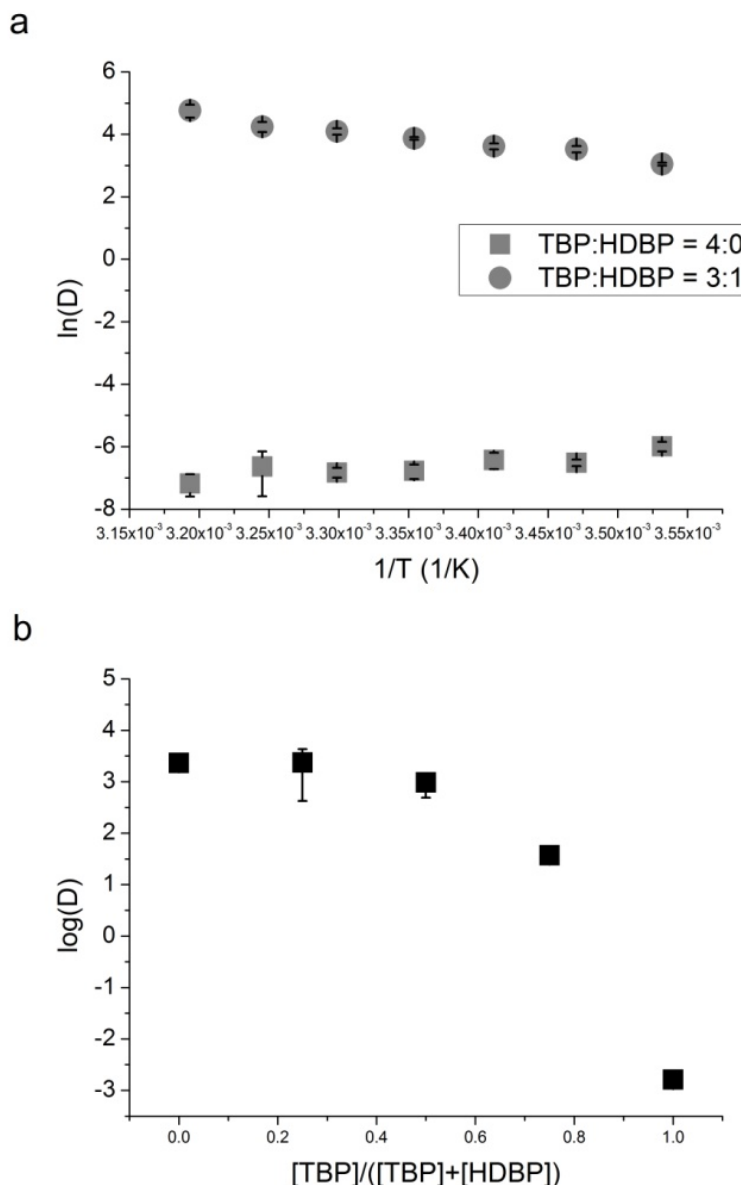


Figure 31:(a) Van't Hoff plots for given TBP:HDBP ratios in the extraction of Dy^{3+} from 0.2 M HNO_3 . (b)representative distribution plot of data used to construct Van't Hoff plots. All uncertainties represent one standard deviation. All plots show total 1 M extractant (TBP+HDBP) concentration.

Objective III: Use synchrotron radiation techniques, such as small angle X-ray scattering (SAXS) and X-ray absorption spectroscopy (XAS), to characterize and gain an improved understanding of the structure of reverse micelles, how and why they form and their role in metal extraction.

Building on the foundation of results obtained from basic physicochemical studies, extraction and water uptake we carried out various small-angle scattering experiments with synchrotron radiation and neutrons as well as X-ray absorption measurements of Ln and An ion coordination environments. These

investigations were carried out in an attempt to gain morphological information of the reverse micelles and provide details about metal-extractant interactions.

As mentioned above, the amount of effort spent studying the TBP/HDBP system resulted in no other extraction system being studied using these techniques. While this was unfortunate the amount of information obtained for this particular system made us realize the lack of deep understanding on such extraction systems and how much effort is required to obtain an accurate picture of the extraction mechanism. Hence, the results and studies outlined here are exclusively for the TBP/HDBP system.

SAXS

The non-linear behavior in the extraction of metal ions and in the water uptake shown above for Objective I prompted us to investigate the possibility of aggregates in these systems. Over the course of the project a number of samples of the organic phase for the experiment using varying concentration of metal ions and varying types of lanthanides were sent to Argonne National Laboratory for small angle X-ray scattering studies. In most cases a student from UC Irvine, Alex Braatz, traveled to ANL to participate in the collection of the X-ray scattering data. The data was collected at beamline 12-ID-C at the Advanced Photon Source (APS). Figure 32 below show some of the raw X-ray scattering data for a few of the dysprosium samples.

From figure 32 is it possible to see that the scattering of x-rays from analyzing the organic phase contacted with 0.2 M nitric acid is different depending on the molar ratio of extracting reagents. The end members, i.e. 1 M TBP and 1 M HDBP, display less scattering than the 50:50 mixture of TBP:HDBP shown in figure 32 as green dots. Thus, the scattering behavior is not a simple average of the end members, much like the Dy and water extraction.

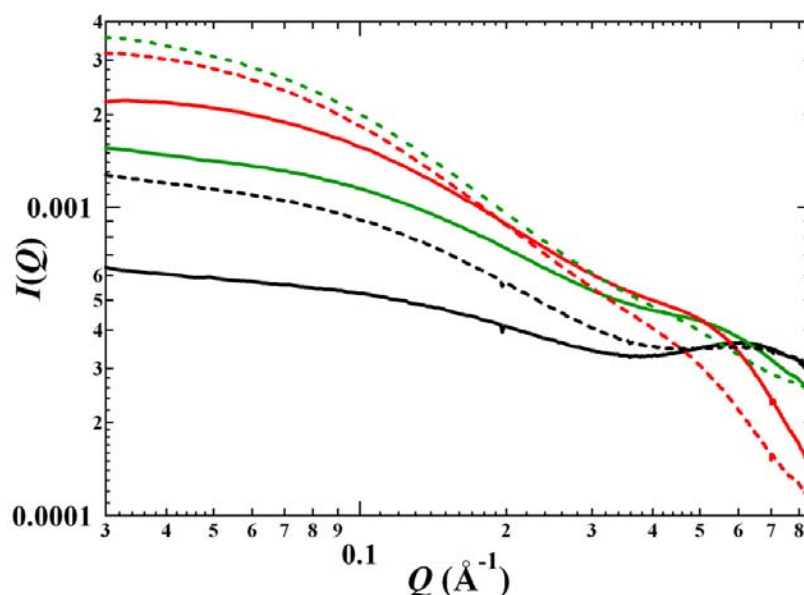


Figure 32. Log-log plot of the SAXS data for: TBP mole ratio of 1: pre-contact (black solid), 0.2 M acid contact (black dotted). TBP mole ratio of 0.5: pre-contact (green solid), 0.2 M acid contact (green dotted). TBP mole ratio of 0: pre-contact (red solid), 0.2 M acid contact (red dotted).

Additional SAXS data is shown in figure 33 where 1×10^{-3} M Lu in 0.2 M nitric acid has been contacted with organic phases containing a total of 1M TBP or HDBP at varying ratios. Again, the raw data indicate that the maximum scattering at low Q take place for the mixture of TBP:HDBP rather than for one of the end members. This behavior is observed for samples using 2 M HNO_3 and for the samples containing lanthanum.

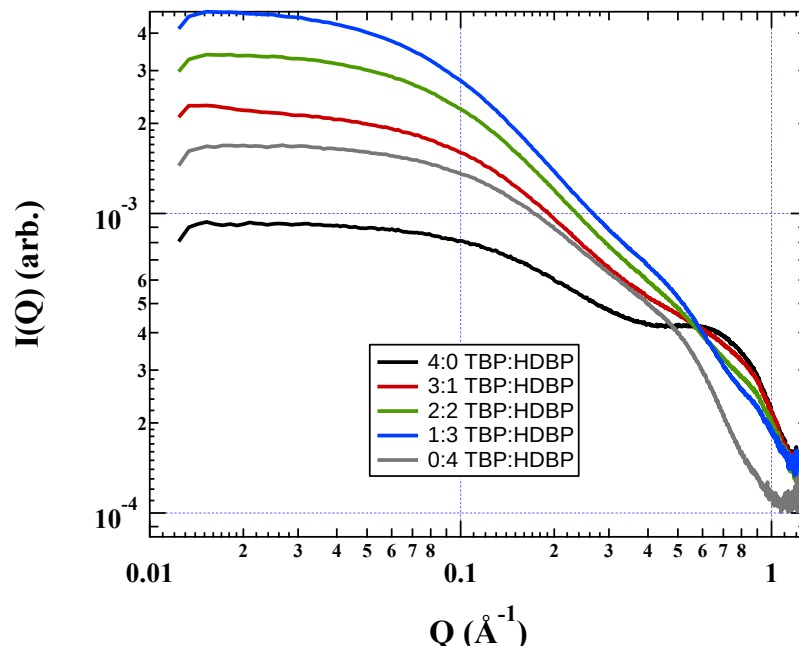


Figure 33: SAXS data of organic phases used to extract Lu from 0.2 M HNO_3 . The legend corresponds to the specific organic phase used.

All data was analyzed using Igor software utilizing APS macros to determine the radius of gyration and the maximum linear extent. Figure 34 shows the radius of gyration for all three metal ions. Figure 35 shows the maximum linear extent for systems containing Dy and, as a comparison, for organic phases contacted with aqueous phase but without any metal ion present. In both figures, the results from the corresponding 'dry' organic phases are shown. These are the organic phases that have not been in contact with any aqueous phase.

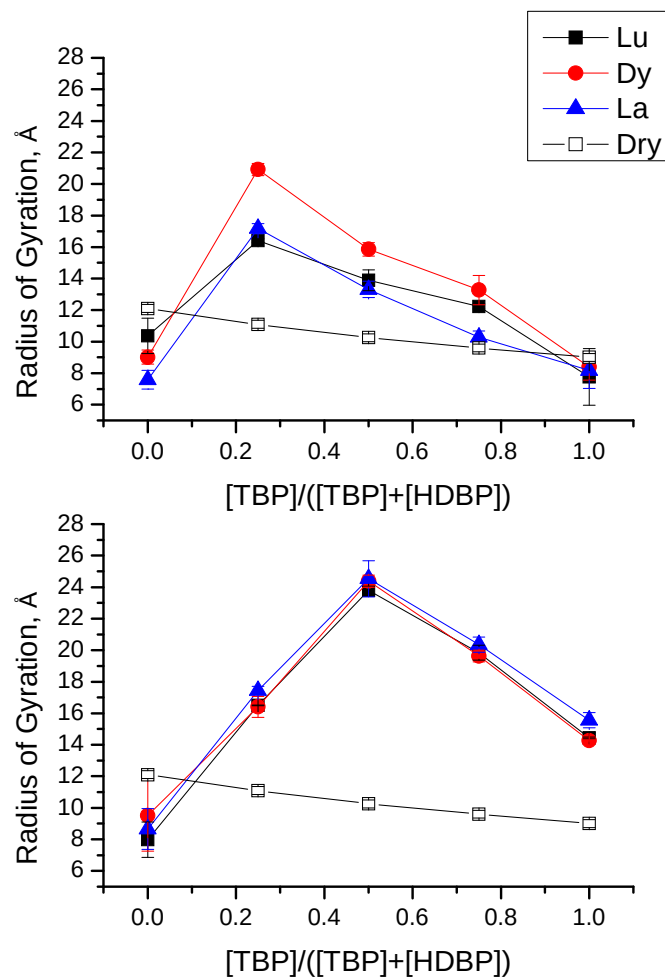


Figure 34: Radius of gyration (R_g , $\text{\AA}$) calculated from the entire scattering curves for the organic phases containing varying ratios of TBP and HDBP with constant 1 M extractant concentrations after contact with 0.2 M HNO_3 (top) and 2 M HNO_3 (bottom) containing either La, Dy or Lu. The radius of gyration for the dry organic phase is shown with open squares.

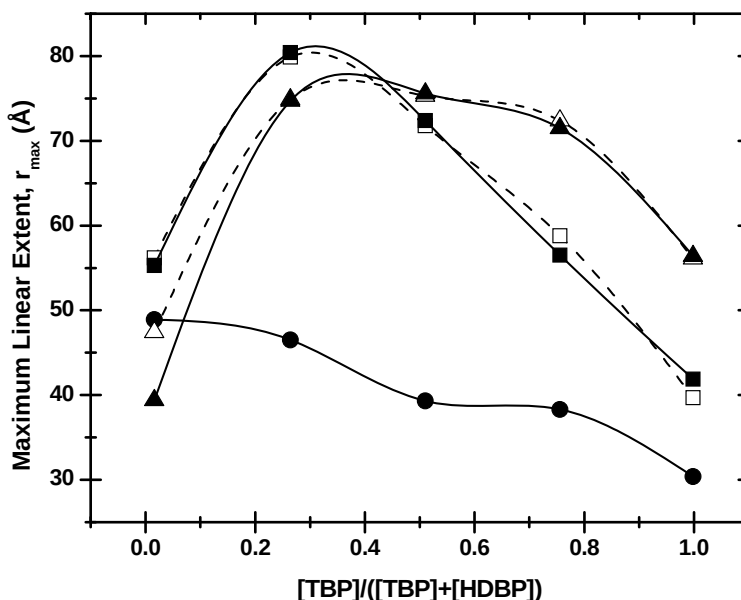


Figure 35. Maximum linear extent (in Å) calculated from the SAXS measurements of organic solutions containing varying ratios of TBP and HDBP with constant, 1 M, extractant concentration, contacted with 2 M HNO₃ (triangles) or 0.2 M HNO₃ + 1.8 M NH₄NO₃ (squares). The open symbols are the results obtained in the absence of Dy³⁺ in the aqueous phase, whereas the filled symbols show the results with aqueous solutions containing 10⁻⁴ M Dy³⁺. The filled circles refer to blank, non-pre-equilibrated (or “dry”) organic phases.

Two important conclusions may be drawn from the data in figures 34 and 35. First, the size of the aggregates has no apparent correlation with the type of metal ion that is extracted. Second, the presence of a metal ion does not appear to have any effect on the size of the aggregates formed in the organic phase. What is important though is that the organic phase be contacted with some aqueous phase, as the 'dry' organic solutions display no significant aggregate formation.

It is interesting to note that the largest radius of gyration when using 0.2 M HNO₃ exist for the 1:3 ratio of TBP:HDBP while for the organic solutions contacted with 2 M HNO₃ the largest radius of gyration is seen for the 2:2 mixture of TBP:HDBP. Furthermore the largest aggregates at the 1:3 TBP:HDBP mole ratio for 0.2 M acid concentration fit well with the increased water and high metal ion extraction at this mole ratio and could suggest that mixed aggregates formed under these conditions are effective in trapping water and dysprosium. However, the large aggregates observed at 2 M nitric acid are not as easy to explain since the metal and water uptake do not show any synergy. It has been shown before that nitric acid uptake by TBP will result in aggregates and it is possible that what we are observing at 2 M nitric acid is really two different aggregates coexisting in the organic phase that result in an overall increase in aggregate size at 2:2 mole ratio of TBP:HDBP.

Additional information about particle morphology can be obtained from the $p(r)$ functions, shown in Figure 36, obtained by the GIFT treatment of the SAXS data. For simplicity, only the $p(r)$ functions for the extraction of Dy from 2 and 0.2 M HNO₃ and the dry organic phases will be shown in this text. The same analysis for the extraction of La and Lu from 2 and 0.2 M HNO₃ solutions were carried out and will be reported in upcoming manuscripts. The extended, tail like decay of the $p(r)$ functions indicates elongated reverse micelles that are typically between globular/ellipsoidal in nature to cylindrical. In the dry organic phases the intensity of the first peak decreases with increasing HDBP concentration,

indicating a deviation from a globular system. Additionally, the formation of a second peak has been attributed to interactions between rod-shaped aggregates as a solution becomes more structured. Analogous studies of nonionic surfactant micelles in aqueous and oil diluents observed similar secondary peaks in the GIFT-generated $p(r)$ functions. After contact with an aqueous phase, the ordering across the series with the mixed system differs from the dry organic phases and indicates larger, more elongated structures than the end members when a mixture of TBP and HDBP exists. Additionally, the formation of a second peak is far more pronounced after contact with an aqueous solution than the corresponding dry organic phases, indicating a higher degree of order for the organic phases after contact with an aqueous phase.

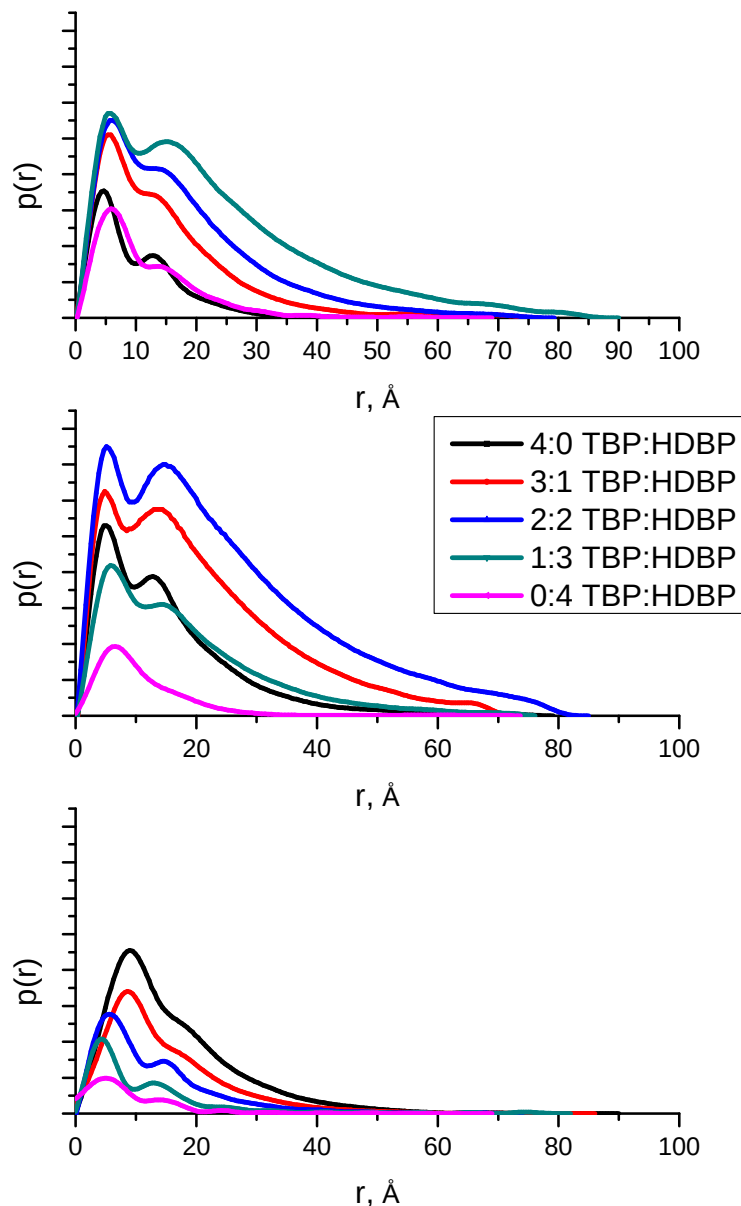


Figure 36: $P(r)$ functions for the extraction of Dy from 0.2 M HNO_3 (Top), 2 M HNO_3 (middle) and the corresponding dry organic phases (bottom).

EXAFS

Over the course of the project we have studied a number of sample sets for the TBP/HDBP system by use of Extended X-Ray Absorption Fine Structure (EXAFS). Aqueous solutions of 1.25×10^{-3} M metal ion, Dy, La or Lu in both 2 M and 0.2 M HNO_3 were created and contacted with organic phases containing 1 M TBP/HDBP at varying ratios. The metal ion concentration was chosen to avoid third phase formation but keep the concentration high enough in the organic phase to produce a sufficient signal for XAS. The organic ratios chosen were identical to the conditions discussed above to be comparable to previous data.

The data collected was analyzed by using a variety of programs, including QSE, WinXAS, Athena, SIXPack, etc., to provide averaged and normalized background-subtracted data, see figure 37 for an example. This data was used as input data into EXAFSPAK for further metrical analysis. The purpose of this technique was to determine the coordination number of the metal ion and to determine the interatomic distance of the closest atoms to the metal core. We followed standard procedures for treating the data.

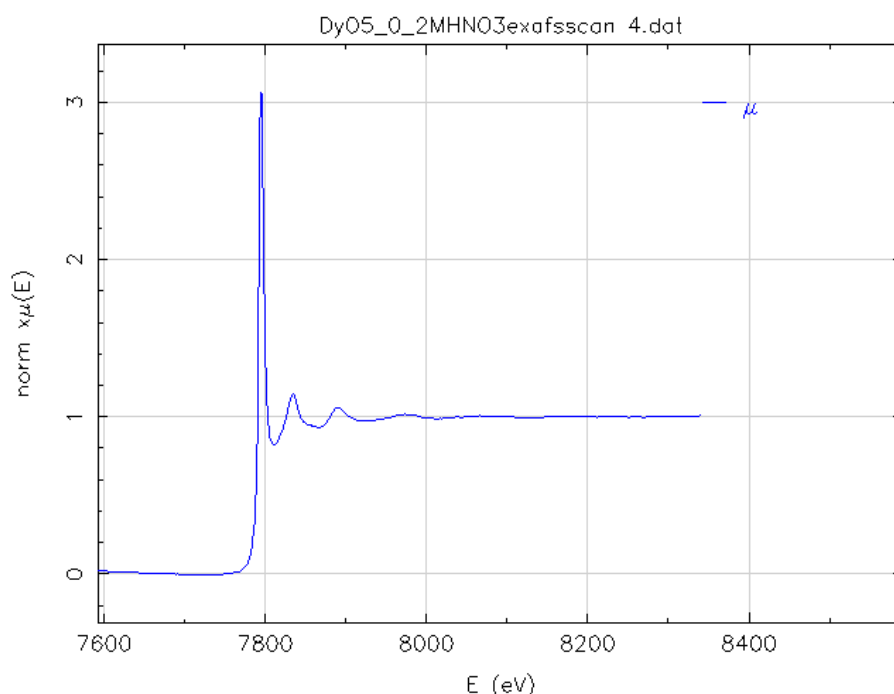


Figure 37: Normalized Dy L_3 -edge XAS data for 1.25×10^{-3} M Dy in 0.2 M HNO_3 contacted with 1 M HDBP in *n*-dodecane. The small oscillations beyond the intense L_3 edge peak contain information about the Dy coordination environment in terms of interatomic distances and coordination numbers.

The $k^3\chi(k)$ EXAFS data for the complexes formed by extraction from aqueous phase into an organic phase containing TBP, HDBP or a mix of both are shown in Figure 38. The corresponding FT (Fourier transforms) and fits are shown in Figure 39. L_3 -edge X-ray absorption spectroscopy for the lanthanide elements was chosen due to the easily accessible X-ray energies (approx. 6–9 keV) at synchrotron radiation user facilities and for the wealth of published absorption spectra involving L_3 -edge EXAFS of lanthanides.

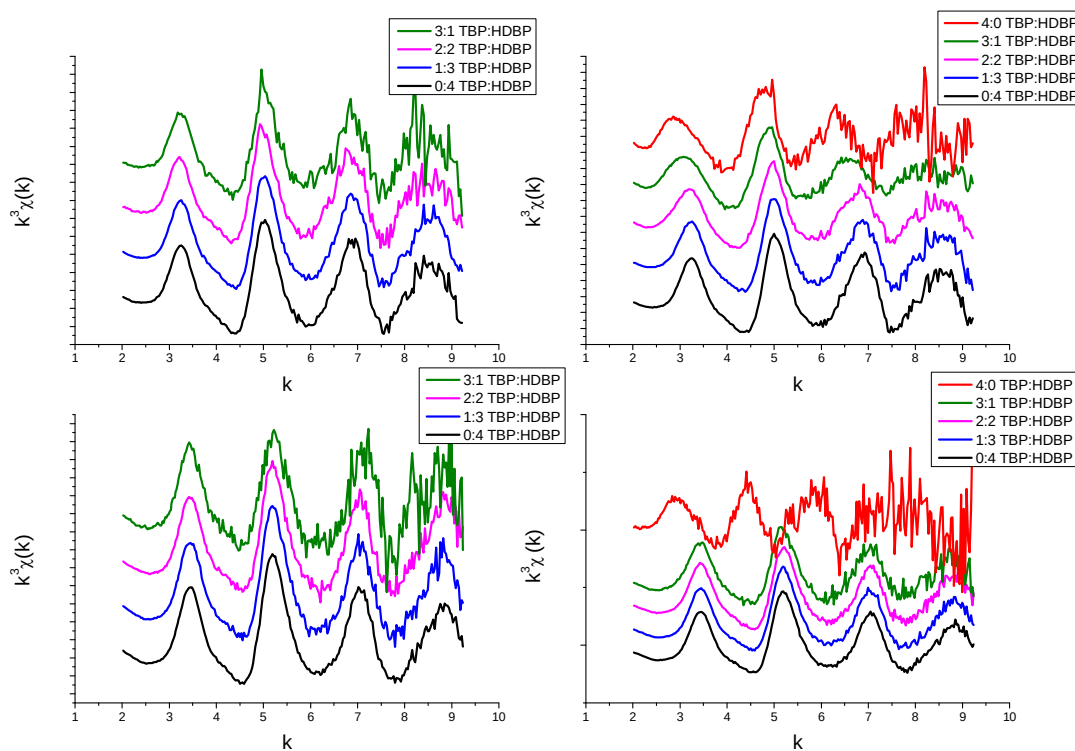


Figure 38: $k^3\chi(k)$ EXAFS data of organic phases extracting from aqueous phases containing 1.25×10^{-3} M Dy in 0.2 M HNO_3 (top left), 1.25×10^{-3} M Dy in 2 M HNO_3 (top right), 1.25×10^{-3} M Lu in 0.2 M HNO_3 (bottom left), and 1.25×10^{-3} M Lu in 2 M HNO_3 (bottom right).

Unfortunately, EXAFS experiments involving La^{3+} proved to be uninformative due to the closeness of the L_2 and L_3 -edges, yielding insufficient fine structure information. Hence, no additional analysis could be completed with reasonable accuracy with our current experimental configuration. The FT data of the organic phases show two peaks of physical significance: an intense peak at 1.8-1.95 Å attributed to the nearest O neighbor, and a medium peak at 3.3-3.45 Å attributed to the distant P atoms.

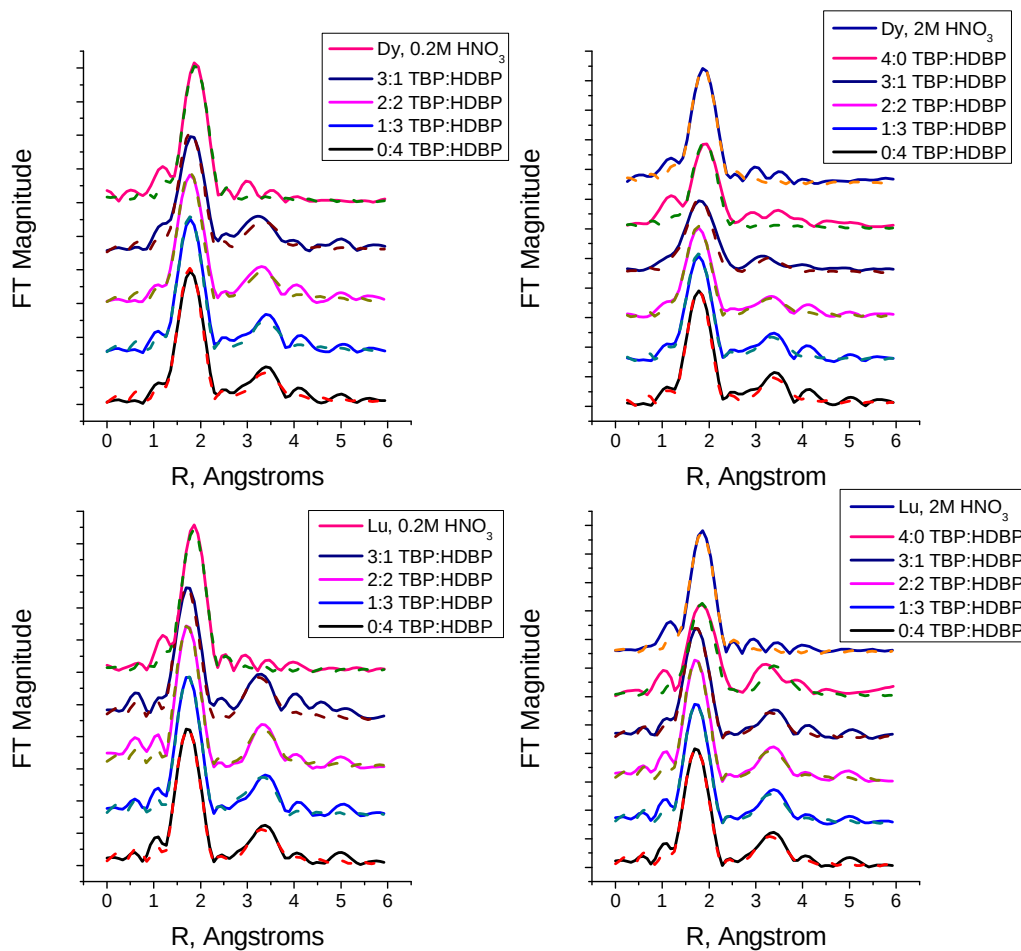


Figure 39: Fourier transform data of the $k^3\chi(k)$ EXAFS and the corresponding fits (dashed lines).

Based on the appearance of the Ln-O and Ln-P interactions in the FT data, all of the $\text{Ln } k^3\chi(k)$ EXAFS for the organic phases were fit using a two shell (O and P) backscattering model, with the exception of the 1 M TBP samples which showed no distant Ln-P interactions due to the low metal ion concentration in the organic phase yielding insufficient signal to differentiate the peak from noise. Metrical results of the fits are collected in Table 2 and Table 3.

Table 2: Ln-O and Ln-P EXAFS fit data for Dy^{3+} and Lu^{3+} extraction from 2 M HNO_3 into the organic phase. R is the interatomic distance, CN is the coordination number, σ^2 is the Debye-Waller Factor, ΔE is the energy threshold values.

2M HNO_3									
Organic Composition		$r/\text{\AA}$	err	CN	err	$\sigma^2/\text{\AA}^2$	err	$\Delta E/\text{eV}$	err
0:4 TBP:HDBP	Dy-O	2.25	0.002	5.8	0.2	0.0053	0.0004	-2.6	0.3
	Dy-P	3.80	0.005	3.2	0.2				
	Lu-O	2.19	0.002	6.8	0.2	0.0061	0.0003	0.3	0.2

1:3 TBP:HDBP	Lu-P	3.75	0.004	4.4	0.2				
	Dy-O	2.25	0.003	5.7	0.2	0.0061	0.0004	-2.9	0.3
	Dy-P	3.80	0.005	3.2	0.2				
	Lu-O	2.19	0.002	6.7	0.8	0.0057	0.0003	0.2	0.2
2:2 TBP:HDBP	Lu-P	3.76	0.004	4.2	0.3				
	Dy-O	2.26	0.003	5.9	0.2	0.0087	0.0005	-4.4	0.3
	Dy-P	3.80	0.006	2.9	0.3				
	Lu-O	2.18	0.002	6.7	0.2	0.0056	0.0004	0.1	0.3
3:1 TBP:HDBP	Lu-P	3.75	0.004	4.2	0.3				
	Dy-O	2.30	0.005	7.4	0.4	0.0147	0.0009	-4.4	0.5
	Dy-P	3.86	0.013	3.6	0.5				
	Lu-O	2.19	0.003	6.9	0.3	0.0071	0.0006	-0.2	0.4
4:0 TBP:HDBP	Lu-P	3.76	0.007	4.1	0.4				
	Dy-O	2.38	0.008	6.6	0.6	0.0096	0.0014	-2.7	0.8
	Lu-O	2.31	0.011	8.1	1.0	0.0111	0.0019	-0.3	0.9

The results of the fit indicate that Dy and Lu are six-coordinate with O atoms with organic phases containing any concentration of HDBP, though Lu and Dy do indicate closer to 8 coordinate with O atoms when extracted by 1 M TBP alone from 2 M HNO₃ though the errors associated with the coordination number determination are high due to low metal ion concentrations in the organic phase. There is an increase in the O coordination number from 6 with 100 % HDBP to 8 for 100% TBP as the TBP concentration is increased to its final concentration of 1 M TBP. The 8 O CN is lower than but consistent with the 9 O coordinate TBP-trisolvates of Ln(III), which have 6 O atoms from three bidentate inner-sphere nitrate anions and 3 O atoms from three solvating TBP molecules.

Unfortunately, the concentration of metal ion was too low with the extraction from 0.2 M HNO₃ by TBP alone to obtain a sufficient signal so the Ln-O coordination number for the 1 M TBP organic phase is solely from the 2 M HNO₃ extractions. The results of the fit for the Ln-P coordination numbers indicate Dy and Lu are between 3-5-coordinate with P, though the errors are high due to low fluorescent signal obtained as we move further away from the metal ion center because of the $1/r^2$ dependence of the EXAFS signal strength.

Table 3: Ln-O and Ln-P EXAFS fit data for Dy³⁺ and Lu³⁺ extraction from 0.2 M HNO₃ into the organic phase. R is the interatomic distance, CN is the coordination number, σ^2 is the Debye-Waller Factor, ΔE is the energy threshold values.

0.2M HNO₃									
Organic Composition		r/Å	err	CN	err	$\sigma^2/\text{Å}^2$	err	$\Delta E/\text{eV}$	err
0:4 TBP:HDBP	Dy-O	2.25	0.003	5.9	0.2	0.0055	0.0004	-2.4	0.3
	Dy-P	3.80	0.006	3.2	0.3				
	Lu-O	2.19	0.002	6.7	0.2	0.0056	0.0003	0.5	0.2
	Lu-P	3.75	0.004	4.3	0.2				
1:3 TBP:HDBP	Dy-O	2.25	0.002	5.9	0.2	0.0052	0.0004	-2.4	0.3
	Dy-P	3.81	0.005	3.2	0.2				
	Lu-O	2.19	0.002	6.8	0.2	0.0054	0.0004	0.4	0.3
	Lu-P	3.75	0.005	4.3	0.3				

2:2 TBP:HDBP	Dy-O	2.25	0.003	6.1	0.3	0.006	0.0005	-3	0.4
	Dy-P	3.77	0.007	3.5	0.3				
	Lu-O	2.18	0.002	6.2	0.2	0.0039	0.0004	-0.1	0.3
	Lu-P	3.74	0.005	4.1	0.3				
3:1 TBP:HDBP	Dy-O	2.26	0.005	5.5	0.4	0.0058	0.0009	-1.8	0.6
	Dy-P	3.78	0.009	3.6	0.5				
	Lu-O	2.18	0.006	6.5	0.5	0.0056	0.0009	-0.3	0.7
	Lu-P	3.71	0.010	5.1	0.7				

For organic phases that contain TBP alone, it was found that Dy³⁺ and Lu³⁺ is likely eight coordinate with O, which is more consistent with the known aqua ions of the Ln³⁺ series and to be expected due to TBP being a neutral extraction reagent and thus extracting by a solvation mechanism as opposed to an ion exchange mechanism. With this in mind, 6 O coordination of Ln³⁺ with HDBP and TBP is consistent with precedent, as is the apparent 8 O coordination with TBP alone. The question that arises with regard to the coordination number is the source of the O, as EXAFS alone only yields coordination numbers and interatomic distances. This O could arise from the HDBP ligand alone in a monomer or monodeprotonated dimer form. We could also be observing monodentate or bidentate bonding of the HDBP to the metal ion with either water and/or nitrate ions. We could also be observing a mixed complex system with HDBP and TBP, which has been suggested in literature as the possible mechanism for synergism, or some combination of all of those possibilities contributing to the inner coordination sphere about the metal. For insights into the source of these oxygen atoms we turn to the analysis of the more distant Ln-P interactions.

The results in Table 2 and 3 show the Ln-P distances span the range from 3.7-3.8 Å. In an attempt to rule out the possibility of a bidentate binding of HDBP to the metal ion, we must simply look at the interatomic distances of the Ln-O and Ln-P interactions. Gannaz, *et al.* observed that the interatomic distances of the Ln-O interaction would be too long and the Ln-P distances would be too short for a bidentate bound HDEHP extractant around Eu³⁺. (Gannaz, B.; Antonio, M. R.; Chiarizia, R.; Hill, C.; Cote, G. *Dalton transactions* 2006, 4553-4562) Applying a similar model to our system yields the same effect, that the interatomic distances for Ln-O and Ln-P interactions are more in line with a monodentate model, as shown in Figure 40, since a bidentate bonding of the HDBP molecules about the metal centers does not match the experimental interatomic distances. The O-P-O angle is fixed at 109.5, assuming the phosphate group maintains a perfect tetrahedral geometry.

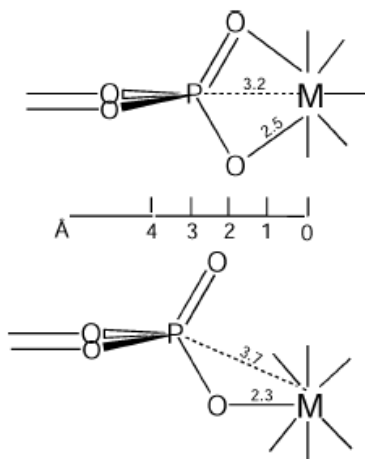


Figure 40: Model depicting a bidentate, edge sharing of two phosphate O with M (top) and a monodentate binding of one phosphate O with M. Figure reproduced from Gannaz, et al.

A value of 6 P would be consistent with the coordination of three monodeprotonated dimers to Ln^{3+} to form a neutral species $\text{Ln}(\text{HDBP} \cdot \text{DBP})_3$ or due to a mixed complex system of $\text{Ln}(\text{DBP})_3 \cdot \text{TBP}_3$ that maintains charge neutrality but still yields 6 P coordination. The EXAFS determined coordination numbers for the Ln-P interaction, however, do not show 6 P but rather a range of coordination numbers from 3-5 P. This could suggest a different speciation than those previously explored in these types of systems. To determine if the complex is $\text{Ln}(\text{HDBP} \cdot \text{DBP})_3$, $\text{Ln}(\text{DBP})_3 \cdot \text{TBP}_3$, or a mixture of both possibilities or perhaps even a dinuclear species that yield less than 6 phosphorus atoms in the second coordination shell, further analysis must be carried out with the obtained EXAFS spectra.

XANES

Utilization of XANES can yield further insight into the coordination environment of the Ln(III) ions in the TBP:HDBP systems and lend further support for the observed coordination of 6 oxygen atoms about the metal centers. The normalized L_3 -edge XANES for all samples are shown in Figure 41. The intense L_3 -edge peaks are characteristic of dipole-allowed (2p-to-5d) electronic transitions for Ln(III) and the responses are essentially equivalent, which suggests that the Ln(III) coordination environments in the TBP/HDBP organic systems are consistent across the latter half of the period.

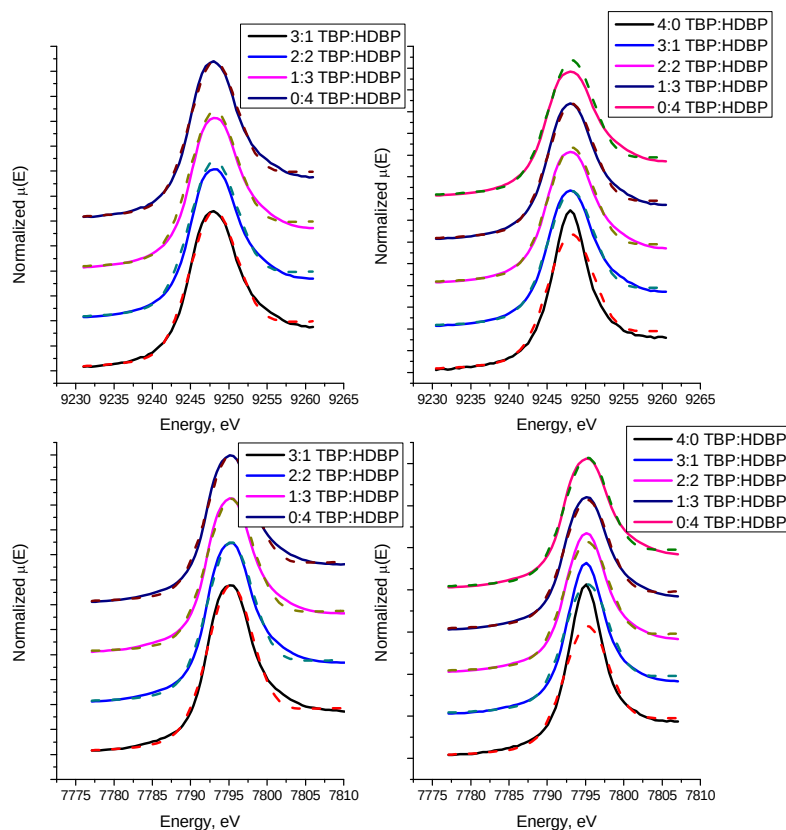


Figure 41: Normalized L_3 -edge peaks for Lu in 0.2 M HNO_3 (top left), Lu in 2 M HNO_3 (top right), Dy in 0.2 M (bottom left), and Dy in 2 M HNO_3 (bottom right). Corresponding fits are shown as dashed lines.

Further investigation of the XANES region and further evidence of the six O coordination environments can be obtained by taking the second derivative of the L_3 -edge peak. The differentiation is done to remove

the edge step in a convenient manner, which improves the ease of visualization of the response. The second derivative data for both metal ions at all conditions are shown in Figure 42. For the extraction from low nitric acid, there is evidence of two minima in the 2nd derivative of the L₃-edge peak for all conditions investigated. This double minima is evidence of crystal field splitting and also indicative of an octahedral geometry, namely a complex containing 6 ligands about a metal center, assuming monodentate binding. For the high acid data, an evolution in the crystal field splitting is apparent in the 2nd derivative data as the concentration of TBP increases. This evolution lends direct and independent support to the coordination number changing from 6 to 8 in O as the concentration of TBP is increased.

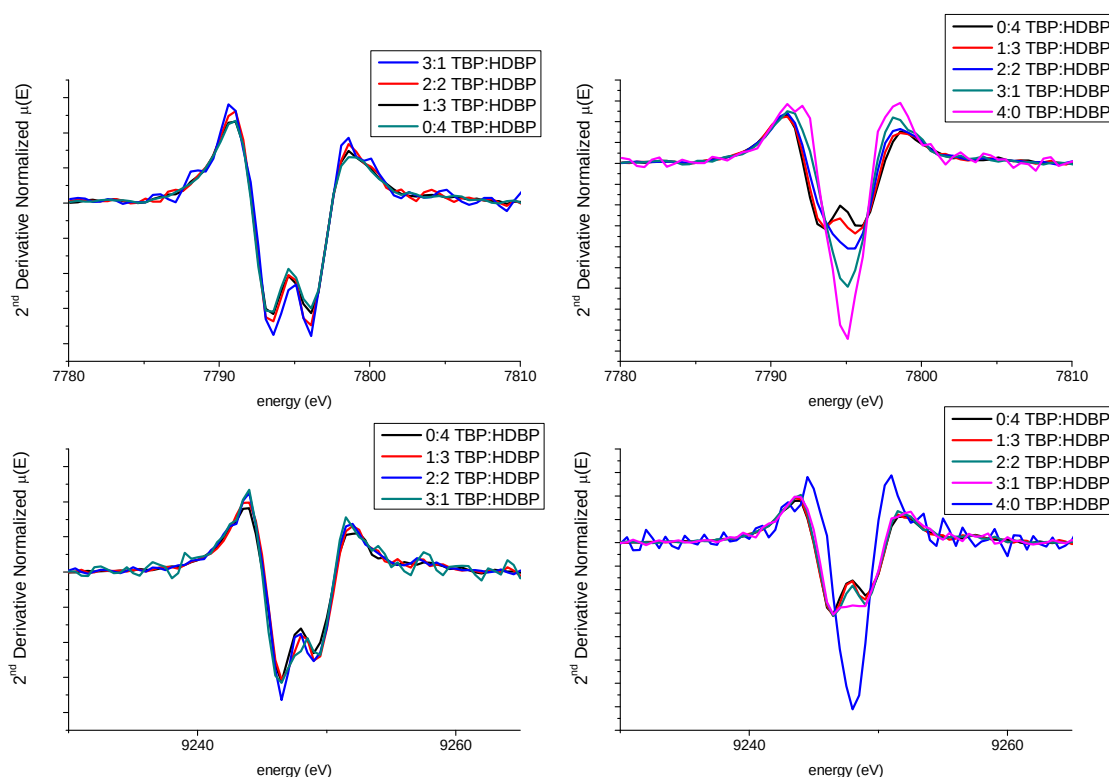


Figure 42: 2nd derivatives of the normalized L₃-edge peaks for Dy in 0.2 M (top left), and Dy in 2 M HNO₃ (top right), Lu in 0.2 M HNO₃ (bottom left), Lu in 2 M HNO₃ (bottom right).

While the lanthanum samples were not useful for obtaining any EXAFS data we will still be able to use the XANES data from these samples. This is the focus of an ongoing analysis and will not be ready in time to include in this report. We will include it in our future manuscript with credit to the funding agency and the project.

Principal Component Analysis

Principal component (factor) analysis (PCA) and linear regression analysis was utilized to further probe the binary extractant system after extraction from 2 M HNO₃. The 1M TBP and 1M HDBP organic phases were used as reference phases and compared against the mixed phases. For PCA, all five data sets for each metal ion extracted from 2 M HNO₃ were first analyzed identically. For the EXAFS analysis the data was truncated at $k = 9.25 \text{ \AA}^{-1}$ to reduce the possibility of adverse effects of the experimental noise at high k on the PCA. The results were the same for both metal ions investigated (dysprosium and lutetium),

namely that two principal components accounted for all the data. This result, though purely mathematical in nature, is consistent with the notion that the single extractant systems with HDBP and TBP alone are the so-called end-member species. Most importantly, the implication of the PCA results is that the EXAFS data for the binary extractant system are adequately described as an arithmetic sum of the EXAFS data for the two single extractant systems, meaning mixed complexes may not be present in the extraction of metal ions by mixtures of these two extractants. To strengthen this treatment of the data, Linear combination fitting was implemented on the primary, normalized spectra, I_f/I_0 vs. energy (keV), of the binary extractant systems using again the spectra for the single component extraction as the two limiting end members. The results of the linear combination show similar results to the PCA analysis, namely that the binary extractant mixtures are simple additions of the end member species. Additionally, the linear combination shows that the predominant species formed is one with only HDBP, as shown in figure 43. This finding is in line with the well known fact that TBP does not tend to extract trivalent metal ions and is also supported by findings that similar acidic organophosphorus reagents form monodeprotonated dimers to extract trivalent metals.

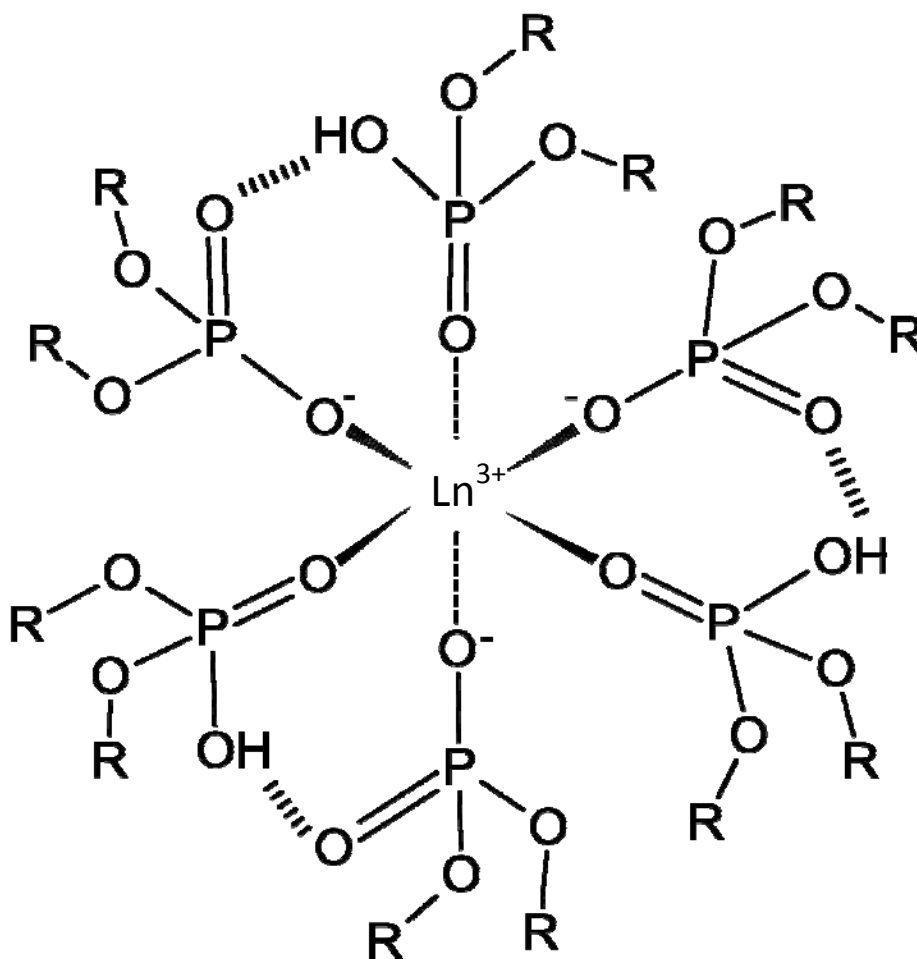


Figure 43. Suggested structure for HDBP complexation of a trivalent lanthanide.

Discussion

While the SAXS data indicate that aggregates exist in this system we are still not sure about the role of these aggregates play in the extraction mechanism. For example, recent work from the ICSM in France by Poirot et al. (Chem. Phys. Chem. 10.1002/cphc.201600305) clearly demonstrates that the extraction of

Nd(III) from nitrate media requires aggregation of malonamide extractants in aliphatic diluents in addition to simple Nd-malonamide coordination chemistry. The data from the EXAFS studies indicate that the metal ions are coordinated directly by the strongest extraction reagent and do not exist as part of a water droplet in a reverse micelle type aggregate. Furthermore, the data thus far indicates that it is very unlikely that there are mixed complexes of TBP and HDBP under the conditions in our studies.

Objective IV: Compile the accumulated systems knowledge, perspectives and insights obtained from the coordinated experimental and theoretical efforts in a database to allow us to describe, understand and predict the mechanisms and formation of reverse micelle effects and stable water-in-oil microemulsions in the extraction of metal ions.

As has been mentioned previously in this report, the combination of TBP and HDBP ended up much more complex than we had anticipated. Hence, significant effort was spent investigating this system in great detail and for the other extraction systems studied we have some metal and water uptake data but no detail regarding the existence of aggregates or stable microemulsion.

During this project one student (self funded through a NSF fellowship) was recruited to look at the TBP/n-dodecane extraction system using MD simulations. This was done in an attempt to gain some understanding on the kinetics of aggregate formation and the possible chemical pathways for this phenomenon. The preliminary work carried out by the student formed the basis of another project that is currently funded through DOE NEUP where one of the goals are to carry out MD simulations of extraction systems coupled with careful experimental validations. In order to make sense of a large compilation of experimental data these simulations may be a tool to improve understanding, but only if the data is used as a validation for the simulations.

Conclusions for the project and Future work

What can be said, based on the knowledge that we have gained from the TBP/HDBP system, is that while aggregates and synergistic extraction exist simultaneously there is no evidence, *in this particular system*, that the reverse micelles accommodate the metal ions and cause the synergy. As the goal of this project was to investigate the connection between the two it appears that we were mostly unsuccessful in proving any connection. Rather, we were successful in disproving it.

One thing that may be of interest to investigate further is the effect that microemulsions have on the physicochemical properties of the organic phase. It is possible that the changes in dielectric constant, conductivity, viscosity etc create a more favorable environment for the metal-ligand complexes that form in an extraction system and therefore it would appear as the extraction increases.

Publications and presentations.

During this project we have published 4 peer reviewed journal papers (P1-P4), 3 peer reviewed conference proceedings (CP1-CP3) and 1 non-peer reviewed conference proceeding (CP4) based on the work carried out here.

- P1. Ellis, R.J.; Anderson, T.L.; Antonio, M.R. Braatz, A.; Nilsson, M. A SAXS Study of Aggregation in the Synergistic TBP–HDBP Solvent Extraction System, *J. Phys. Chem. B*, **117**, 5916–5924, 2013. [dx.doi.org/10.1021/jp401025e](https://doi.org/10.1021/jp401025e)

- P2. Anderson, T.L.; Braatz, A.; Ellis, R.J.; Antonio, M.R.; Nilsson, M. Synergistic Extraction of Dysprosium and Aggregate Formation in Solvent Extraction Systems Combining TBP and HDBP, *Solvent Extr. Ion Exch.*, **31**(6), 617–633, 2013. DOI: 10.1080/07366299.2013.787023
- P3. Braatz, A., Nilsson, M. Fluorescence studies of metal complexes in synergistic extraction systems combining dibutyl phosphoric acid and tri-n-butyl phosphate. *J. Radioanal. Nuclear Chem.*, **303**(2):1105-1109. DOI 10.1007/s10967-014-3487-1.
- P4. Vo, Q.N., Hawkins, C.A, Dang, L.X., Nilsson, M., Nguyen, H.D. Computational Study of Molecular Structure and Self-Association of Tri-n-butyl Phosphates in n-Dodecane, *J. Phys. Chem. B*, 2015, 119 (4), pp 1588–1597. DOI: 10.1021/jp510365c
- CP1. Braatz, A., Ellis, R., Antonio, M., Nilsson, M. (2013). Investigation of Metal Ion Extraction and Aggregate Formation Combining Acidic and Neutral Organophosphorus Reagents. In *Nuclear Energy at a Crossroads. GLOBAL-2013: International Nuclear Fuel Cycle Conference*, Salt Lake City, USA.
- CP2. Jackson, A. S., Zalupski, P. R., Nilsson, M. (2014). Investigation of Heat of Formation of Reverse Micelles using Isothermal Titration Calorimetry and Temperature Dependent Extractions. In *Proceedings from the International Solvent Extraction Conference. ISEC' 2014*, (pp. 1156-1161). Würzburg, Germany.
- CP3. Nilsson, M., Braatz, A., Jackson, A., Zalupski, P., Ellis, R., Antonio, M. (2014). Microemulsions and Aggregation Formation in Extraction Processes for Used Nuclear Fuel. In *Proceedings from the International Solvent Extraction Conference. ISEC' 2014*, (pp. 551-556). Würzburg, Germany.
- CP4. Nilsson, M., Braatz, A., Jackson, A., Vo, Q., Nguyen, H. D., Zalupski, P., Ellis, R., Antonio, M. (2014). Microemulsions and Aggregation Formation in Extraction Processes for Used Nuclear Fuel. In *Proceedings from 13IEMPT. OECD/NEA 13th Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation*, Seoul, South Korea.

In addition to these publications the data collected is currently being compiled in at least 3 additional publications for peer reviewed journals.

The work has been presented at a number of international and domestic conferences as well as invited seminars at various educational and research institutions. In total 18 oral presentations and 7 poster presentations have been given by the PI or students from his group. Below is a list of all the presentations in reverse chronological order, the presenter is underlined.

- | | |
|-----------|--|
| 8/11/2015 | "Microemulsions and Aggregation Formation in Extraction Processes for UNF", MRWFD Campaign Working Group Meeting, US Department of Energy, Gaithersburg, MD, USA, Oral Presentation, <u>Nilsson, M.</u> |
| 7/16/2015 | "Chemical Interactions in Nuclear Fuel Cycles: The Role of Microemulsions and Aggregates", Pacific Northwest National Laboratory, Richland, WA, USA, Oral Presentation, <u>Nilsson, M.</u> |
| 6/8/2015 | "Chemical Interactions in Nuclear Fuel Cycles: The Role of Microemulsions and Aggregates", Chemistry Department Seminar Series, Washington State University, Pullman, WA, USA, Oral Presentation, <u>Nilsson, M.</u> |
| 5/20/2015 | "Structural investigations of metal-ion complexation and aggregate formation combining TBP and HDBP: insights from spectroscopy and scattering |

studies", 39th Annual Actinide Separations Meeting, Salt Lake City, UT, USA, Poster Presentation, Braatz, A., Antonio, M., Ellis, R., Nilsson, M.

5/20/2015 "Synergism and Aggregate Formation in Solvent Extraction Systems", 39th Annual Actinide Separations Meeting, Salt Lake City, UT, USA, Poster Presentation, Jackson, A., Nilsson, M.

4/16/2015 "Structural Investigations of Metal-ion Complexation and Aggregate Formation Combining TBP and HDBP: Insights from X-ray Absorption Spectroscopy", MARC X:Tenth International Conference on Methods and Applications of Radioanalytical Chemistry, Kona, HI, USA, Oral Presentation, Braatz, A., Ellis, R., Antonio, M., M. Nilsson.

1/30/2015 "Chemical interactions in separation processes for used nuclear fuel", Florida Power & Light Distinguished Nuclear Lecture Series, Florida International University, Miami, FL, USA, Oral Presentation, Nilsson, M.

10/29/2014 "Insights in Extraction Synergy and Aggregation Formation in Extraction Systems for Actinides and Lanthanides", 18th Symposium on Separation Science and Technology, Oak Ridge National Lab, TN, USA, Oral Presentation, Nilsson, M., Braatz, A., Jackson, A., Vo, Q., Bui, S., Nguyen, H. D., Zalupski, P., Ellis, R., Antonio, M.

11/18/2014 "A Computational Study of Molecular Structure and the Self-Association of Tri-n-butyl Phosphate in n-Dodecane Diluent", 2014 AIChE Annual Meeting, American Institute of Chemical Engineering, Atlanta, GA, USA, Oral Presentation, Vo, Q. N., Hawkins, C., Dang, L. X., Nilsson, M., Nguyen, H. D.

10/27/2014 "Insights of Metal Ion Aggregation Formation Combining Acidic and Neutral Organophosphorous Reagents", 18th Symposium on Separation Science and Technology, Oak Ridge National Lab, TN, USA, Poster Presentation, Braatz, A., Ellis, R., Antonio, M., Nilsson, M.

9/24/2014 "Microemulsions and aggregation formation in extraction processes for used nuclear fuel", 13th Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation, OECD/NEA, Seoul, Republic of Korea, Oral presentation, Nilsson, M., Braatz, A., Jackson, A., Vo, Q., Nguyen, H. D., Zalupski, P., Ellis, R., Antonio, M.

9/11/2014 "Microemulsions and Aggregation Formation in Extraction Processes for Used Nuclear Fuel", 20th International Solvent Extraction Conference, ISEC' 2014, Würzburg, Germany, Oral Presentation, Braatz, A., Jackson, A., Zalupski, P., Ellis, R., Antonio, M., Nilsson, M.

9/8/2014 "Investigation of Heat of Formation of Reverse Micelles using Isothermal Titration Calorimetry", 20th International Solvent Extraction Conference, ISEC' 2014, Würzburg, Germany, Poster Presentation, Jackson, A., Zalupski, P., Nilsson, M.

5/22/2014 "Microemulsions and Aggregation Formation in Extraction Processes for Used Nuclear Fuel", 38th Annual Actinide Separations Meeting, Albuquerque, NM, USA, Oral Presentation, Braatz, A., Jackson, A., Vo, Q., Nguyen, H. D., Zalupski, P., Ellis, R., Antonio, M., Nilsson, M.

5/20/2014 "The Use of Isothermal Titration Calorimetry and Metal Ion Extraction Experiments to Investigate Reverse Micelle Formation", 38th Annual Actinide Separations Meeting, Albuquerque, NM, USA, Poster Presentation, Jackson, A., Zalupski, P., Nilsson, M.

10/1/2013 "Investigation of Metal Ion Extraction and Aggregate Formation Combining Acidic and Neutral Organophosphorous Reagents", Global 2013:

	International Nuclear Fuel Cycle Conference, Salt Lake City, UT, USA, Oral Presentation, <u>Braatz, A.</u> , Ellis, R., Antonio, M., Nilsson, M.
9/25/2013	"Fluorescence Studies of Complex Stoichiometry of Metal ions in Synergistic Extraction Systems Combining Dibutyl Phosphoric Acid and Tri-n-butyl Phosphate", 5th Asia-Pacific Symposium on Radiochemistry, APSORC'13, Kanazawa, Japan, Oral Presentation, <u>Braatz, A.</u> , Nilsson, M.
6/25/2013	"Metal Ion Extraction and Aggregate Formation of Systems Combining Acidic and Neutral Organophosphorous Reagents", 37th Annual Actinide Separations Meeting, Spokane, WA, USA, Oral Presentation, <u>Braatz, A.</u> , Ellis, R., Antonio, M., Nilsson, M.
8/19/2012	"Thermodynamic signatures of aggregate formation in solvent extraction systems", 244st ACS National Meeting, Philadelphia, PA, USA, Oral Presentation, <u>Nilsson, M.</u>
8/1/2012	"Investigation of metal ion extraction and aggregate formation combining acidic and neutral organophosphorous reagents", 20th International Conference On Nuclear Engineering, ICONE 20, Anaheim, CA, USA, Oral Presentation, Braatz, A., Anderson, T., Ellis, R., Antonio, M., <u>Nilsson, M.</u>
5/22/2012	"Investigation of Metal Ion Extraction and Aggregate Formation Combining Acidic and Neutral Organophosphorous Reagents", 36th Annual Actinide Separations Meeting, Chattanooga, TN, USA, Poster Presentation, <u>Braatz, A.</u> , <u>Anderson, T.</u> , Ellis, R., Antonio, M., Nilsson, M.
3/28/2012	"Extraction Trends and Effects of Synergy for Lanthanides and Actinides in Combining Neutral and Acidic Phosphorous Containing Reagents", MARC IX:Ninth International Conference on Methods and Applications of Radioanalytical Chemistry, Oral Presentation, Braatz, A., Ellis, R., Antonio, M., <u>Nilsson, M.</u>
3/27/2012	"Investigation of metal ion extraction and aggregate formation combining acidic and neutral organophosphorous reagents", 243rd ACS National Meeting, San Diego, CA, USA, Oral Presentation, <u>Braatz, A.</u> , Anderson, T., Ellis, R., Antonio, M., Nilsson, M.
10/25/2011	"Investigations on the Synergistic Effects in Solvent Extraction Systems Combining TBP and DBP", 17th Symposium on Separation Science and Technology, Gatlinburg, TN, USA, Oral Presentation, Anderson, T., Braatz, A., <u>Nilsson, M.</u>
10/25/2011	"Synergistic Extraction of Dy and La in a System Combining TBP and DBP", 17th Symposium on Separation Science and Technology, Gatlinburg, TN, USA, Poster Presentation, <u>Braatz, A.</u> , Anderson, T., Nilsson, M.

Outcomes and markers of success

As this was a project led from a university one of most important products was the education and training of students. Over the course of this project 3 graduate students (Alex Braatz, Andy Jackson and Quynh Vo) and 3 undergraduate students (Timothy Anderson, Leanne Bautista, Steven Bui) were involved in the work. All undergraduate students graduated and found jobs in industry. One of the graduate students, Alex Braatz, graduated in Nov 2015 and is currently a post-doctoral scientist at ORNL. The 2 other graduate student passed their qualifying exam during the course of this project and will graduate in the 2016-2017 academic year. The graduate students were given chances to visit the national labs. Alex visited ANL on several occasions and worked with Dr. Antonio while staying there. Andy visited INL on

two separate occasions to carry out calorimetry work under the direction of Dr. Zalupski. These visits not only helped the students in their research projects but also helped build important connections for their future careers.

Finally, this project resulted, so far, in 9 publications and 25 presentations with more publications underway. In all the publications and presentations, we acknowledged the funding source for this work.