Sigma Team for Minor Actinide Separation: PNNL FY 2011 Status Report

Fuel Cycle Research & Development

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SUMMARY

Work conducted at Pacific Northwest National Laboratory (PNNL) in Fiscal Year 2011 addressed two lines of inquiry. The two hypotheses put forth, along with a summary of the work conducted to test these hypotheses, follow:

1. *A multifunctional neutral extractant can be combined with an acidic extractant to form a single process solvent for separating trivalent actinides from the trivalent lanthanides and other fission products in acidic high-level nuclear waste.* In this regard, a solvent system was investigated that combined the bifunctional neutral extractant from the TRUEX[a] process (CMPO)[b] with the acidic extractant from the TALSPEAK[c] process (HDEHP)[d] into a single process solvent. (Note: The process using the combined CMPO/HDEHP solvent will hereafter be referred to as the "TRUSPEAK" process.) Investigations of the fundamental chemistry have revealed that CMPO and HDEHP interact with one another in *n*-dodecane to form a CMPO·HDEHP adduct and that CMPO and HDEHP act synergistically in the extraction of trivalent actinides and lanthanides, forming extracted species of the type $[M(AHA)_2(A)]$ and $[ML(AHA)_2(A)]$, where M is a trivalent lanthanide or actinide ion, L is CMPO, AHA is the deprotonated HDEHP dimer, and A = deprotonated monomeric HDEHP. The synergic effect is stronger for Nd(III) and Am(III) than it is for Eu(III). A proof-of-principle experiment was performed to demonstrate the feasibility of applying the TRUSPEAK process to the raffinate from the uranium extraction (UREX) process. In this test, co-extraction of the lanthanides and actinides was readily achieved and americium was selectively stripped from the lanthanides using 0.05 M DTPA+1.5 M citrate at pH ~ 3.5. Although Zr was strongly extracted by the TRUSPEAK solvent, a method was developed to co-strip the Zr with the lanthanide elements. Molybdenum can be routed to the high-level waste stream by scrubbing it from the loaded TRUSPEAK solvent with a citrate buffer prior to stripping of the actinides.

2. *Higher oxidation states (e.g., +5 and +6) of Am can be stabilized in solution by complexation with stereognostic uranophilic ligands, and this chemistry can be exploited to separate Am from Cm.* Work conducted to date suggests that the available stereognostic ligands would likely provide only a marginal improvement in stabilizing higher actinide oxidation states when compared to ligands with similar functionality but no stereognostic features (i.e., iminodiacetate). Thus improvements in stereognostic design are needed to advance this chemistry.

(a) TRUEX = transuranic extraction
(b) CMPO = octyl(phenyl)-N,N-diisobutyl-carbamoylphosphine oxide
(c) TALSPEAK = trivalent actinide-lanthanide separations by phosphorus-reagent extraction from aqueous complexes
(d) HDEHP = bis(2-ethylhexyl)phosphoric acid

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TABLES

ACRONYMS

CMPO	octyl(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide
DTPA	diethylenetriaminepentaacetic acid
EETAC	tris-N,N',N''-[2-(2-carboxy-phenoxy)ethyl]-1,4,7-triazacyclononane
FY	fiscal year
HDEHP	bis(2-ethylhexyl)phosphoric acid
Ln/An	lanthanide/actinide
NPB	tris(3-(2-carboxy-phenoxy)propyl)amine
PNNL	Pacific Northwest National Laboratory
SXLSQI	FORTRAN program for modeling solvent extraction equilibria
TALSPEAK	trivalent actinide-lanthanide separations by phosphorus-reagent extraction from aqueous complexes
TBP	tributyl phosphate
TRU	transuranic
TRUEX	transuranic extraction
TRUSPEAK	combined TRUEX and TALSPEAK process
UREX+	uranium extraction plus

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1.   INTRODUCTION

Advanced concepts for closing the nuclear fuel cycle typically include separating the minor actinides (i.e., Np, Am, and Cm) from other fuel components. The reason for separating these elements stems from their long-term effects on the performance of geologic repositories for irradiated fuel. Separating these elements from the material going to the repository and subsequently converting them (e.g., by fission with fast neutrons) to stable or short-lived nuclides would greatly reduce the long-term risks associated with nuclear power. Separating Cm also has near-term benefits for the repository by reducing its heat load. Recent efforts in the United States have considered separating the transuranic (TRU) elements (Np, Pu, Am, Cm) from irradiated nuclear fuel as a single group. Including the minor actinides with the Pu makes the Pu less desirable for weapons production and thus improves the proliferation resistance of the fuel cycle compared to conventional fuel recycling schemes (which separate pure Pu) (Todd and Wigeland 2006).

One of the critical challenges in this regard is separating the transuranic (TRU) elements (especially Am and Cm) from the lanthanide fission products. The lanthanides are generally neutron poisons and thus reduce the efficiency of destruction processes for the TRU elements. Although there are active programs worldwide investigating the separation of TRU elements from the lanthanides, recent work in the United States has focused on the "uranium extraction plus" (UREX+) suite of separation processes. One of the disadvantages of this approach is the complexity of the process. For example, in the "UREX+1a" concept for irradiated fuel recycling, a series of four solvent extraction processes are proposed to partition the fuel into useful products and fission product waste (Regalbuto 2011). The Minor Actinide Separation Sigma Team was established within the Fuel Cycle Research and Development Program to discover and develop new, more efficient methods for separating the TRU elements from the lanthanide elements and for separating Am from Cm. This report summarizes work conducted at Pacific Northwest National Laboratory (PNNL) in Fiscal Year (FY) 2011 as part of the Minor Actinide Separation Sigma Team.

Work conducted at PNNL in FY 2011 addressed two lines of inquiry. The two hypotheses put forth were:

1. A multifunctional neutral extractant can be combined with an acidic extractant to form a single process solvent for separating trivalent actinides from the trivalent lanthanides and other fission products in acidic high-level nuclear waste.

2. Higher oxidation states (e.g., +5 and +6) of Am can be stabilized in solution by complexation with stereognostic uranophilic ligands, and this chemistry can be exploited to separate Am from Cm.

Experiments performed to test each of these hypotheses are summarized in this report.

2.   SIGNIFICANCE

2.1   TRUSPEAK Task

Developing a single process that combines the attributes of the transuranic extraction (TRUEX) and trivalent actinide-lanthanide separations by phosphorus-reagent extraction from aqueous complexes (TALSPEAK) processes would benefit the development of advanced closed fuel cycles by reducing the complexity of operations required to recover the minor actinides. Converting the transuranic elements to short-lived or stable nuclides requires separation from the lanthanide elements, which are generally

neutron poisons and thus reduce the efficiency of fissioning processes. As previously mentioned, the "UREX+" suite of separation processes recently developed and investigated in the U.S. suffers the disadvantage of process complexity because of the number of different solvent extraction steps required. Combining two of these solvent extraction steps into a single process to reduce the complexity of materials handling has significant potential value in reducing the process complexity and thereby improving the economics of advanced fuel cycle recycle technology. Two processes that might be suited to "blending" are the TRUEX and the TALSPEAK processes. Section 3 presents the background material concerning these two processes.

2.2   Stabilization of Am(V)/Am(VI)

Managing Cm in a closed nuclear fuel cycle is a significant challenge, especially with regard to handling this element in fabricating fuels or targets for burning the TRU elements in fast reactors. One option is to separate the Cm from the other TRU elements and store it for decay. However, separating Am from Cm is a significant technical challenge because of the very similar chemistries of Am^{3+} and Cm^{3+}. One key distinction between Am and Cm is that Am can be oxidized to Am(V) and Am(VI) in aqueous media. The accessibility of the higher Am oxidation states can be exploited to separate Am from Cm, but the higher Am oxidation states are difficult to maintain. Stabilizing either Am(V) or Am(VI) by complexing with ligands selective for linear trans-dioxo actinyl ions would provide opportunities to separate Am from Cm (e.g., by precipitation or solvent extraction). For this reason, we have undertaken a study to determine whether ligands that are known to strongly bind to uranyl ion (the so-called uranophiles) can be used to stabilize Am(V) or Am(VI) in aqueous solution.

3.   APPROACH

3.1   TRUSPEAK Task

3.1.1   TRUSPEAK: Background

The TRUEX process separates the TRU elements (Np, Pu, Am, Cm) and the lanthanide fission products from the other fission products in 1 to 3 M HNO_3. This is achieved by extracting the TRU elements with octyl(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide (CMPO, Figure 3.1a) into an aliphatic hydrocarbon diluent. Tributyl phosphate (TBP) is added to the TRUEX solvent as a modifier to prevent third-phase formation at high solvent loading (Horwitz et al. 1985). The TALSPEAK process uses bis(2-ethylhexyl)phosphoric acid (HDEHP, Figure 3.1b) as the extractant (Nilsson and Nash 2007). In this case, an aqueous-soluble complexant, diethylenetriaminepentaacetic acid (DTPA), is used to complex the actinide ions and prevent their extraction into the organic phase (or to strip the actinides from the organic phase in the so-called "reverse TALSPEAK" method). Because DTPA binds the lanthanide ions less strongly than the actinide ions, the lanthanides are extracted by HDEHP in the presence of DTPA, thereby achieving a separation of the lanthanides from the actinides.

In UREX+1a, the TALSPEAK process is applied to the raffinate from TRUEX (after adjustment) to separate the TRU elements from the lanthanides. In this report, we describe a process in which the TRUEX and TALSPEAK functions are combined into a single solvent extraction process, referred to here as "TRUSPEAK." In the TRUSPEAK process, the TRUEX extractant (CMPO) is combined with the TALSPEAK solvent (HDEHP in dodecane). In doing this, it was envisioned that the CMPO chemistry would dominate under conditions of high acidity (≥ 1 M HNO_3), resulting in co-extraction of the TRU and lanthanide elements into the organic phase. After suitable scrubbing steps, contacting the loaded solvent with a buffered DTPA solution at pH ~3 to 4 should result in a condition in which the HDEHP chemistry dominates, and the system should behave in a manner analogous to a "reverse TALSPEAK"

process. The greater affinity of DTPA for the TRU ions versus the lanthanides should cause the TRU elements to be selectively stripped into the aqueous phase, thereby separating them from the lanthanides.

a) CMPO   b) HDEHP

Figure 3.1. Chemical Structures of the Extractants Used in a) the TRUEX Process and b) the TALSPEAK Process

In FY 2009, the feasibility of the TRUSPEAK concept was established (Lumetta et al. 2009, 2010a). It was established that for a TRUSPEAK solvent consisting of 0.1 M CMPO + 1 M HDEHP in *n*-dodecane, the distribution ratios for the extraction of Am(III) and Eu(III) from 1 M HNO_3 are comparable to those obtained in the TRUEX process solvent (0.2 M CMPO + 1.4 M TBP in *n*-dodecane or normal paraffin hydrocarbon). In the TRU "stripping regime" (0.05 M DTPA at pH 3 to 4), the best lanthanide/actinide (Ln/An) separation factors were achieved when citrate ion was used as the buffer. Separation factors of 12 or greater were achieved with 0.05 M DTPA and 1.5 M citrate.

Although these results are promising, there are certain aspects of the TRUSPEAK solvent system that indicate our original hypothesis (i.e., that CMPO and HDEHP act independently) was somewhat naïve. First, the presence of CMPO significantly influences the Ln/An separation factor. In the TALSPEAK process, the lowest Ln/An separation factor is achieved for Nd. But for 0.1 M CMPO + 1 M HDEHP, Sm displays the minimum separation factor. Second, the Eu/Am separation factor decreases with increasing CMPO concentration in the solvent formulation. Third, there is a significant synergistic interaction between CMPO and HDEHP in the extraction of Am and Nd, but a much weaker synergism in the corresponding extraction of Eu. Understanding the fundamental chemistry involved (e.g., the nature of the extracted species formed and interactions between CMPO and HDEHP) might allow the extraction system to be modified to improve lanthanide/actinide separation performance. For this reason, work in FY 2010 and 2011 focused on gaining an understanding of the fundamental chemistry underlying the TRUSPEAK process. However, some work was conducted in FY 2011 directed at certain practical aspects of the TRUSPEAK process, such as managing Zr and Mo in the process.

3.1.2   TRUSPEAK: Approach

The TRUSPEAK investigations at PNNL in FY 2011 were directed at quantifying the equilibria involved in this extraction system. It was desirable to use a surrogate for Am in these studies because macro quantities of the metal ion would be required. Because of the relatively high Nd/Am separation factor observed in TRUSPEAK (Lumetta et al. 2010a) compared to the TALSPEAK process, it was hypothesized that CMPO synergizes the extraction of Nd(III) much in the same way as it does for Am(III). Experiments were performed to test this hypothesis, and this was shown to be the case (Lumetta et al. 2010b). So Nd(III) was chosen for use as a surrogate for Am(III) in the TRUSPEAK equilibria studies. Although previous results have suggested better Ln/An separation factors are obtained when citrate is used as a buffer, we chose to use lactate as buffer, primarily because it has only one protonation

reaction to consider, but also because most related studies reported in the literature have been carried out using lactate buffer. The following key lines of inquiry were pursued in FY 2011:

1. Distribution ratios were determined for the extraction of Nd(III) and Eu(III) from 1.5 M lactic acid at pH 1.0 with *n*-dodecane solutions of HDEHP as a function of the HDEHP concentration

2. Distribution ratios were determined for the extraction of Nd(III) and Eu(III) from 1.5 M lactic acid at pH 1.0 with 0.1 M HDEHP in *n*-dodecane as a function of added CMPO

3. The data collected in 1 and 2 were analyzed using the computer program SXLSQI to model the extraction equilibria involved

4. Spectroscopic measurements—Fourier transform infrared (FTIR) spectroscopy and ultravioliet/visible (UV/Vis) spectrophotometry—were made to probe speciation in the Ln/HDEHP/CMPO/ *n*-dodecane systems (Ln = Nd or Eu)

5. The behavior of Mo(VI) and Zr(IV) in the TRUSPEAK process was investigated, including means keep these fission products out of the TRU product stream.

6. A batch proof-of-principle TRUSPEAK experiment was performed using a simulated UREX raffinate solution.

3.2   Stabilization of Am(V)/Am(VI)

3.2.1   Stabilization of Am(V)/Am(VI): Background

A variety of solvent extraction and ion exchange methods have been reported for separating trivalent Am and Cm (Lumetta et al. 2006), but these methods typically require the use of very high-salt solutions, so they are not attractive for large-scale use in processing commercial irradiated fuel. At the Savannah River Site, Americium was separated from Cm by oxidizing Am(III) to Am(V) in K_2CO_3 solution, causing the double salt $K_5AmO_2(CO_3)_3$ to precipitate at 85 °C (Groh et al. 1965). But again, this method uses significant quantities of salt, which would require disposal, and it is unproven at the industrial scale required to support advanced fuel cycles for commercial irradiated fuel. Thus, new methods to separate Cm from Am are needed that work efficiently at industrial scale and that do not lead to the creation of large amounts of secondary TRU waste.

One key distinction between Am and Cm is that Am can be oxidized to Am(V) and Am(VI) in aqueous media, forming the trans-dioxo cations AmO_2^+ and AmO_2^{2+}, respectively. The accessibility of the higher Am oxidation states can be exploited to separate Am from Cm, but the higher Am oxidation states are difficult to maintain. In this work, we have undertaken a study to determine whether ligands that are known to strongly bind to uranyl ion (the so-called uranophiles) can be used to stabilize Am(V) or Am(VI) in aqueous solution. In the 1990s, Raymond and co-workers proposed that enhanced selectivity for *trans*-dioxo cations could be obtained by designing ligands that simultaneously form coordinate bonds to the equatorial region of the metal center and N-H hydrogen bonds to the axial oxygen atoms (Franczyk et al. 1992). This has been referred to as stereognostic ligand design and as is conceptually illustrated in Figure 3.2. In this work, we investigated the ligands shown in Figure 3.3 as potential stabilizing ligands for Am(V) or Am(VI). Tris-N,N',N''-[2-(2-carboxy-phenoxy)ethyl]-1,4,7-triazacyclononane (EETAC) and tris(3-(2-carboxy-phenoxy)propyl)amine (NPB) were prepared according to the literature methods (Franczyk et al. 1992, Walton and Raymond 1995, respectively) and were isolated as the hydrochloride salts for use in this work. The Rebek ligand was provided by researchers at the Scripps Research Institute (Sather et al. 2010).
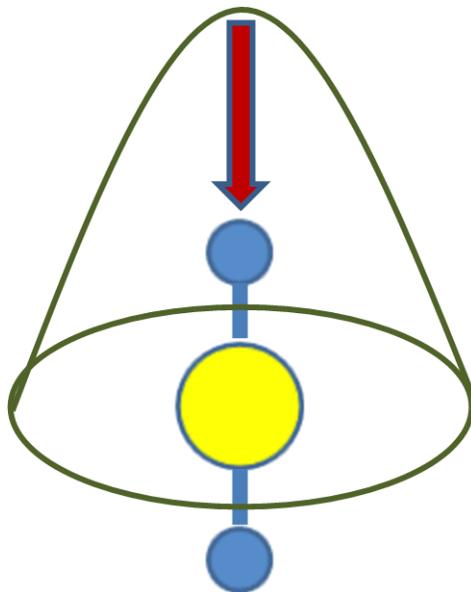
Figure 3.2. Conceptual Illustration of the Stereognostic Ligand Design Concept in Which a Ligand Binds an Actinyl Ion in the Equatorial Plane, but the Complex Is Also Stabilized Through Hydrogen Bonding (depicted by the arrow) to an Axial Oxygen Atom
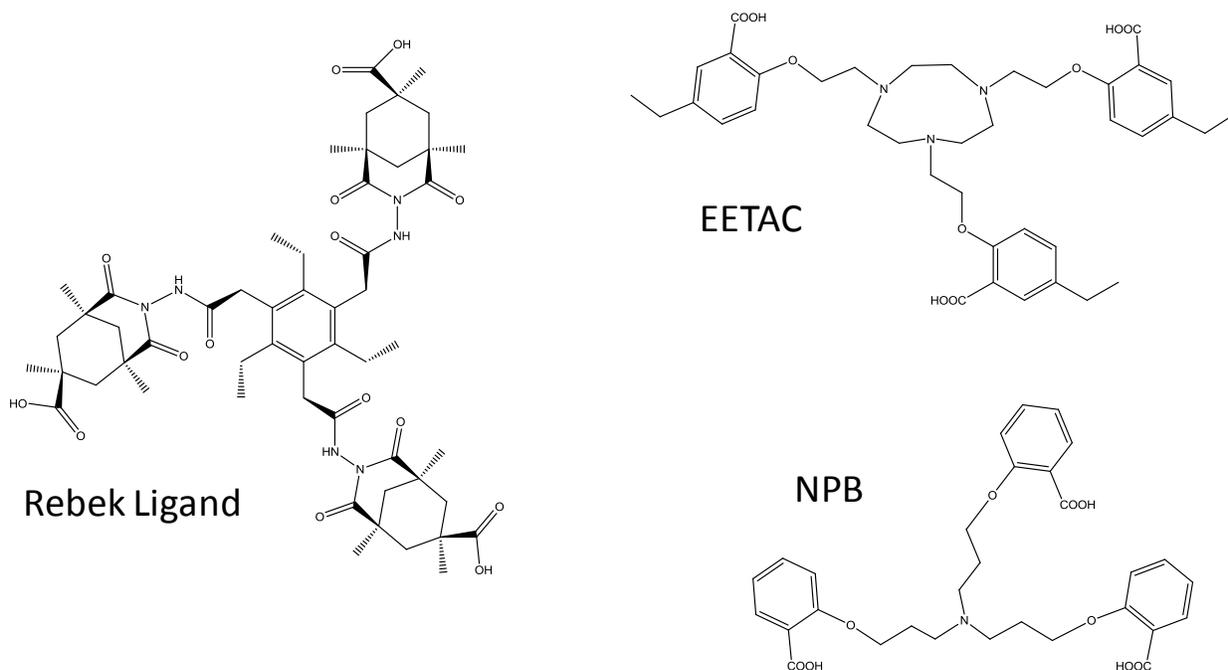

Figure 3.3. Structure of the Uranophilic Ligands Used in this Work

3.2.2   Stabilization of Am(V)/Am(VI): Approach

To assess the potential applicability of the stereognostic ligands in stabilizing higher oxidation states of Am, we began by measuring the binding constants for these ligands with more readily available Am analogs. Specifically, we investigated complexation to Nd(III), Np(V), and Pu(VI), representing the +3, +5, and +6 oxidation states of Am (Lumetta et al. 2010b). These spectrophotometric studies used 80%
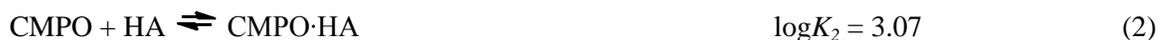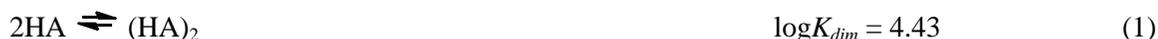
methanol/20% water as the solvent system. However, the Am(VI) is very unstable in this solvent mixture. So that the affinity of the ligands for Am(VI) could be explored in strictly aqueous media, a resin was prepared by physically sorbing the EETAC onto the inert support Amberlite® XAD-7. An analogous resin was prepared using the Rebek ligand. Batch K_d values were obtained with these two resins for sorption of Am(III) and U(VI). For comparison, K_d values were measured for Chelex®-100, which is an ion exchange resin containing the stereognostically blind iminodiacetate group.

4.   SUMMARY OF RESULTS

4.1   TRUSPEAK Results

Extraction of Nd(III) and Eu(III).

The distribution ratios, D, for the extraction of Nd(III) and Eu(III) from 1.5 mol/L lactic acid at pH 1 by HDEHP in *n*-dodecane are presented in Figure 4.1a as a function of the initial HDEHP concentration. Based on the mean experimental values, the slopes of the log$D$ versus log*[HDEHP]* plots are 2.0 and 2.1 for Nd(III) and Eu(III), respectively. These slope values are less than those typically reported for extraction of Ln ions from mineral acids with HDEHP, for which slopes of 2.5 to 3.0 are typically observed (Peppard et al. 1957, 1958; Lundqvist et al. 1983; Sánchez et al. 1999). Applying simple slope analysis methods to these data would lead to the conclusion that the stoichiometry of the extracted Nd(III) or Eu(III) complex is different from the commonly accepted [Ln(DEHP·HDEHP)₃] formulation (Nilsson 2007). For this reason, an equilibrium thermodynamic model (SXLSQI) (Baes 1998) was applied in interpreting the data. The data in Figure 4.1a were combined with the Nd(III) and Eu(III) distribution data obtained as a function of the CMPO concentration (Figure 4.1b) and both data sets were modeled together using SXLSQI. The best SXLSQI fits to the Nd(III) and Eu(III) extraction data shown in Figure 4.1 were obtained by including the following equilibrium reactions:

$$2HA \rightleftharpoons (HA)_2 \qquad\qquad \log K_{dim} = 4.43 \qquad\qquad (1)$$

$$CMPO + HA \rightleftharpoons CMPO{\cdot}HA \qquad\qquad \log K_2 = 3.07 \qquad\qquad (2)$$

$$LacH \rightleftharpoons H^+ + Lac^- \qquad\qquad pK_a = 3.86 \qquad\qquad (3)$$

$$Ln^{3+}(aq) + 5HA(org) \rightleftharpoons Ln(AHA)_2(A)(org) + 3H^+(aq) \qquad\qquad (4)$$

$$Ln^{3+}(aq) + CMPO + 5HA(org) \rightleftharpoons Ln(CMPO)(AHA)_2(A)(org) + 3H^+(aq) \qquad\qquad (5)$$

where Lac = $CH_3CH(OH)COO$ and HA = HDEHP. The equilibrium constants for Reactions 1 and 3 were taken from the literature, (Gen and Wang 1982, Portanova et al. 2003) and these were held constant during refinement of the model. The equilibrium constant for Reaction 2 was previously determined by our group using ^{31}P nuclear magnetic resonance (NMR) spectroscopy (Lumetta et al. 2010b); this value was also held constant during refinement of the model.

Table 4.1 presents the refined equilibrium constants for Reactions 4 and 5 for both Nd(III) and Eu(III). The calculated values for D_{Nd} and D_{Eu} are plotted as the solid black lines in Figure 4.1. Excellent agreement between the experimental and calculated values was obtained with the simple model represented by Equations 1 through 5. As one would expect for the higher charge density of Eu(III) compared to that of Nd(III), the complexation by HDEHP (Reaction 4) is an order-of-magnitude stronger for Eu(III) than for Nd(III); this is reflected in the higher Eu(III) distribution ratios. On the other hand, the interaction of CMPO (Reaction 5) with Eu(III) is somewhat weaker than that with Nd(III). This is indicated by the smaller difference between the logK_4 and logK_5 values for Eu(III) [logK_5– logK_4 = 1.64]

compared to Nd(III) [$\log K_5 - \log K_4 = 2.46$]. The relatively weak interaction of Eu(III) with CMPO explains the flat dependence of D_{Eu} versus the CMPO concentration up to 0.01 mol/L CMPO, whereas the stronger CMPO complexation to Nd(III) explains the initial rise in D_{Nd} as the CMPO concentration is increased. In both cases, Reaction 2 causes the D values to decline rapidly above 0.03 mol/L CMPO.
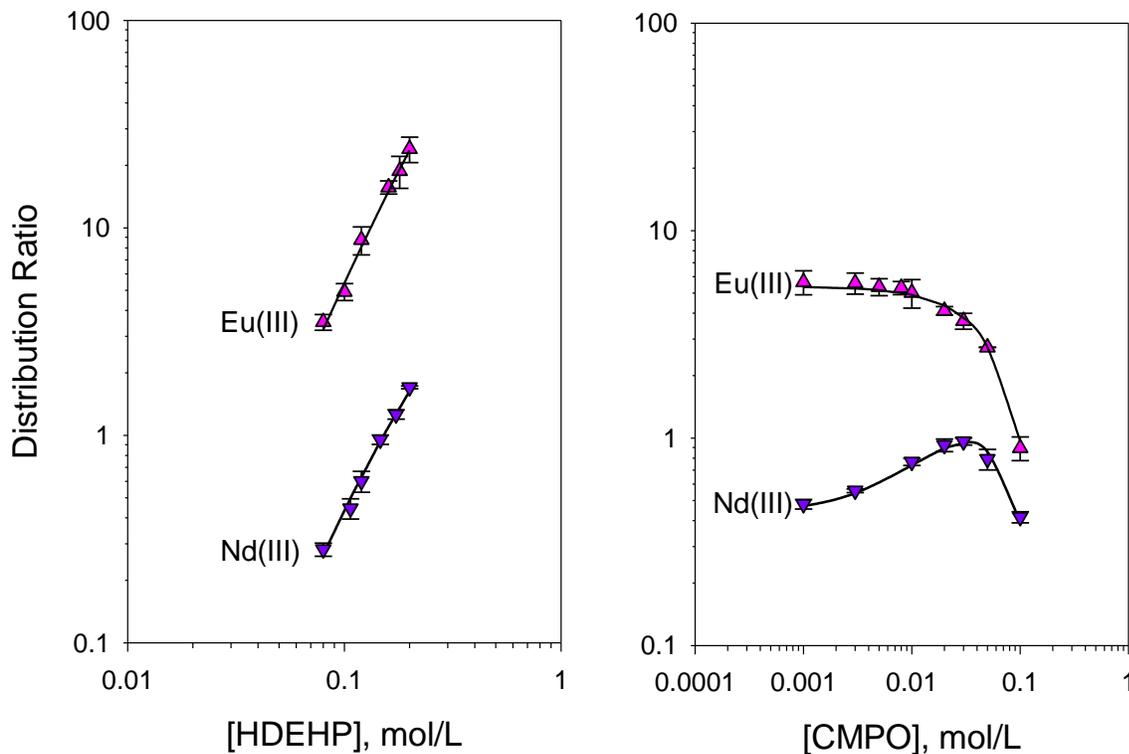

Figure 4.1. Extraction of Nd(III) and Eu(III) from 1.5 mol/L Lactic Acid at pH = 1.0 by a) Variable Concentrations of HDEHP in *n*-dodecane and b) Variable Concentrations of CMPO in 0.1 M HDEHP/*n*-dodecane. All data points were obtained in at least duplicate; in some cases, up to nine measurements were made. Only the mean values are shown on the plot. The solid lines are calculated values based on the model described in the text.

Table 4.1. Equilibrium Constants for Reactions 4 and 5 for Extraction of Neodymium(III) and Europium(III) from 1.5 mol/L Lactic Acid Solution at pH =1.0

	$\log K_4$ [a]	$\log K_5$ [b]
Nd(III)	16.38 ± 0.04	18.84 ± 0.03
Eu(III)	17.69 ± 0.03	19.33 ± 0.10

[a] Equilibrium constant for Reaction 4
[b] Equilibrium constant for Reaction 5

TRUSPEAK Proof-of-Principle Experiment

A series of batch contacts were performed to represent the extraction (1 M HNO_3 in the feed), scrub (0.5 M HNO_3), Am stripping (0.05 M DTPA/1.5 M citrate at pH 3.5), and Ln/Zr stripping (0.25 M TEDGA[a] + 1 M HNO_3) steps of the TRUSPEAK process. The distribution ratios for Am and the lanthanides in the extraction step were all greater than 3, with the exception of La for which the *D* value was only 1.4. In the Am stripping steps, the observed *D* values, both for Am and the lanthanides, were somewhat larger than those expected based on previously measured extraction data, but the measured separation factors generally agreed quite well with the expected values.

Molybdenum was co-extracted with the trivalent lanthanides and Am during the extraction step, with the mean $D_{Mo} = 135$. The Mo was retained in the organic phase during the 0.5 M HNO_3 scrub ($D_{Mo} = 205$), but it was stripped quantitatively during the first Am stripping contact. This result indicated that Mo should be removed from the solvent before Am stripping so that the Am product is not contaminated with Mo. This can readily be achieved by implementing a second scrubbing step in which the loaded TRUSPEAK solvent is contacted with a citrate buffer.

The lanthanides and yttrium were efficiently stripped from the TRUSPEAK solvent by contact with 0.25 M TEDGA + 1 M HNO_3. The lanthanide *D* values were typically less than 0.1 during the Ln/Zr stripping steps. The Zr distribution ratio was approximately 100 during the first Ln/Zr stripping contact, but fell below a value of 1 for the subsequent stripping steps. This suggests that Zr can be stripped from the TRUSPEAK solvent with 0.25 M TEDGA + 1 M HNO_3, but optimization is needed to avoid Zr reflux in the stripping sections. Zirconium stripping in the first Ln/Zr stripping contact might have been limited by the amount of TEDGA available to complex the Zr^{4+}, so increasing the amount of TEDGA in the stripping solution (either by increasing the concentration or by adjusting the organic-to-aqueous phase ratio) might improve Zr stripping.

4.2   Stabilization of Am(V)/Am(VI) Results

Figure 4.2 presents the batch K_d values for the EETAC and Rebek ligand resins for sorption of Am(III) and U(VI) as a function of the measured pH. For comparison, the Am(III) and U(VI) K_d values obtained for Chelex-100 are also shown. For the Rebek ligand resin, the maximum difference in the $\log K_d$ values between U(VI) and Am(III) was 1.75 at pH ~4.5. This selectivity for U(VI) over Am(III) was no better than that seen for Chelex-100, which displayed a maximum $\log K_d^{U(VI)} - \log K_d^{Am(III)}$ value of 1.8 at pH 0.85 to 1.3. The EETAC resin only displayed a slight enhancement in the U(VI)/Am(III) selectivity over the Chelex-100 resin, with a maximum $\log K_d^{U(VI)} - \log K_d^{Am(III)}$ value of 2.3 at pH ~2.6.

Given the relatively weak enhancement in the affinity of the EETAC resin for U(VI) over Am(III) (and virtually no enhancement for the Rebek ligand) compared to Chelex-100, it may be best to investigate alternative stereognostically-designed ligands for stabilizing Am(V) or Am(VI). Computer-aided design of improved stereognostic ligands will be pursued in future work.

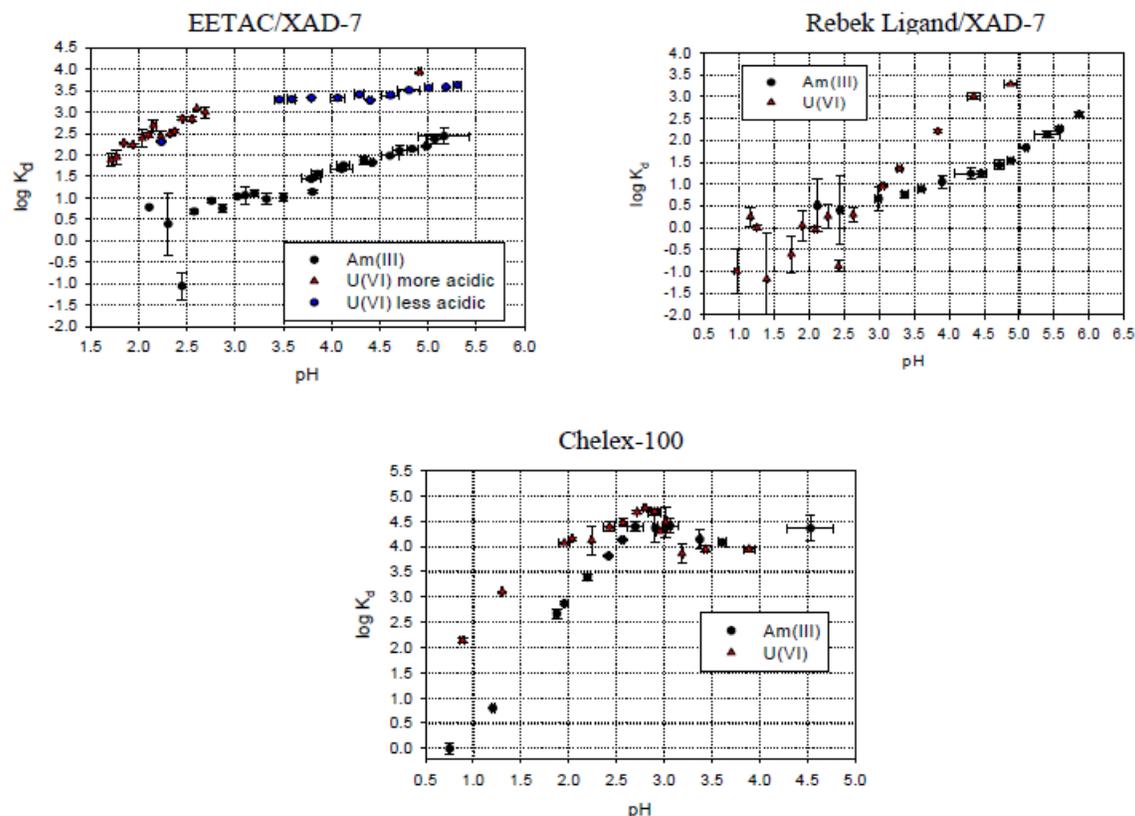[a]   TEDGA = N,N,N',N'-tetraethyldiglycolamide

Figure 4.2. Batch K_d values for sorption of Am(III) and U(VI) onto the two candidate stereognostic resins and the Chelex-100 control.

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6.   INDICATORS OF PROJECT QUALITY AND PRODUCTIVITY

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7.   COLLABORATORS AND PARTICIPANTS

The key researchers involved in this work are:

- Gregg Lumetta, Principal Investigator, responsible for overall project technical content and design and execution of TRUSPEAK experiments

- Sergey Sinkov, Senior Research Scientist, responsible for design and execution of Am oxidation/complexation experiments

- Tatiana Levitskaia, Senior Research Scientist, responsible for equilibrium modeling of solvent extraction data

- Doinita Neiner, Research Scientist, responsible for measuring activity coefficients and performing NMR measurements

- Jenifer Braley, Research Scientist, responsible for design and execution of solvent extraction and other experiments

- Jennifer Carter, Technician, responsible for execution of experiments as directed by the project scientists

- Marvin Warner, Senior Research Scientist, responsible for leading ligand synthesis

- Jonathan Pittman, Masters Intern, responsible for ligand synthesis

- Stan Latesky, visiting scientist from the University of the Virgin Islands; leads a faculty and student team (two students each summer) working on various aspects of Nd extraction chemistry