Separating the Minor Actinides Through Advances in Selective Coordination Chemistry

Fuel Cycle Research & Development

Prepared for
U.S. Department of Energy
Sigma Team for Minor Actinide Separation
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SUMMARY

This report describes work conducted at the Pacific Northwest National Laboratory (PNNL) in Fiscal Year (FY) 2012 under the auspices of the Sigma Team for Minor Actinide Separation, funded by the U.S. Department of Energy Office of Nuclear Energy. Researchers at PNNL and Argonne National Laboratory (ANL) are investigating a simplified solvent extraction system for providing a single-step process to separate the minor actinide elements from acidic high-level liquid waste (HLW), including separating the minor actinides from the lanthanide fission products. Currently, Am and Cm are the only minor actinide elements being considered; however, inclusion of Np and Pu in the actinide product stream may ultimately be considered as an option.

The separation of the minor actinides from the other HLW constituents by solvent extraction is based on the selective complexation of certain metal ions in either the aqueous or organic phase. The solvent system investigated in FY 2012 combined octyl(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide (CMPO) with 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester acid (HEH[EHP]), both of which were dissolved in *n*-dodecane. CMPO is known to extract trivalent actinide and lanthanide ions from nitric acid media by forming complexes of the type $[M(NO_3)_3(CMPO)_3]$ in the organic phase. Most other fission products form weaker complexes with CMPO and are therefore not extracted; a notable exception is Zr(IV), which is strongly extracted by CMPO. At low aqueous phase acid concentrations (e.g., pH 2 to 4), HEH[EHP] forms lipophilic complexes with a number of metal ions, including the trivalent actinide and lanthanides. However, by employing a complexing agent (e.g., a polyaminocarboxylate) that preferentially binds the actinides in the aqueous phase, the actinides can be separated from the lanthanides. In this case, the polyaminocarboxylate binds the actinides in the aqueous phase while the lanthanides are complexed by HEH[EHP] in the organic phase. In this work we investigated both practical aspects of the CMPO + HEH[EHP] system, and the fundamental chemistry involved.

The extraction behavior in the CMPO + HEH[EHP] extraction system displays regimes in which the HEH[EHP] chemistry dominates (i.e., low HNO_3 concentrations) and those in which the CMPO chemistry dominates (i.e., high HNO_3 concentrations). At 0.1 mol/L HNO_3 the lanthanide distribution ratios for the 0.2 mol/L CMPO + 1.0 mol/L HEH[EHP] solvent system follow the general trend of increasing D with increasing atomic number. Because a similar trend is seen with 1.0 mol/L HEH[EHP] in *n*-dodecane without CMPO present, the chemistry of the combined solvent is dominated by the chemistry of HEH[EHP] at 0.1 mol/L HNO_3, with CMPO playing little, if any role. Above 0.5 mol/L HNO_3 the nitric acid dependence for the extraction of Am and the lanthanides into the 0.2 mol/L CMPO + 1.0 mol/L HEH[EHP] solvent displays a pattern in which the D values increase until approximately 1 mol/L HNO_3, then decline at higher HNO_3 concentrations. This pattern is that expected for the situation in which CMPO is dominating the extraction chemistry. From a practical standpoint, the extraction behavior for the CMPO + HEH[EHP] extraction system is more favorable than that previously determined for the CMPO + HDEHP (bis(2-ethylhexyl)phosphoric acid) system because the distribution ratios remain high above 1 mol/L HNO_3.

The minor actinide stripping behavior of the CMPO + HEH[EHP] system is also more favorable than that for the CMPO + HDEHP system. The latter is highly sensitive to the aqueous phase solution pH. The dependence on pH is greatly reduced when HEH[EHP] is used as the acidic extractant in the solvent formulation. Furthermore, it should be possible to operate the minor actinide stripping section at lower pH, which is another advantage because it will reduce downstream solution adjustments required for conversion of the minor actinides to their oxide forms.

Fourier transform infrared (FTIR) spectroscopic and visible spectrophotometric investigations qualitatively indicate that CMPO binds to Nd(III) in the HEH[EHP] system more weakly than in the analogous HDEHP system. Quantification of this effect is in progress.

CONTENTS

FIGURES

TABLES

ACRONYMS

CMPO	octyl(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide
DTPA	diethylenetriaminepentaacetic acid
FTIR	Fourier transform infrared
FY	fiscal year
HEDTA	N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid
HEH[EHP]	2-ethylhexylphosphonic acid mono-2-ethylhexyl ester acid
HDEHP	bis(2-ethylhexyl)phosphoric acid
ICP-OES	inductively coupled plasma atomic emission spectroscopy
Ln/An	lanthanide/actinide
PNNL	Pacific Northwest National Laboratory
TALSPEAK	trivalent actinide-lanthanide separations by phosphorus-reagent extraction from aqueous complexes
TBP	tributyl phosphate
TEDGA	N,N,N',N'-tetraethyldiglycolamide
TRU	transuranic
TRUEX	transuranic extraction
UREX+	uranium extraction plus

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 to mitigate their long-term effects on the performance of geological 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 greatly reduces 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, and 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). The work described here is focused on separating the trivalent actinides Am and Cm, but inclusion of Np and Pu in the actinide product scheme could be considered as an option.

A critical challenge in this regard is separating the minor actinide 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 minor actinide elements. Although there are active programs worldwide investigating the separation of minor actinide 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 its complexity. 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 Sigma Team for Minor Actinide Separation was established within the Fuel Cycle Research and Development Program to discover and develop new, more efficient methods for separating the minor actinide 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) 2012 as part of the Sigma Team for Minor Actinide Separation.

The work conducted at PNNL in FY 2012 focused primarily on testing the hypothesis that 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. This notion exploits subtle differences in the coordination chemistry of the actinide elements compared to the lanthanide elements. In particular, the slight preference of the actinide ions for soft donor ligands, such as amines, is used to selectively remove the actinides from a solvent phase loaded with both the lanthanides and actinides.

2.   SIGNIFICANCE

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 United States 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 has significant potential to reduce the process complexity, 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.

3.   APPROACH

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 3.1) 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). Similar processes have been developed using diamide extractants, such as the DIAMEX process (Courson et al. 2000; Malmbeck et al. 2000), and tetraalkyldiglycolamide extractants (Modolo et al. 2007, 2008; Magnusson et al. 2009). All of these methods involve co-extraction of the TRU and lanthanide elements into a hydrocarbon solvent containing the neutral extractant, followed by co-recovery of the TRU elements and lanthanides into a dilute acid stripping solution.

The TALSPEAK process uses bis(2-ethylhexyl)phosphoric acid (HDEHP, Figure 3.1) as the extractant (Nilsson and Nash 2007). In this case, an aqueous-soluble complexant, diethylenetriaminepentaacetic acid (DTPA, Figure 3.1), 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. Although it has been demonstrated to be effective at separating the minor actinide elements from the lanthanides, the TALSPEAK process suffers some limitations; specifically, the process chemistry is not completely understood and is difficult to model, the extraction kinetics are slow, and the process is highly sensitive to pH. Recently, a variant of the TALSPEAK process was proposed in which HDEHP is replaced by its phosphonic acid analog, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester acid (HEH[EHP], Figure 3.1), and DTPA is replaced by N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid (HEDTA, Figure 3.1) (Braley et al. 2012). The HEH[EHP]/HEDTA system offers the advantage of more predictable extraction behavior, faster kinetics, and less dependence on pH.

In UREX+1a, the TALSPEAK process is applied to the actinide/lanthanide product from TRUEX (after adjustment) to separate the TRU elements from the lanthanides. In this report, we describe the progress made towards combining the functions of the TRUEX and TALSPEAK processes into a single process capable of both separating the minor actinide elements from acidic high-level liquid waste and from the lanthanide fission products.[a] The approach taken combines a bifunctional neutral extractant (CMPO) with an acidic extractant (HDEHP or HEH[EHP]) to form a single process solvent. The CMPO chemistry was expected to dominate under conditions of high acidity ($\geq$ 1 M HNO_3), resulting in co-extraction of the minor actinide 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 was expected to result in a condition in which the HDEHP chemistry dominates, and the system would behave in a manner analogous to a "reverse TALSPEAK" process. The greater affinity of DTPA for the actinide ions versus the lanthanides was expected to cause the minor actinide elements to be selectively stripped into the aqueous phase, thereby separating them from the lanthanides. Work in previous fiscal years indicated that CMPO + HDEHP is perhaps not the ideal combination of neutral and acidic extractants, so work in FY 2012 focused mainly on the CMPO + HEH[EHP] system. Structures for the various extractants and complexants used in this study are given in Figure 3.1.

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[a]   This report focuses on the work conducted at PNNL. A parallel, yet coordinated, effort is underway at Argonne National Laboratory. Results of the latter study will be reported separately.
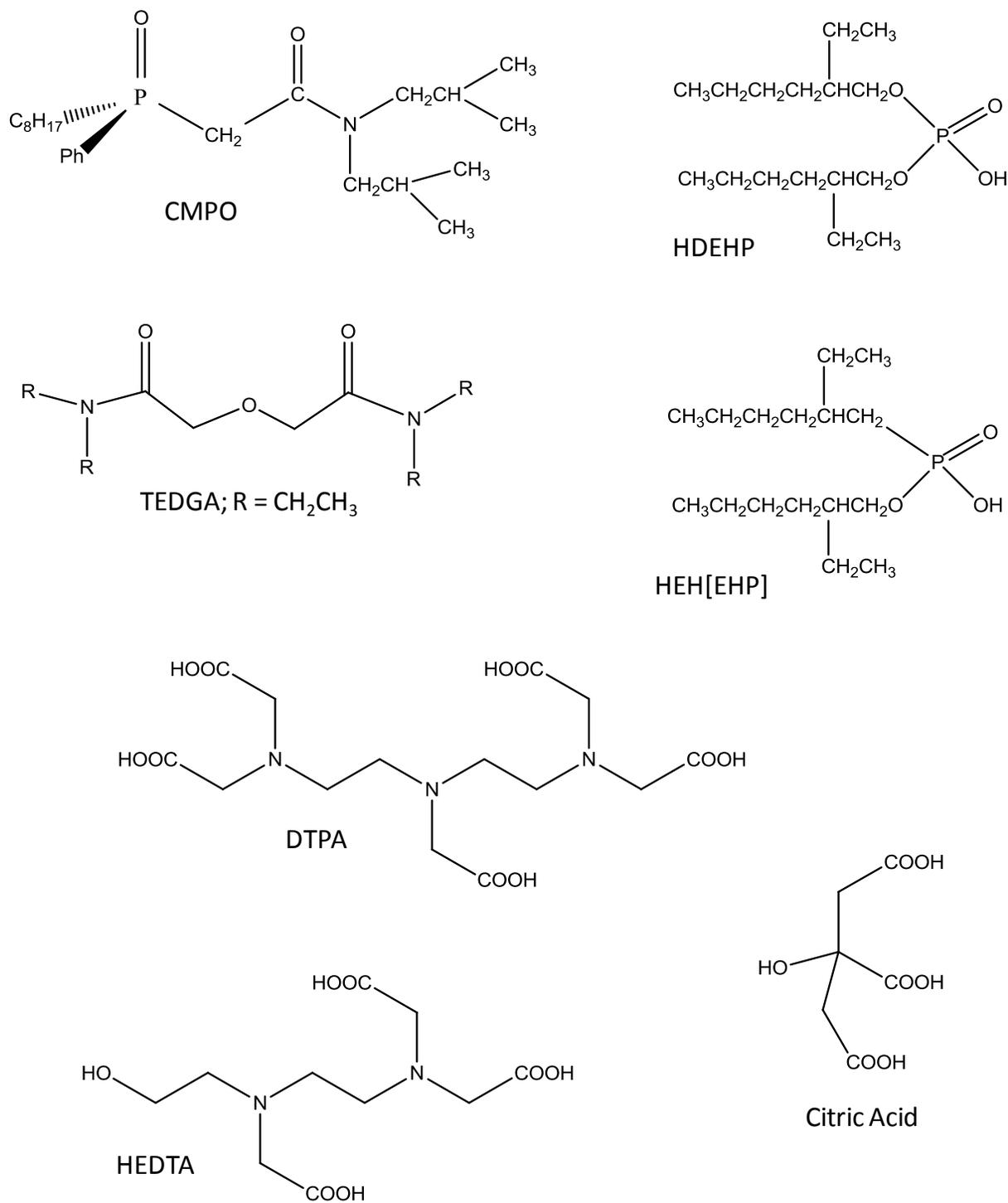
Figure 3.1.   Chemical structures of the extractants and complexants used in this study.

4.   SUMMARY OF RESULTS

4.1   Extraction of Americium and the Lanthanides from Nitric Acid

Lumetta et al. (2009, 2010a,b) established the feasibility of combining CMPO with HDEHP into a single process solvent for extracting and separating the minor actinides in FY 2009 and 2010. They determined that, for a solvent consisting of 0.1 mol/L CMPO + 1 mol/L HDEHP in *n*-dodecane, the distribution ratios (*D* = organic phase concentration ÷ aqueous phase concentration) for the extraction of Am(III) and Eu(III) from 1 mol/L HNO_3 are comparable to those obtained in the TRUEX process solvent (0.2 mol/L CMPO + 1.4 mol/L TBP in *n*-dodecane or normal paraffin hydrocarbon). However, they also determined that increasing the nitric acid concentration above 1 mol/L resulted in decreases in the Am(III) and Eu(III) distribution ratios (Figure 4.1a). This extraction behavior is similar to that seen for HDEHP, without any CMPO present, although CMPO does increase the Am and Eu distribution ratios at 1 to 3 mol/L HNO_3. In many respects, the CMPO/HDEHP system is dominated by the HDEHP chemistry, even at high HNO_3 concentrations. This is an undesirable feature of the combined CMPO + HDEHP system; it would be preferable for the *D* values to remain above 1 for HNO_3 concentrations greater than 1 mol/L.

TRUSPEAK Nitric Acid Dependence

0.1 M CMPO/1.0 M HDEHP/dodecane

0.2 M CMPO/1.0 M HEH[EHP]/dodecane
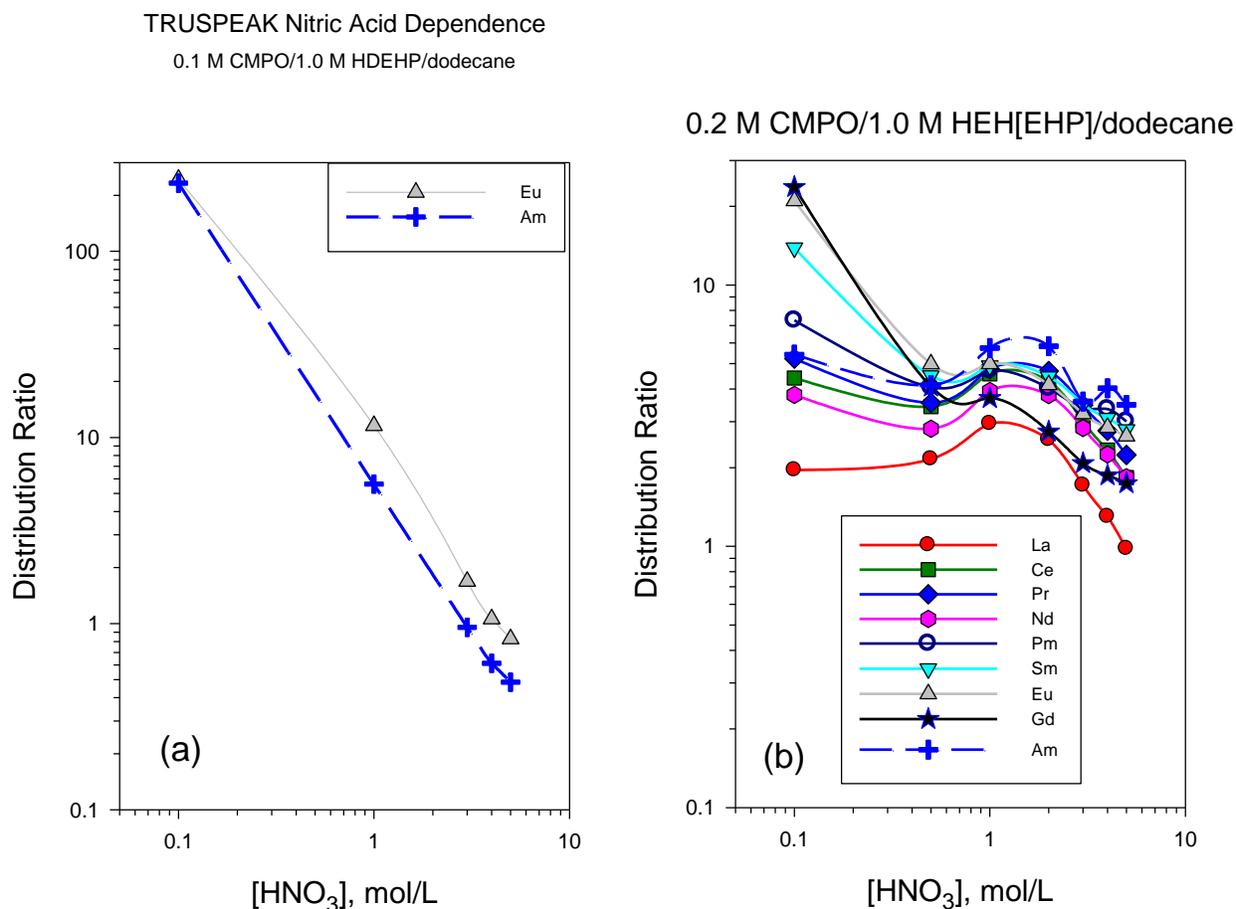
Figure 4.1. Extraction of Am(III) and trivalent lanthanides by (a) 0.1 mol/L CMPO + 1.0 mol/L HDEHP in *n*-dodecane (Lumetta et al. 2012a), and (b) 0.2 mol/L CMPO + 1.0 mol/L HEH[EHP] in *n*-dodecane (this work), as a function of HNO_3 concentration. Each lanthanide ion was

initially present at approximately 2 mmol/L in the aqueous phase. Note that the ordinate scales are different for (a) and (b) and that the spline curves are included only to guide the eye.

Switching the acidic extractant from HDEHP to HEH[EHP] improves the extraction profile. Figure 4.1b presents the dependence of the extraction of Am and relevant lanthanide ions on the HNO_3 concentration, using 0.2 mol/L CMPO + 1.0 mol/L HEH[EHP] in *n*-dodecane as the extraction solvent. The extraction behavior in the CMPO/HEH[EHP] extraction system displays regimes in which the HEH[EHP] chemistry dominates (i.e., low HNO_3 concentrations) and those in which the CMPO chemistry dominates (i.e., high HNO_3 concentrations). At 0.1 mol/L HNO_3, the lanthanide distribution ratios for the 0.2 mol/L CMPO + 1.0 mol/L HEH[EHP] solvent system follow the general trend of increasing *D* with increasing atomic number, with the exception of Nd, which is out of sequence. This trend is also seen with 1.0 mol/L HEH[EHP] in *n*-dodecane without CMPO present. The distribution ratios for the extraction of Nd, Sm, Eu, and Gd from 0.1 mol/L HNO_3 into 1.0 mol/L HEH[EHP] (with no CMPO present) were measured to be 0.62, 8.65, 19.4, and 19.6, respectively (the *D* values for La, Ce, and Pr were below the detection limit for the inductively coupled plasma atomic emission spectroscopy [ICP-OES] method used). Hence at 0.1 mol/L HNO_3, the chemistry of the combined solvent is dominated by the chemistry of HEH[EHP], with CMPO playing little, if any role.

Above 0.5 mol/L HNO_3, the nitric acid dependence for the extraction of Am and the lanthanides into the 0.2 mol/L CMPO + 1.0 mol/L HEH[EHP] solvent displays a pattern in which the *D* values increase until approximately 1 mol/L HNO_3, then decline at higher HNO_3 concentrations. Such a pattern is seen for the TRUEX solvent, which consists of CMPO modified with TBP (Horwitz et al. 1985). This extraction behavior can be explained by the formation of $[M(NO_3)_3(CMPO)_3]$ species in the organic phase (Horwitz et al. 1987), which is favored by increasing nitrate concentration in the aqueous phase. However, at high HNO_3 concentration, competition from the extraction of HNO_3 into the organic phase reduces the effective CMPO concentration, thus lowering the distribution ratios for the M(III) ions. The observation of a maximum in the *D* values suggest that above ~0.5 mol/L HNO_3, the extraction chemistry in the CMPO + HEH[EHP] system is dominated by that of CMPO.

4.2   Selective Stripping of the Minor Actinides

Once the minor actinides and the lanthanides have been co-extracted into the combined process solvent (and after any required scrubbing steps), the minor actinides must be selectively stripped from the solvent, leaving the lanthanide elements in the organic phase. As is done in the TALSPEAK process, this is achieved by contacting the solvent with a carboxylate-buffered solution containing a polyaminocarboxylate ligand. Figure 4.2 shows the Am and lanthanide distribution ratios for the 0.1 mol/L CMPO + 1 mol/L HDEHP/*n*-dodecane solvent system using 0.05 mol/L DTPA in a 1.5 mol/L citrate buffer as the Am-selective stripping solution (Lumetta et al. 2012a). The data indicate that, much like the TALSPEAK process, the distribution ratios for the CMPO + HDEHP solvent system are highly dependent on pH in the minor actinide stripping regime. To achieve high lanthanide/actinide separation factors, the pH must be tightly controlled (approximately ± 0.1 pH unit) around pH 3.4.

If HEH[EHP] is used as the acidic extractant in the combined solvent formulation, the dependence on pH is greatly reduced. Figure 4.3 shows the Am and lanthanide distribution ratios for the 0.2 mol/L CMPO + 1.0 mol/L HEH[EHP]/*n*-dodecane solvent system using 0.1 mol/L HEDTA in a 0.1 mol/L citrate buffer as the Am-selective stripping solution. Although this system is not completely optimized, the data do indicate that the minor actinide stripping process is much less sensitive to pH when HEH[EHP] is used as the acidic component in the extraction solvent. Furthermore, it should be possible to operate the minor actinide stripping section at lower pH, which is another advantage; it will reduce downstream solution adjustments required for conversion of the minor actinides to their oxide forms.
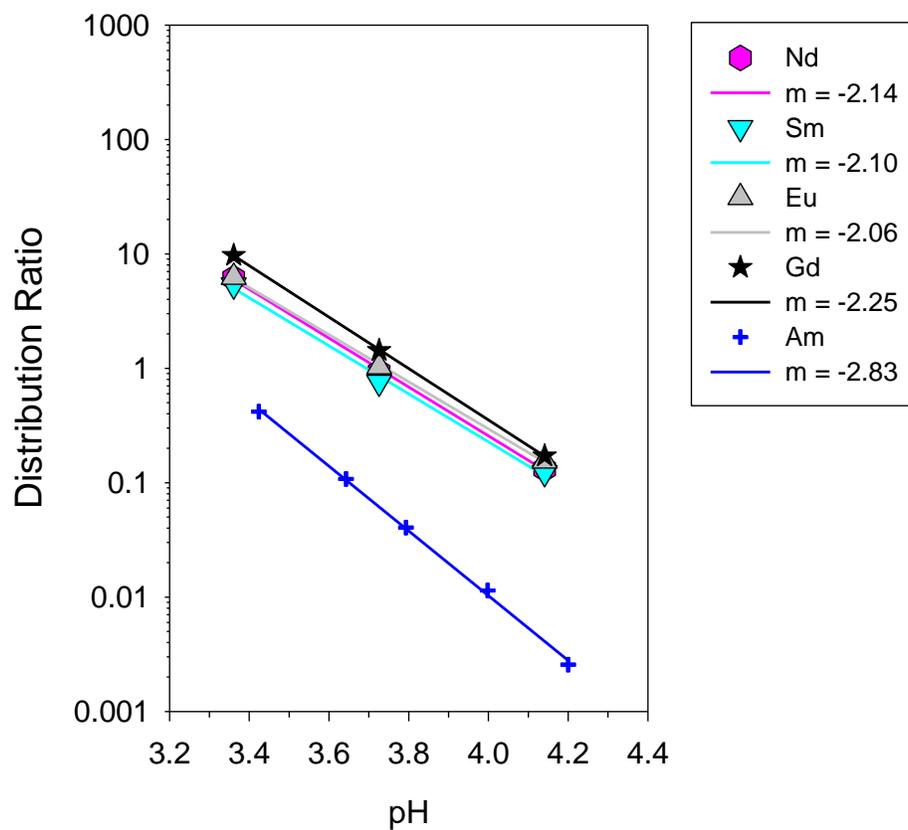
Figure 4.2. Extraction of Am, Nd, Sm, Eu, and Gd by 0.1 mol/L CMPO + 1 mol/L HDEHP in
n-dodecane as a function of equilibrium pH at 1.5 mol/L citrate and 0.05 mol/L DTPA (from
Lumetta et al. 2012a).
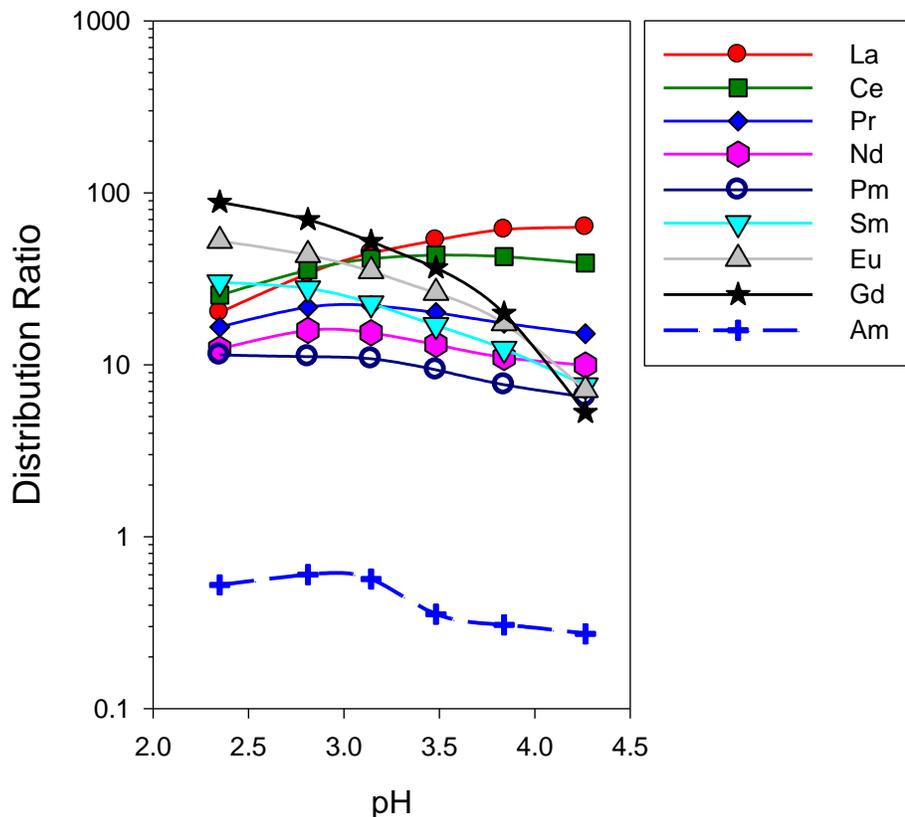
Figure 4.3.   Extraction of Am(III) and Ln(III) by 0.2 mol/L CMPO + 1.0 mol/L HEH[EHP] in
n-dodecane as a function of pH from citrate-buffered solutions; aqueous conditions:
0.1 mol/L citrate, 0.1 mol/L HEDTA; each lanthanide ion was initially present at
approximately 2 mmol/L in the aqueous phase.

   Further experimentation suggested 0.15 mol/L HEDTA + 0.15 mol/L citrate would provide more
optimal selective stripping of the minor actinides from the 0.2 mol/L CMPO + 1.0 mol/L HEH[EHP] in
n-dodecane solvent. Figure 4.4 shows the behavior of most of the relevant lanthanides and Am(III) using
this formulation for minor actinide stripping. In this experiment, the lanthanides were extracted into
0.2 mol/L CMPO + 1.0 mol/L HEH[EHP] in *n*-dodecane from 2 mol/L HNO_3. After scrubbing with
0.15 mol/L citrate solution (initial pH = 3, final pH =2), the loaded solvent was contacted with 0.15 mol/L
HEDTA + 0.15 mol/L citrate at several different pH conditions. A separate portion of 0.2 mol/L CMPO +
1.0 mol/L HEH[EHP] in *n*-dodecane was loaded in identical manner, but with [241]Am tracer added. All
contacts were performed at an organic-to-aqueous phase ratio of one, with mixing achieved by vortex
mixing for 15 min at 1,900 rpm. The results indicate good separation of the lanthanides from Am can be
achieved, especially above pH 2.5. It should be noted that Pm(III) was not included in this experiment.
The data in Figure 4.3 suggest that the Pm/Am separation factor might be slightly less than the Nd/Am
separation factor, so the separation factors plotted in Figure 4.4 are probably slightly higher than would be
achieved if Pm were present.
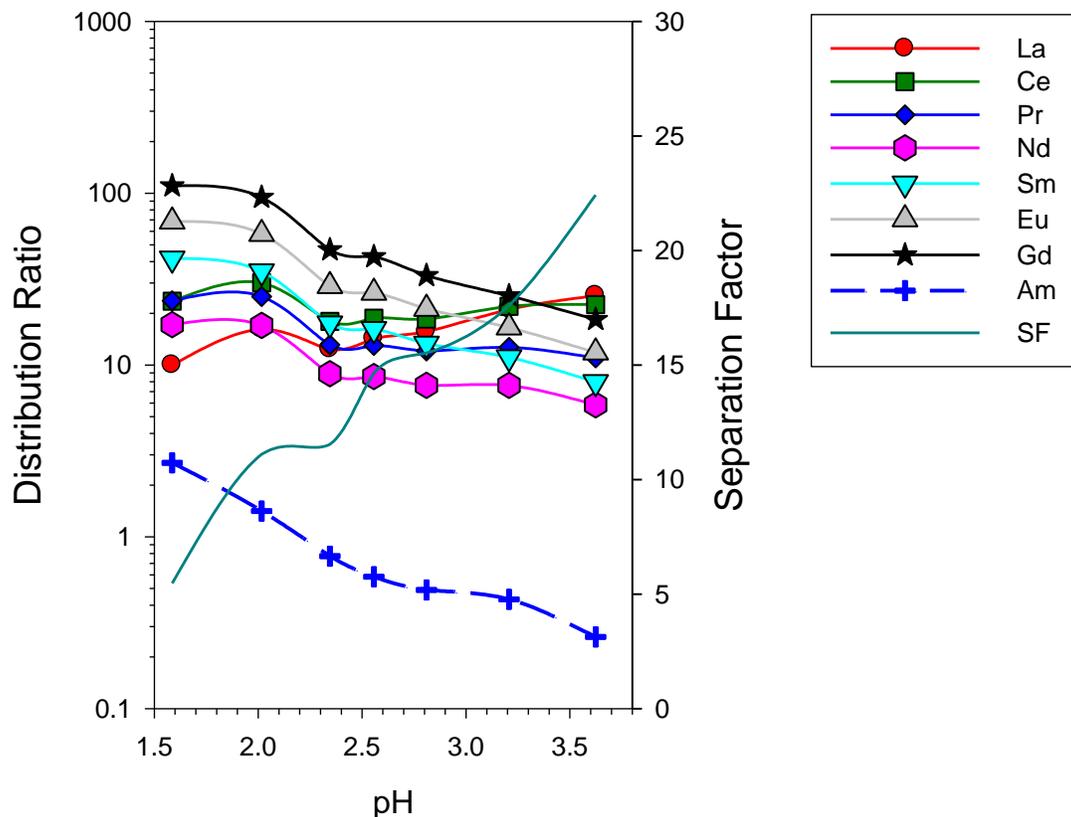
Figure 4.4. Back-extraction of Am(III) and Ln(III) from 0.2 mol/L CMPO + 1.0 mol/L HEH[EHP] in *n*-dodecane as a function of pH; aqueous conditions: 0.15 mol/L citrate, 0.15 mol/L HEDTA; each lanthanide ion was initially present at approximately 2 mmol/L in the organic phase.

4.3   Fission Product Behavior

Investigation of the extraction behavior of the transition metal fission products Zr(IV), Mo(VI), and Ru(III) was initiated in FY 2012, along with investigation of the behavior of Fe(III). The distribution ratios for the extraction of Fe(III) and Ru(III) from nitric acid into 0.2 mol/L CMPO + 1.0 mol/L HEH[EHP] in *n*-dodecane were too low to be reliably determined by ICP-OES. Zirconium(IV) and Mo(VI) were strongly extracted at all nitric acid concentrations examined (Figure 4.5a).

Under the conditions expected for stripping of the minor actinides, the Zr(IV) distribution ratios remain high, but those of Mo(VI) and Fe(III) are below one (Figure 4.5b). Molybdenum(VI) can be removed from the solvent by scrubbing with an aqueous citrate solution before the minor actinide stripping step. Indeed, when a solution of 0.2 mol/L CMPO + 1.0 mol/L HEH[EHP] in *n*-dodecane, pre-loaded with Mo(VI), Zr(IV), and the lanthanides was contacted with 0.25 mol/L citrate at an initial pH of 3, the measured Mo(VI) distribution ratio was 0.04. This indicates that Mo(VI) should be readily scrubbed from the solvent with a citrate solution. Zirconium(IV) remained in the organic phase when contacted with 0.25 mol/L citrate solution. The distribution ratios for La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), and Gd(III) were all greater than 10 under these conditions. Fe(III) can also be scrubbed from the solvent with citrate solution. The citrate scrub also has the advantage that it would "condition" the solvent phase for the minor actinide stripping step, which also utilizes a citrate-based aqueous phase.
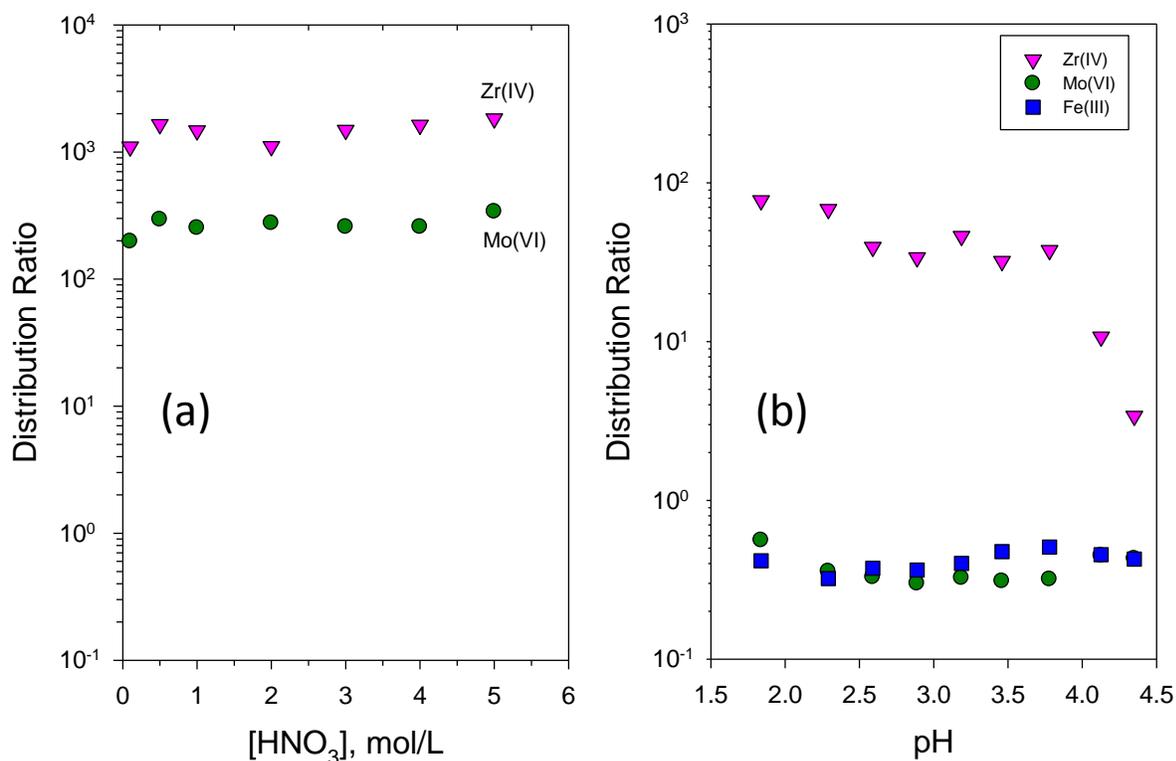
Figure 4.5. Distribution ratios for Zr(IV), Mo(VI), and Fe(III) for extraction into 0.2 mol/L CMPO + 1.0 mol/L HEH[EHP] in *n*-dodecane from (a) nitric acid media, and (b) 0.15 mol/L HEDTA + 0.25 mol/L citrate.

Stripping the Zr(IV) from the CMPO + HEH[EHP] solvent remains an important challenge. Previous work suggests that an acidic solution of N,N,N',N'-tetraethyldiglycolamide (TEDGA) should be capable of stripping the Zr(IV) from the solvent along with the lanthanides (Lumetta et al. 2012a). However, the Zr(IV) distribution ratio was 34 when the lanthanide and Zr-loaded 0.2 mol/L CMPO + 1.0 mol/L HEH[EHP] solution was contacted with 0.025 mol/L TEDGA in 1 mol/L HNO_3. It is possible that complexation of the TEDGA by the lanthanides present in this system reduced the free TEDGA concentration to the point that it was ineffective at stripping the Zr(IV). If this is the case, increasing the TEDGA concentration might lead to more effective Zr(IV) stripping. However, further experimentation is needed to verify this.

4.4   Synergic Extraction Behavior

Studies of the CMPO + HDEHP combined solvent system revealed a strong synergic interaction of CMPO and HDEHP in the extraction of Am and Nd from buffered DTPA solutions (Lumetta et al. 2011). This synergic behavior is detrimental to the process because it reduces the lanthanide/actinide separation factors compared to those achieved in the TALSPEAK process. Yet another advantage of the CMPO + HEH[EHP] solvent system is that the synergism in the extraction of the trivalent actinides and lanthanides is greatly reduced. Figure 4.6 presents the Am and lanthanide distribution ratios for extraction from a lactate-buffered HEDTA solution into mixed CMPO + HEH[EHP] solvents with varying CMPO mole fraction. The data indicates that there is mild synergism for extraction of the light lanthanides under these conditions, but the synergic behavior decreases with increasing Z for the lanthanides. There is no evidence of synergic extraction behavior for the lanthanides from Sm and higher. Likewise, only a

relatively weak synergism is observed for the extraction of Am by CMPO/HEH[EHP] mixtures. Interestingly, the lanthanide/Am separation factors increase with increasing proportion of CMPO in the solvent mixture. This contrasts with the CMPO/HDEHP system for which the opposite was observed (Lumetta et al. 2010a). A separation factor (Nd/Am) of ~80 was obtained at a CMPO mole fraction of 0.5.
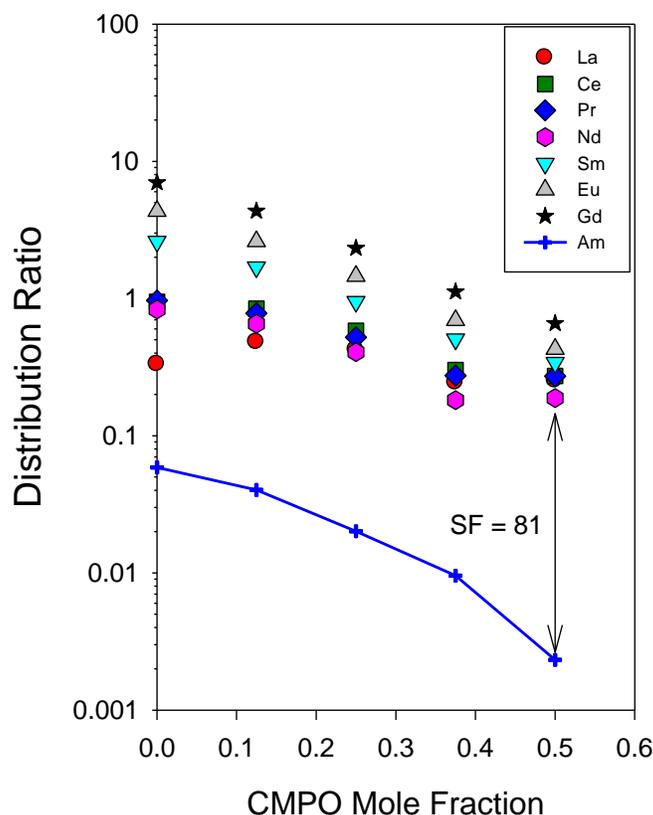
Figure 4.6. Extraction of Am(III) and Ln(III) by CMPO + HEH[EHP] solutions with variable CMPO mole fraction, but with the total [CMPO] + HEH[EHP] = 0.2 mol/L; diluent = *n*-dodecane; aqueous phase = 0.02 mol/L HEDTA + 1 M lactate at pH = 3.6.

4.5   Fundamental Chemistry of the Extraction Systems

Ultimately, to model and control a lanthanide/actinide separation process based on a combined extraction solvent, it is necessary to understand the fundamental chemical equilibria involved and the species that are formed in solution. Spectral studies were undertaken to probe the fundamental aspects of the solution chemistry involved in the combined solvent systems, using Nd(III) as a prototypical extracted metal ion. A series of *n*-dodecane solutions of HEH[EHP] with varying concentrations of Nd(III) were prepared by contacting 0.5 mol/L HEH[EHP] with equal volumes of aqueous 0.011, 0.0055, or 0.0011 mol/L NdCl$_3$. Figure 4.7 shows the visible electronic spectra of these three Nd(III) solutions. The spectral features are independent of the Nd(III) concentration in the HEH[EHP] solution, suggesting that a single species exists in solution under the examined conditions. Indeed, the same spectrum was obtained under highly loaded conditions in which the 0.5 mol/L HEH[EHP] solution was contacted six successive times with equal volumes of 0.11 M NdCl$_3$
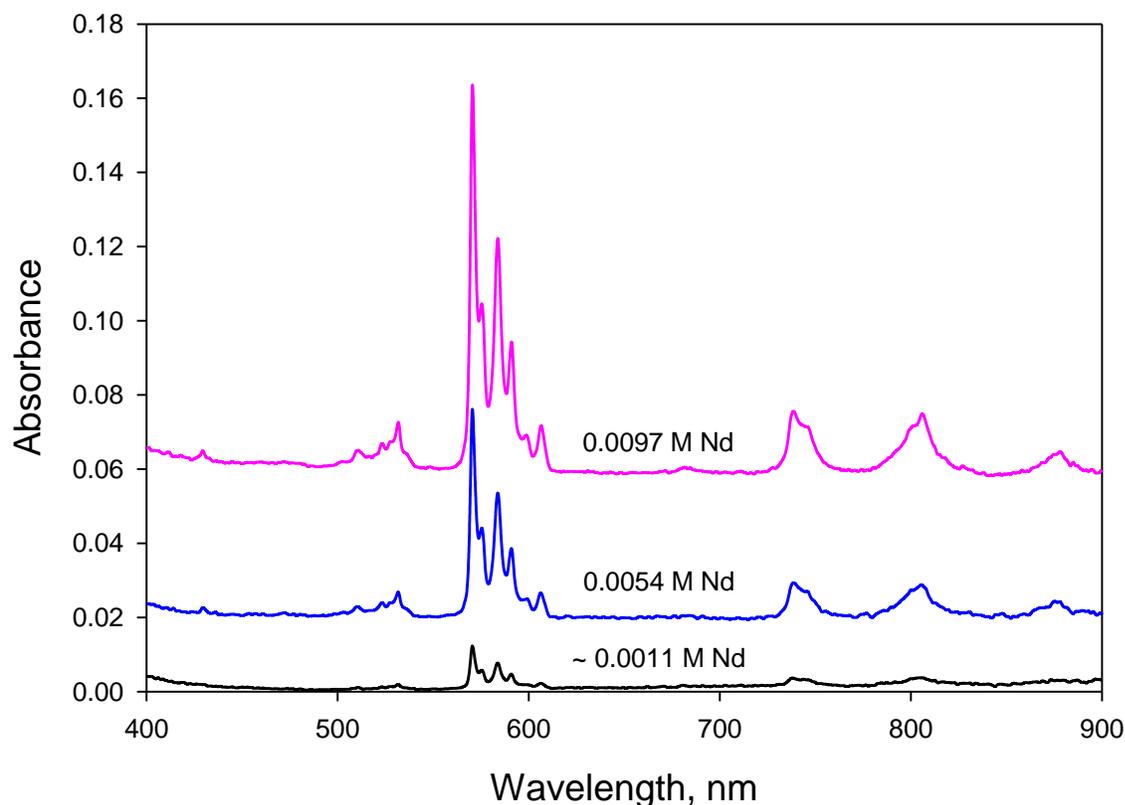
Figure 4.7.   Visible spectrum of 0.5 mol/L HEH[EHP] solutions in *n*-dodecane at different Nd loadings.
Spectra are arbitrarily offset for clarity.

Figure 4.8 compares the fourier transform infrared (FTIR) spectrum[a] of neat HEH[EHP] to that of 0.5 mol/L HEH[EHP] in *n*-dodecane. For the latter, the contribution of *n*-dodecane to the spectrum was removed by subtracting the spectrum of *n*-dodecane (subtraction factor = 0.86) using GRAMS/AI version 7.02 (Thermo Electron Corp.). The HEH[EHP] FTIR spectrum in *n*-dodecane agrees very well with that for neat HEH[EHP], except that the vibrational bands are generally shifted to slightly higher energy for the solution-phase spectrum. Table 4.1 presents the key band assignments for HEH[EHP].

Neodymium(III) was loaded into the 0.5 mol/L HEH[EHP]/*n*-dodecane solution by contacting three successive times with aqueous 0.11 mol/L $NdCl_3$ at an organic-to-aqueous phase ratio of 2. This procedure resulted in 0.0193 mol/L Nd in the HEH[EHP] solution.[b] The FTIR spectrum of HEH[EHP] is compared to that of the Nd–HEH[EHP] complex in Figure 4.9. The spectrum of the latter was obtained by subtracting first the spectrum of *n*-dodecane (subtraction factor = 0.86), the subtracting the contribution of HEH[EHP] to the spectrum (subtraction factor = 0.85). Band assignments for the Nd–HEH[EHP] complex are presented in Table 4.1. Upon complexation to Nd(III), the ν(P=O) band of HEH[EHP] shifts from 1,198 to 1,163 cm^{-1} indicating complexation through the phosphoryl oxygen. The broad band at 1679 cm^{-1} in the HEH[EHP] solution , attributed to the hyrdogen-bonded O–H stretch, disappears upon compexation to Nd(III). This suggests the disruption of the dimeric HEH[EHP] structure (Tkac et al.

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[a]   FTIR spectra were recorded on a Bruker Alpha-P spectrometer equipped with a diamond attenuated total reflectance (ATR) cell.

[b]   The organic-phase Nd concentration was determined by stripping the Nd into 6.2 mol/L HNO_3 and analyzing the resulting aqueous solution by ICP-OES.

2012). The ν(P–O) band of HEH[EHP] at 983 cm^{-1} disappears upon complexation to Nd(III), but another band appears at 868 cm^{-1}, which might be the associated complexed ν(P–O) band. If this is the case, it would indicate a strong interaction of the second oxygen in the HEH[EHP] ligand with the Nd(III) center. This in turn would suggest a complex of the type NdA$_3$ rather than Nd(AHA)$_3$ where A represents the deprotonated HEH[EHP] anion and AHA represents a mono-deprotonated HEH[EHP] dimer. Further investigation of this hypothesis is needed.
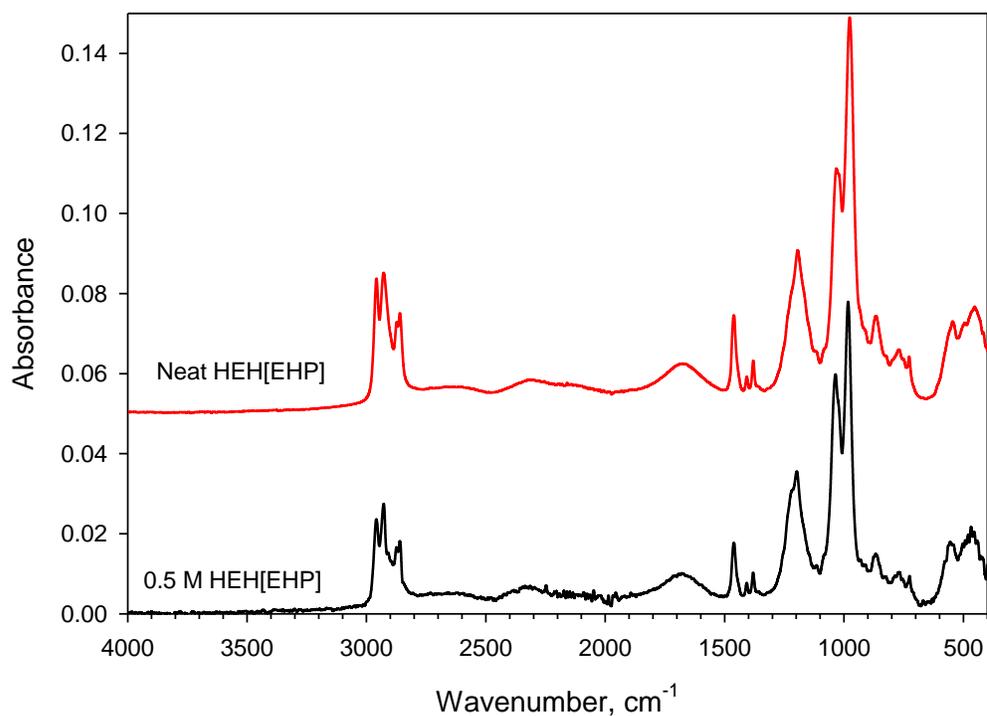
Figure 4.8. Comparison of the FTIR spectrum of neat HEH[EHP] to that of 0.5 mol/L HEH[EHP] in *n*-dodecane.

Table 4.1. FTIR band assignments for HEH[EHP] and the Nd-HEH[EHP] complex. [a]

| | **HEH[EHP]** | |
Band Assignment	**Neat/0.5 mol/L**[b]	**Nd-HEH[EHP] Complex**[c]
P=O	1194/1198	1163
O–H (H-bonded)	1675/1679	Not observed
P–O	976/983	868 (tentative)
C–O–P	1032/1036	1055,1066

[a] Band assignments are made based on those made by Tkac et al. (2012); all values reported in units of cm^{-1}.
[b] 0.5 mol/L in *n*-dodecane.
[c] 0.0193 mol/L Nd loaded into 0.5 mol/L HEH[EHP].
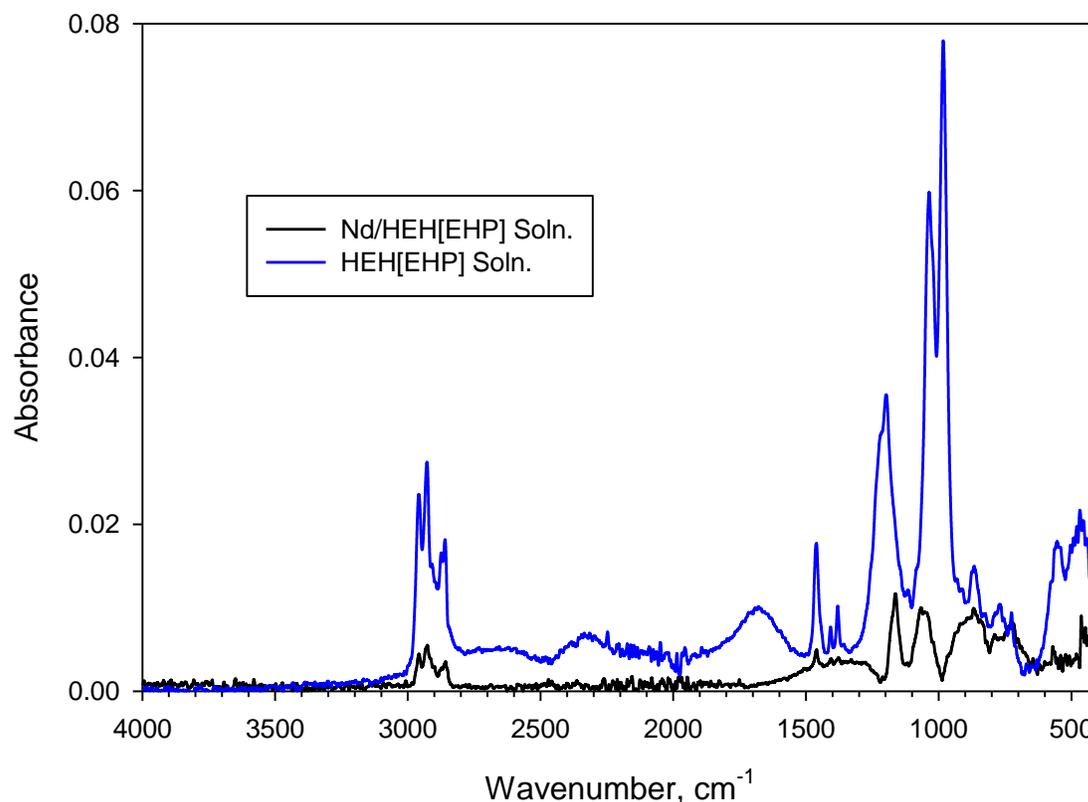
Figure 4.9. FTIR spectrum of 0.5 mol/L HEH[EHP] in *n*-dodecane, before and after loading with
0.0193 mol/L Nd.

To explore the complexation of CMPO to the Nd-HEH[EHP] complex, a series of *n*-dodecane solutions containing constant total HEH[EHP] concentration (0.25 mol/L), constant total Nd concentration (9.66×10^{-3} mol/L), and variable CMPO concentration (0 to 0.1 mol/L) was prepared, and the visible spectrum of each was recorded. Figure 4.10 presents an overlay of the spectra obtained. At the time of writing, full analysis of this spectral data set to determine the complexation constant for the Nd-HEH[EHP]-CMPO ternary complex had not been completed. However, some qualitative observations concerning the strength of CMPO binding in this system can be made. As indicated by the relatively small changes in the hypersensitive $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ transitions (560 – 610 nm), the complexation of CMPO to the Nd-HEH[EHP] complex appears to be much weaker than for the analogous HDEHP system. Significant spectral changes were observed for the hypersensitive bands after adding CMPO to the Nd-HEDHP system (Lumetta et al. 2012b).

The visible spectrum of the Nd-HEH[EHP]-CMPO ternary complex was isolated by subtracting the spectrum of the Nd-HEH[EHP] complex (spectrum α in Figure 4.10) from the spectrum obtained when 0.1 mol/L CMPO was added (spectrum L in Figure 4.10) (subtraction factor = 0.55). Figure 4.11 shows the resulting spectrum. Also shown in Figure 4.11 is the spectrum obtained for the Nd-HDEHP-CMPO system at a CMPO/Nd ratio of ~4. Two points can be made regarding these data. First, in the case of the Nd-HEH[EHP]-CMPO system, at a CMPO/Nd ratio of ~10, the spectrum attributed to the binary Nd-HEH[EHP] complex had to be mathematically subtracted to reveal the spectrum of the ternary Nd-HEH[EHP]-CMPO complex. In contrast, no spectral manipulation was necessary to reveal the spectrum of the Nd-HDEHP-CMPO ternary complex, even at a lower CMPO/Nd ratio of 4. Again, this supports the notion that the complexation of CMPO to Nd(III) in the HEH[EHP] system is significantly weaker than in the HDEHP system. Second, the visible spectra of the ternary complexes is very similar in both the

HEH[EHP] and HDEHP systems, suggesting that the structural aspects of the complexes are the same in both systems.
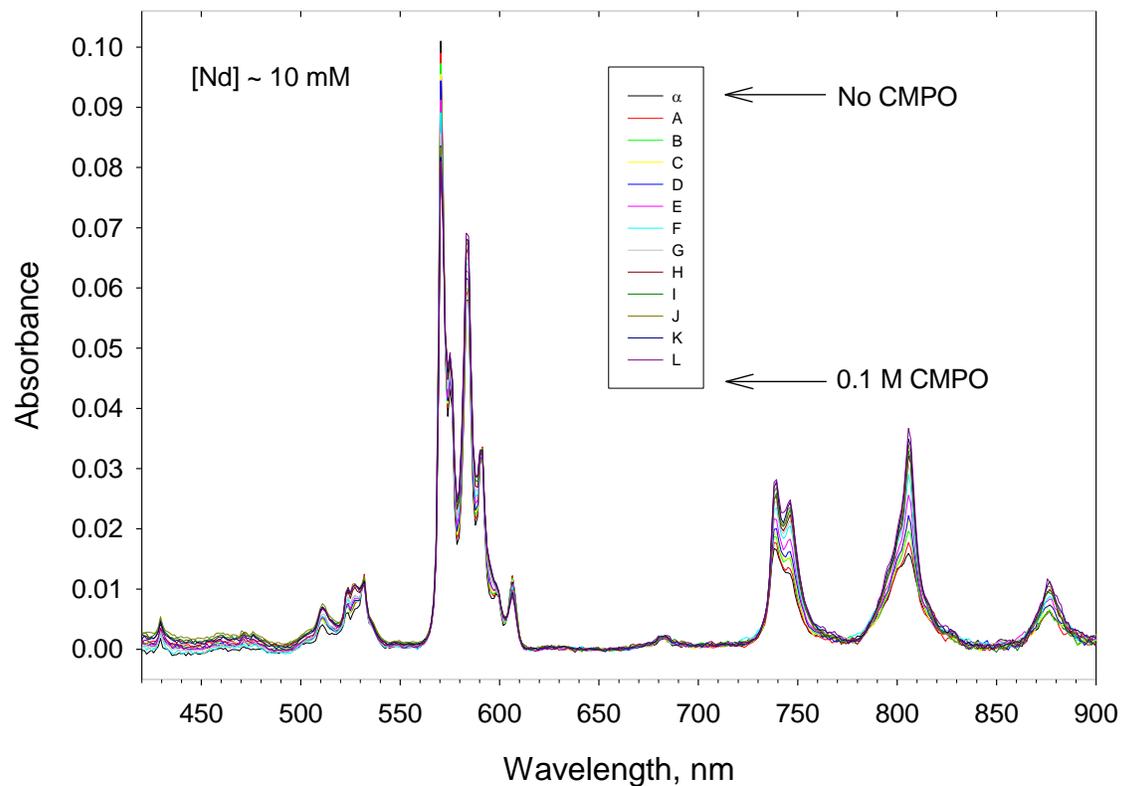
Figure 4.10. Overlay of the visible spectra obtained for 0.25 mol/L HEH[EHP] + 9.66 × 10^{-3} mol/L Nd + variable CMPO system.
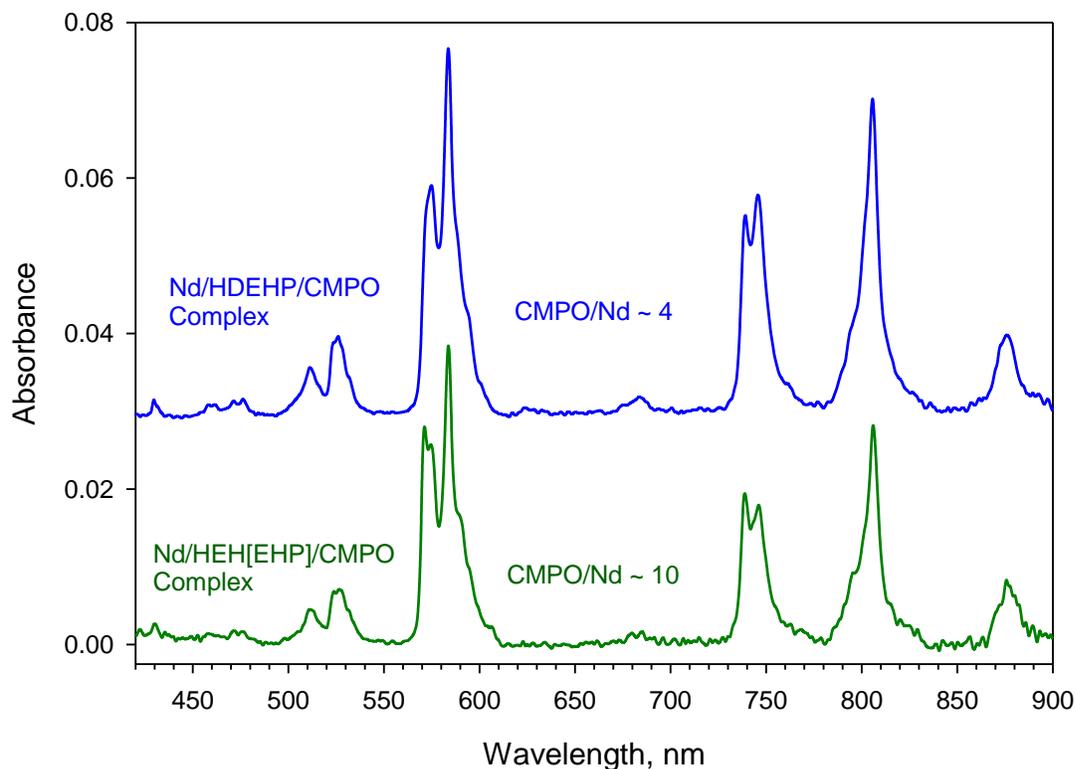
Figure 4.11. Visible spectra of the Nd-HEH[EHP]-CMPO and Nd-HDEHP-CMPO ternary complexes. See text for details.

4.6   Conclusion

Combining the extractants CMPO and HEH[EHP] into a single solvent with *n*-dodecane as the diluent is a promising approach for developing a single-step process for separation of the minor actinides from acidic high-level liquid waste. The CMPO + HEH[EHP] system has a number of advantages over the analogous CMPO + HDEHP system, including:

1. improved performance for the co-extraction of lanthanides and actinides from nitric acid media

2. less sensitivity to the pH during the stripping of the minor actinides

3. reduced synergistic extraction behavior, which in turn leads to higher lanthanide/actinide separation factors.

The transition metal fission products Mo(VI) and Zr(IV) are extracted into the CMPO + HEH[EHP] solvent. Molybdenum can be easily scrubbed out by contacting with citrate solution. Zirconium remains in the solvent through the minor actinide stripping step. Ideally, the Zr(IV) would be stripped along with the lanthanides, but methods to achieve this must still be developed and demonstrated.

Spectroscopic studies suggest the binding of CMPO to Nd(III) in the HEH[EHP] system is significantly weaker than in the analogous HDEHP system. This is perhaps because of the higher basicity of the deprotonated HEH[EHP] anion compared to the deprotonated HDEHP anion. It can be envisioned that the higher basicity of the HEH[EHP] anion leads to greater electron density at the Nd(III) center, thereby reducing the strength of the CMPO-Nd coordinate bond.

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7.   COLLABORATORS AND PARTICIPANTS

The key PNNL 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

- 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

Our collaborators at Argonne National Laboratory are Artem Gelis, Peter Tkac, and George Vandegrift.