

AN ABSTRACT OF THE DISSERTATION OF

Brian J. Gullekson for the degree of Doctor of Philosophy in Nuclear Engineering
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Title: Organic Phase Inter-Ligand and Metal-Ligand Speciation in TALSPEAK and
ALSEP Solvent Extraction Systems

Abstract approved:

Alena Paulenova

Partitioning of trivalent actinides (in particular, americium and curium) from the fission produced light lanthanides is a major concern of used nuclear fuel reprocessing for the purposes of waste disposal. Several solvent extraction processes have been developed to address these chemically difficult separations. The historically employed TALSPEAK Process utilizes di-2-ethylhexyl phosphoric acid (HDEHP), a cation exchange extractant as an organic phase extractant, while the Advanced TALSPEAK Process utilizes 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEH[EHP]), its phosphonic acid analog as an organic extractant to alleviate processing problems. The newly developed mixed extractant ALSEP Process utilizes either HDEHP or HEH[EHP] in conjunction with either tetraoctyldiglycolamide (TODGA) or tetra-2-ethylhexyldiglycolamide (T2EHDGA), collectively DGA, to perform two separation steps in a single process. The nature of organic phase chemical interactions in these systems must be clarified in order to effectively model and operate them on an engineering scale.

Neodymium speciation in HDEHP organic phases, the organic extractant used in the TALSPEAK Process, have been subject to multiple interpretations necessitating further investigations. UV-Visible spectroscopy coupled with Karl-Fischer titrations reveal that water in the inner neodymium coordination sphere results in an increase in the metal coordination number. Furthermore, the extraction of water was found to be independent of metal concentration, but was dependent on the HDEHP concentration. Investigating across the lanthanides revealed that light f-elements (americium, praseodymium, and

neodymium) can contain inner-coordination sphere water, while heavier lanthanides (samarium, holmium, and erbium) cannot, presumably due to their smaller ionic radii. For HEH[EHP] organic phases, the Advanced TALSPEAK extractant, water extraction was found to be similarly independent of metal concentration and dependent on HEH[EHP] concentration, although a weaker water extractant. Compared the HDEHP, only the lightest lanthanide measured (praseodymium) revealed a change in UV-Vis spectra resembling a speciation change, suggesting that only the lightest of lanthanides can occupy water in the inner-metal coordination sphere.

Characterization of the organic phase of the ALSEP Process is necessary to advise scaling efforts and to identify any potential difficulties which may exist due to inter-ligand interactions. The ALSEP ligand combinations tested were HDEHP - T2EHDGA, HEH[EHP] - TODGA, and HEH[EHP] - T2EHDGA. IR spectroscopy shows that the ability of the ALSEP ligand combinations to form intermolecular adducts in metal-free organic phases are relatively similar, although approximately an order of magnitude lower for the HDEHP - CMPO combination proposed for the previously developed TRUSPEAK system. Metal loaded IR spectroscopy shows that, when trivalent lanthanides are extracted from an aqueous phase which should not allow for the formation of neutral DGA solvates, the nature of the DGA carbonyl bond is shifted for the HDEHP - T2EHDGA system and the HEH[EHP] - TODGA system, but not for the HEH[EHP] - T2EHDGA system. Job's Method further reveals that, for the ligand combinations which are measured to form ternary species, a 1:6:1 ratio of the cation exchange extractant to the DGA forms with metals in the organic phase. UV-Vis titrations further reveal that HDEHP - T2EHDGA forms ternary species the strongest with extracted metals, followed by HEH[EHP] - TODGA and HEH[EHP] - T2EHDGA. Furthermore, americium forms ternary species the strongest with ALSEP ligand combinations, followed by neodymium and holmium.

Finally, the dependence of organic phase nitrate on the complexation of metals in the ALSEP process was investigated for advising process operations. IR spectroscopy revealed that titration of an organic phase containing a DGA loaded with nitric acid shifts the metal coordination from the cation exchange ligand to the DGA similar to extraction of metal from a high concentration nitric acid aqueous phase. UV-Vis titration addition of nitrate to a metal loaded organic phase reveals that, in general, TODGA is more able to

accommodate metal-nitrate complexes than T2EHDGA and the neodymium more strongly complexes with DGAs in the presence of nitrate than holmium. Also seen is that holmium exists in a complicated coordination environment at higher organic phase nitrate concentration, potentially indicating some process issues.

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Organic Phase Inter-Ligand and Metal-Ligand Speciation in TALSPEAK and ALSEP
Solvent Extraction Systems

by
Brian J. Gullekson

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I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

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I. Experimental Justification and Approach

1.1 Used Nuclear Fuel (UNF) Characteristics

Since its discovery, the released energy and resultant products of nuclear fission have been utilized for commercial, medical, and military uses. The elemental distribution of nuclear reactor fuel, following irradiation in a nuclear reactor, is incredibly complex, containing over half of the periodic table in varying concentrations.¹ Of particular concern are lanthanides and the trivalent minor actinides which are very similar chemically, but possess differing neutronic properties and must be separated for actinide transmutation in fast spectrum nuclear reactors.² Various chemical processes have been developed to separate these two species, however several are dependent on tight processing parameters and most utilize large quantities of hazardous chemicals, making engineering scaling difficult. The work detailed herein entails the development of a new trivalent actinide – lanthanide separation technique designed to reduce the generated chemical waste while improving safety and simplifying the process flowsheet.

Nuclear fission is the cleavage of a heavy nucleus, resulting in the release of energy and the creation of two or more smaller nuclei, or fission products. The fission process also typically releases several neutrons which can perpetuate a fission chain reaction. Actinides are typically used as fuel in nuclear reactors due to their favorable energetics for maintaining a fission chain reaction. Most actinides are fissionable, or able to fission by neutron bombardment. Certain actinides, however, are fissile, meaning that low energy, or thermal neutrons can cause them to fission. Nuclides such as ^{235}U , ^{233}U , ^{241}Pu , and ^{239}Pu are fissile isotopes which can maintain a chain reaction after their fission produced neutrons are reduced in energy. The vast majority of global commercial nuclear power reactors, including all U.S. power reactors, are light water reactors which utilize thermal neutrons for fission, requiring fissile isotopes. Natural uranium contains about 0.7% ^{235}U , which is enriched to about 4 – 5% through mass based separations for use in LWR as uranium dioxide.³

The majority of energy released in the fission process is imparted as kinetic energy to fission products. The total mass of the fission products is equal to the mass and initial energy of the pre-fission nucleus and incident neutron minus the mass of the neutrons produced, their energies, and the energy produced from the fission event. The mass numbers of the fission products are equal to the mass number of the fissioned product and its incident neutron minus the number of neutrons released from the event, with most thermal fission events

producing 2-3 neutrons per fission event.⁴ The masses of the two fission products are distributed between the two products in empirically determined percentages, as shown in Figure 1.1.⁵

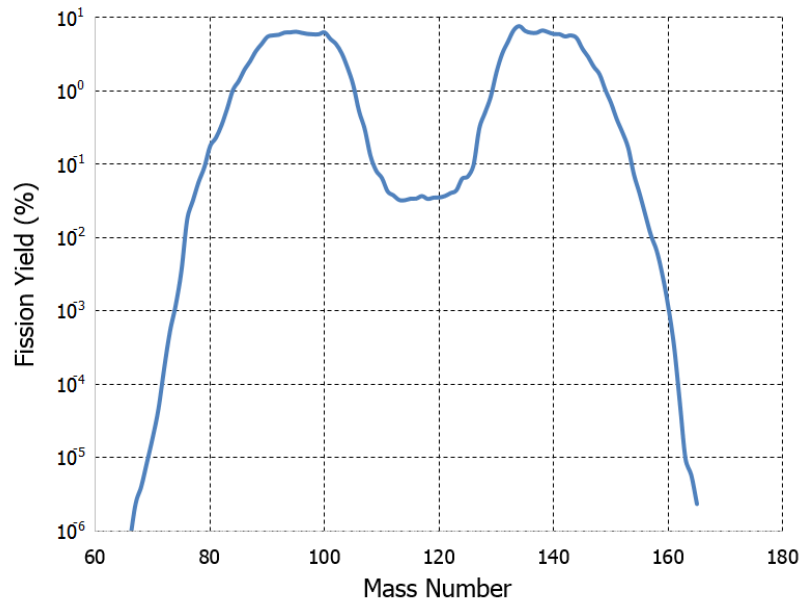


Figure 1.1 – Percentage of Fission Products Produced by U-235 Fission by Mass Number

In Figure 1.1, the total fission yield is equal to 200%, as the masses are distributed between 2 fission products. The majority of the fission products have an excess number of neutrons than what is required for stability, and therefore undergo β^- decay until they attain stability. This results in a variable elemental distribution in the fuel over time. When PWR fuel has produced 33,000 MWd/T, after a 10 year cooling time, the elemental distribution of the fuel is shown in Figure 1.2.¹

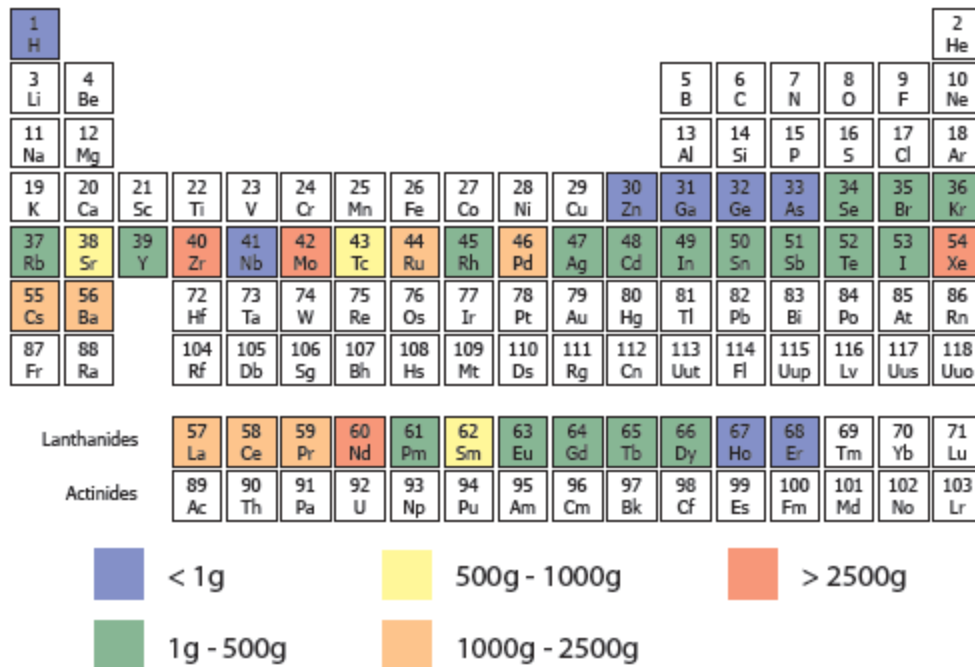


Figure 1.2 – Fission Products in UNF after a 10 Year Cooling Time

Another outcome of subjecting nuclear fuel to high neutron fluxes is neutron capture that does not result in fission, allowing for the breeding of higher atomic number transuranic elements through subsequent β^- decay.⁶ Plutonium and the minor actinides, the term applied to neptunium, americium, curium, and the small quantities of higher actinides produced, account for about 1% of the total mass of UNF.¹ These elements primarily emit alpha particles which are the highest energy form of radiation due to their mass. Furthermore, these elements typically have long decay chains, as they must serial decay down to lighter elements in order to achieve permanent stability. This long term, highly energetic decay makes the transuranic elements the primary radiotoxicity concern after the first thousand years of storage.⁷

One method of mitigating the effects of actinide disposal is by blending them into mixed oxide (MOX) fuels and transmuting them in nuclear reactors. By exposing the transuranic elements to high neutron fluxes in a reactor, more neutron capture can occur which can induce either faster decay or transmutation to fissionable isotopes, reducing the required repository time required by several orders of magnitude. In order to use MOX fuels, the transuranics must be separated from the fission produced-lanthanides as the lanthanides are strong neutron absorbers.^{7,8} This is especially difficult with americium and curium, which have similar ionic radii and the same trivalent oxidation states as many lanthanides, making

them very chemically similar and hard to separate.⁷ Several separation techniques have been developed to partition the lanthanides from americium and curium, however new processes are currently under development to address process non-idealities, reduce chemical waste, and improve safety.

1.2 Solvent Extraction Principles

The most globally developed means of UNF reprocessing is solvent extraction, where the natural immiscibility of two different liquids is utilized to perform chemical separations. Typically, UNF is dissolved into a strong mineral acid aqueous phase (such as nitric acid) and is then contacted with an oily, organic phase. One or both phases contain complexant molecules which affect the partitioning ability of desired metals between the two liquid phases. In the organic phase, extractant molecules contain highly polar regions intended to attract the polar metal cations from the aqueous phase as well as non-polar regions that allow for phase transfer into the bulk organic solution. Aqueous complexants on the other hand mostly contain polar regions intended to attract metals in the aqueous phase and prevent their transfer to the organic phase.

The ability of the chemical species to be extracted into an organic phase is defined by the species' distribution ratio, or D-value. This relationship is shown in Equation 1.1.

$$D_x = \frac{c_{x,org}}{c_{x,aq}} \quad (1.1)$$

In Equation 1.1, “D_x” is the distribution ratio of species x, “c_{x,org}” is the concentration of species x in the organic phase, and “c_{x,aq}” is the concentration of species x in the aqueous phase. Another important value to determine the effectiveness of UNF reprocessing schemes is the so-called separation factor, defined by the relationship in Equation 1.2.

$$SF_{xy} = \frac{D_x}{D_y} = \frac{c_{x,org}/c_{x,aq}}{c_{y,org}/c_{y,aq}} \quad (1.2)$$

In Equation 1.2, “SF_{xy}” is the separation factor of species x from species y, while “D_x” and “D_y” are the distribution ratios of species x and species y respectively. The effectiveness

of a reprocessing scheme depends on both the D-values of the individual species, as well as the separation factors of chemical species that are desirable to separate.⁶

Typical solvent extraction processes have three primary steps: extraction, scrubbing, and stripping. Each of these steps involve multiple stages with countercurrent phase flow intended to optimize efficiency. The extraction stage involves transferring the chemical species of interest from an aqueous feed stream to an extractant containing organic phase. The aqueous phase and any unextracted metal are carried away as a raffinate, while the loaded organic phase, or extract, is carried on to the scrub stage. Next, the scrubbing stage brings the extract into contact with a fresh aqueous phase which does not contain any metal. This helps to back extract any unwanted species which had transferred to the organic phase. The post-scrubbing aqueous phase is combined with the fresh aqueous feed stream in the extraction stage to reextract any desired metals stripped in the scrub stages. Finally, the scrubbed extract is brought into contact with a stripping solution, removing the extracted metal into an aqueous product stream. This type of processing, called counter-current processing, is illustrated in Figure 1.3.⁶

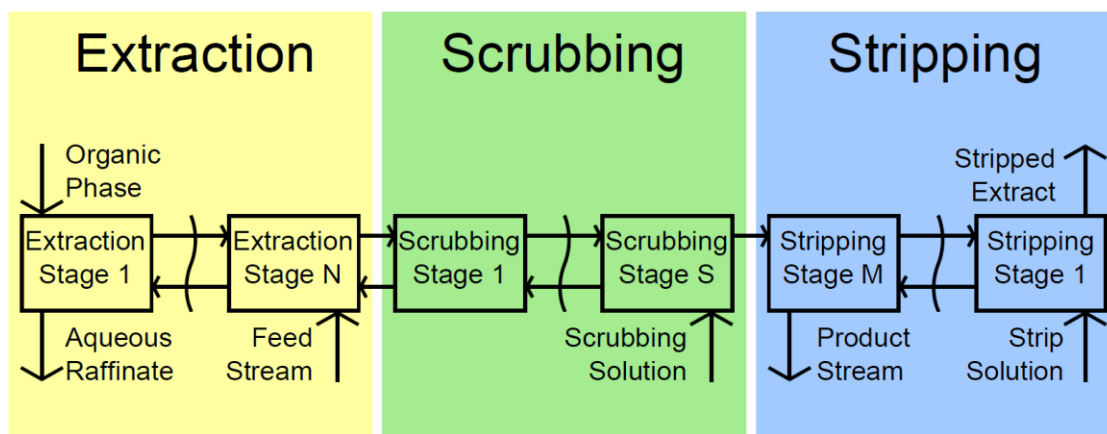


Figure 1.3 – Typical Solvent Extraction Process Operation

One of the most well studied reprocessing schemes, and the typical initial process in multi-process efforts, is the Plutonium Uranium Refining by EXtraction (PUREX) process. The PUREX process was developed in the 1950s out of the Redox Process to isolate uranium and plutonium from all other chemical species in UNF for the purposes of weapons production. UNF in moderate concentration nitric acid ($\sim 2 - 3\text{M}$, although the exact concentration can be tailored to the needs of the process) is contacted with an organic phase

consisting of 30% tributyl phosphate (TBP) in an n-dodecane or kerosene diluent.^{8,9} TBP preferentially binds with tetravalent and hexavalent f-elements, meaning that uranium and plutonium are selectively extracted as UO_2^{2+} and Pu^{4+} to the organic phase while neptunium, americium, and curium, all primarily trivalent or pentavalent, remain in the aqueous phase. Since TBP is a solvating molecule, charge balancing nitrate anions are coextracted with the metal, as shown in Figure 1.4.¹⁰

Once bulk uranium has been removed from the mixed UNF matrix, more individual

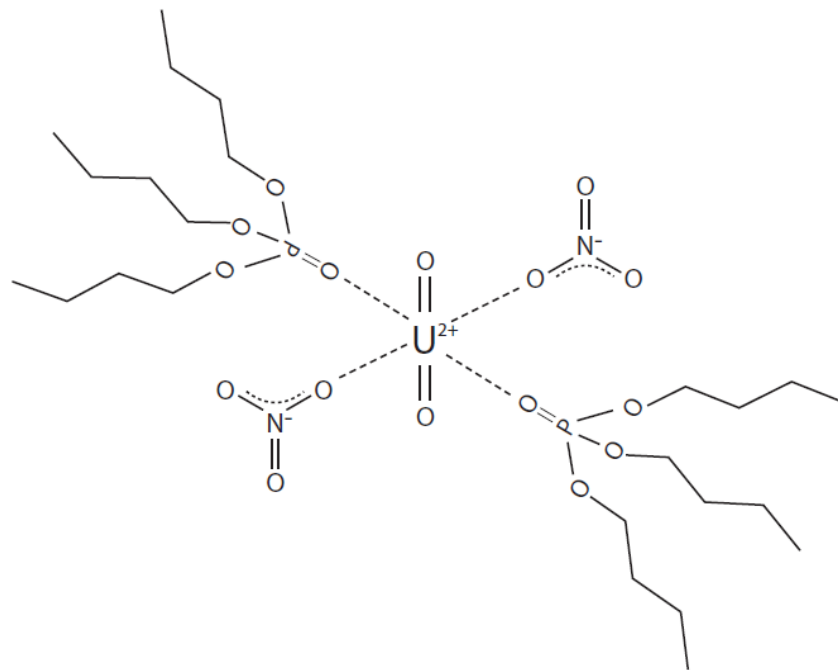


Figure 1.4 – Uranyl Nitrate – TBP Complexes Formed in the PUREX Process

separations can be performed, such as the isolation of radionuclides which potentially pose problems for long-term disposal or those which have the potential for reuse. One process suite developed was UREX+ in the mid-2000s at Argonne National Laboratory. UREX+ combined a number of processes to address several problems of final waste preparation.¹¹ The first process employed was a slight revision to PUREX, named UREX. In the UREX process, a reducing agent acetohydroxamic acid is added to a typical PUREX aqueous phase in order to reduce plutonium to the trivalent oxidation state, preventing its extraction to the organic phase.¹² This removes the bulk of the UNF, extracting all of the uranium (as well as

technetium) from the UNF aqueous phase.¹³ Several other treatments, such as the isolation of cesium and strontium (major heat contributors in the first several hundred years of proposed geologic repositories) and recovery of neptunium and plutonium are also proposed in the UREX+ schemes.^{14,15} The final step in each version of the UREX+ suite is the separation of trivalent minor actinides and lanthanides through two processes; the TRUEX process followed by the TALSPEAK process.

1.3 The TRUEX Process

The TRUEX Process was developed in the 1980s as a means of selectively partitioning trivalent f-elements from PUREX raffinates. Carbamoylmethyl phosphine oxide (CMPO, Figure 1.5) ligands with a single phenyl group and varying alkyl chains were shown to effectively complex americium and lanthanides from high acidity HNO_3 solutions.¹⁶ Phenyl group substitution leads to improved extraction of americium at high acidities and reduced extraction at low acidities, however the solubility of metal loaded organic complexes in the organic phase is reduced.¹⁷ When multiple alkyl chain types were investigated, octyl- and phenyl- groups bound to the phosphine oxide site and two isobutyl- groups bound to the amide site showed the greatest extraction of americium. This extractant tended to form third phases, which are extractant and metal rich regions partially comprised of the organic and aqueous phase. As such, third phases have a density between the densities of the organic and aqueous phase and settle between them in equilibrium. Third phase formation is a very undesirable effect as they are significantly more difficult to physically separate and has potential criticality concerns due to concentration of the complexed metals. Third phase formation was prevented by using slightly polar organic phases, such as aromatic or halogenated organic diluents or in the presence of phase modifiers; other organic phase molecules which prevents the formation of large reverse micelles, which lead to third phases.¹⁸ Tributyl phosphate, the PUREX extractant molecule was seen to be effective at preventing third phase formation.¹⁹ The generic equilibrium model for metal extraction into a CMPO

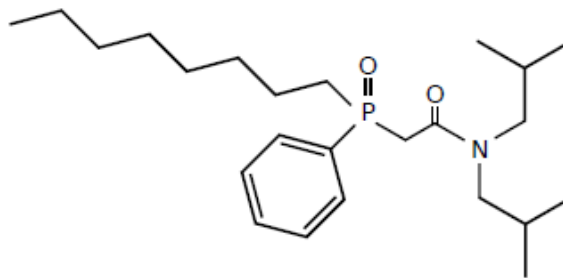
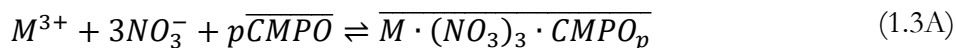


Figure 1.5 – CMPO, the TRUEX Organic Phase Extractant

loaded organic phase is shown in Equations 1.3A with the equilibrium constant defined in Equation 1.3B.



$$K_{ex} = \frac{[\overline{M \cdot (NO_3)_3 \cdot CMPO_p}]}{[M^{3+}][NO_3^-]^3[\overline{CMPO}]^p} \quad (1.3B)$$

Since CMPO is a solvating ligand, metal charge balancing anions must be coextracted to maintain net charge neutrality. As indicated in the equilibrium constant equation, an increase in the concentration of the nitrate anions in the aqueous phase leads to increased metal extraction into the organic phase. This increase in nitrate concentration can be accomplished through the introduction of salts such as NaNO₃ to the aqueous phase or by increasing the acidity of the aqueous phase. For extraction of americium from variable nitric acid concentrations into 0.2M CMPO + 1.2M TBP in an aliphatic hydrocarbon diluent, a maximum extraction is achieved at ~2M HNO₃, slightly decreasing in extraction ability at higher acid concentrations. This is largely believed to be because of the ability of CMPO to extract nitric acid, such that the extractant can be saturated by HNO₃ when extracting from high acidity.

1.4 The TALSPEAK Process

Following the separation of trivalent f-elements from all other constituents of UNF, specialized processes can be used to partition the actinides from lanthanides. The Trivalent Actinide Lanthanide Separation by Phosphorus Extraction of Aqueous Komplexes (TALSPEAK) Process was developed at Oak Ridge National Laboratory in the 1960's as a means of partitioning americium and curium from bulk lanthanides.²⁰ The TALSPEAK process utilizes two competing chemical mechanisms, each with slight favorability toward either actinides or lanthanides which, when combined, can effectively separate them. Di-2-ethylhexylphosphoric acid (HDEHP, Figure 1.6A) is used as an organic extractant in an aliphatic diluent (typically n-dodecane), while diethylene triamine pentaacetic acid (DTPA, Figure 1.6B) is used as an aqueous holdback reagent in a buffered aqueous phase. HDEHP is

a powerful metal complexant with significant oxygenation, making it a hard electron donor which will more preferentially bind with the harder character of lanthanides over trivalent actinides.²¹ DTPA is more nitrogenated making it a slightly softer electron donor, meaning that it

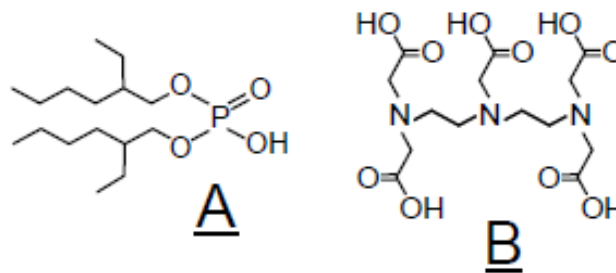


Figure 1.6 – TALSPEAK Metal Complexant Molecules: HDEHP (A) and DTPA (B)

more preferentially binds with softer trivalent actinides as opposed to lanthanides, per Pearson’s HSAB Theory.^{22,23} With these two extractants competing in the TALSPEAK liquid phases, lanthanides are extracted by the HDEHP molecule, while trivalent actinides are retained in the aqueous phase by DTPA, effectively separating them.²²

HDEHP is a cation exchange ligand which must be deprotonated to complex with a metal. Upon complexation, however, the charge of the metal does not need to be offset by an accompanying anion to transfer from the aqueous to the organic phase. Furthermore, it has been observed that, in strongly non-polar solutions such as the aliphatic hydrocarbons used in TALSPEAK, HDEHP almost entirely exists as a bimolecular complex called a “dimer.” Dimerization occurs when the highly polar functional group of HDEHP (or analogous organic-soluble acid) orients itself with the functional group of another acid molecule in solution.²⁴ This orientation is more thermodynamically favorable for organic acids in non-polar solutions as the polarity of the functional group is shielded from the bulk solvent by the outward pointing hydrocarbon tails. The chemical equilibrium of dimerization is shown in Equation 1.4A, while the equilibrium constant is defined by Equation 1.4B.²⁴



$$K_{dim} = \frac{[(\overline{HDEHP})_2]}{[\overline{HDEHP}]^2} \quad (1.4B)$$

It has further been shown that HDEHP dimers, as opposed to monomers complex metals in aliphatic hydrocarbon diluents, meaning that six HDEHP molecules are required to

compensate the charge of a single trivalent metal.²⁵ The generalized chemical equilibrium equation for TALSPEAK metal extraction is shown in Equations 1.5A with the equilibrium constant defined by Equation 1.5B.²²



$$K_{ex} = \frac{[\overline{M \cdot (H(DEHP)_2)_3}][H^+]^3}{[M^{3+}][\overline{(HDEHP)_2}]^3} \quad (1.5B)$$

As indicated in the equilibrium constant equation, an increase in the acidity of the aqueous phase drives the reaction backward, meaning that the metal extraction must be performed from a high pH aqueous phase. Furthermore, HDEHP contributes acid protons to the aqueous phase upon dissociation, altering its acidity. For this reason, a weak acid is used as an aqueous phase to stabilize the pH between 2 and 4, a region where it has been shown that TALSPEAK separations are most effective.²²

DTPA-metal complexes form through the interaction of the metal with one of the eight active sites on the molecule, the five carboxylic acid groups and amine lone pairs. In aqueous solutions, DTPA can form nine possible species based on its possible protonation states. Equilibrium constants have been measured for each protonation reaction by potentiometric titration, allowing for speciation diagrams to be prepared to indicate the nature of DTPA across the range of acidities. Table 1.1 shows these constants for a temperature of 25.0 ± 0.1 °C and an ionic strength of 1M in Na^+ media, while Figure 1.7 shows the speciation of DTPA under these conditions.

Table 1.1. DTPA Protonation Constants at 25.0 ± 0.1 °C and 1M Ionic Strength in Na^+ Media^{26,27}

DTPA Protonation Reactions	log K
$\text{R}^{5-} + \text{H}^+ \leftrightarrow \text{HR}^{4-}$	9.50
$\text{HR}^{4-} + \text{H}^+ \leftrightarrow \text{H}_2\text{R}^{3-}$	8.15
$\text{H}_2\text{R}^{3-} + \text{H}^+ \leftrightarrow \text{H}_3\text{R}^{2-}$	4.11
$\text{H}_3\text{R}^{2-} + \text{H}^+ \leftrightarrow \text{H}_4\text{R}^-$	2.70
$\text{H}_4\text{R}^- + \text{H}^+ \leftrightarrow \text{H}_5\text{R}$	2.19
$\text{H}_5\text{R} + \text{H}^+ \leftrightarrow \text{H}_6\text{R}^+$	1.87
$\text{H}_6\text{R}^+ + \text{H}^+ \leftrightarrow \text{H}_7\text{R}^{2+}$	0.8
$\text{H}_7\text{R}^{2+} + \text{H}^+ \leftrightarrow \text{H}_8\text{R}^{3+}$	-0.1

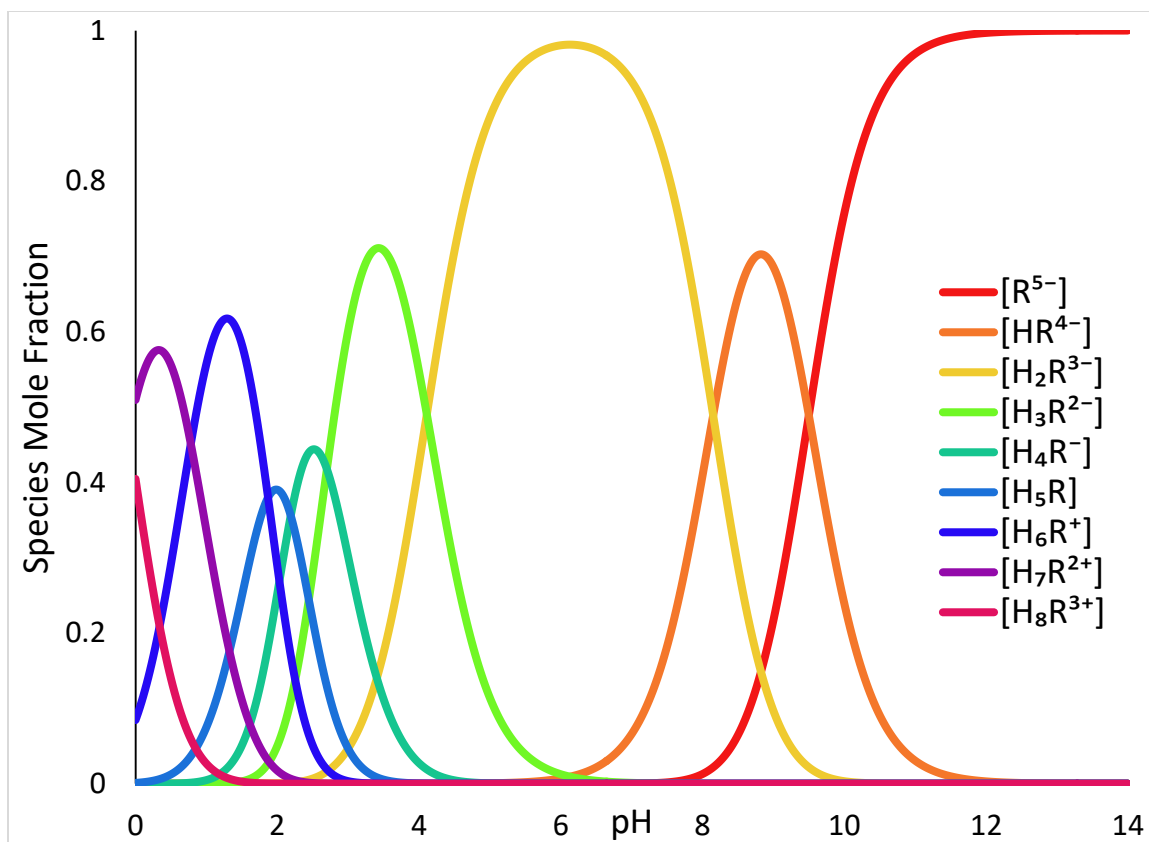


Figure 1.7. DTPA Speciation in Aqueous Solutions of Various Acid Strengths at 25.0 ± 0.1 °C and 1M Ionic Strength in Na^+ Media

As shown in Figure 1.7, for the aqueous phase conditions favorable to the TALSPEAK Process, there are 5 major potential DTPA species: H_2R^{3-} , H_3R^{2-} , H_4R^- , H_5R , and

H_6R^+ . The protonation constants for this system vary in differing environments however, such as with changes in temperature, ionic strength, and ionic media meaning that Figure 1.7 should therefore be considered representative. With trivalent actinides and lanthanides on the other hand, DTPA has been seen to form metal complexes in this acid range by the equilibria defined in Equations 1.6A and 1.6B.²⁸

$$\beta_{101} = \frac{[MR^{2-}]}{[M^{3+}][R^{5-}]} \quad (1.6A)$$

$$\beta_{111} = \frac{[MHR^-]}{[M^{3+}][H^+][R^{5-}]} \quad (1.6B)$$

These two possible metal species (one protonated and one not protonated) are the mechanism by which trivalent actinides are retained in the aqueous phase, however it is plainly evident that the chemical nature of DTPA in the aqueous phase is subject to complicated chemical equilibria.

The buffer selected to maintain the pH in the range of 2 - 4 has a large effect on process operations. Buffers selected must have an acid dissociation constant (pKa) which can keep the pH in the range of effectiveness for the process, but further complications arise as these species can interact with the metals and the metal complexants in solution, potentially increasing the complexity of the system equilibrium. Historically, lactic acid (Figure 1.8) was the preferred buffer for the TALSPEAK process, as its pKa at infinite dilution is 3.86, which allows for the pH to be stabilized in the optimal process range. Lactic acid however, has been seen to complex lanthanides, albeit more weakly than HDEHP or DTPA, and can be co-complexed to the DTPA or co-extracted to the organic phase as a metal-lactate complex or as lactic acid.^{29,30} Furthermore, in the presence of other metals such as zirconium, separation factors are decreased and precipitates can form.³⁰

The chemical equilibria in the TALSPEAK process have been subject to significant amounts of research in the past, however the process is sensitive to a great number of variables. The chemical equilibria can be disturbed by temperature changes, ionic strength changes, ionic media

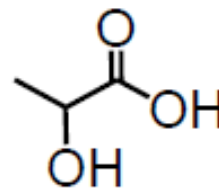


Figure 1.8 – Lactic acid, the TALSPEAK buffer molecule

selection, organic phase diluent selection, changes in the concentrations of the dissolved fuel constituents, and changes in the concentration ratios of the extractants and buffers, among others. Partially due to these complications, a functional, accurate chemical model has not yet been prepared which could predict the behavior of the TALSPEAK process based on process inputs.

1.5 The TRUSPEAK Process

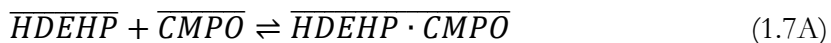
In the development of solvent extraction for UNF reprocessing, several processes have been developed which combine multiple extractant molecules into a single organic phase.³¹ Combining extractants can lead to a system where extraction performance is synergistically improved, or allow for multiple separations in a single stage, reducing waste and simplifying process flowsheets.^{32,33} One proposed mixed extractant scheme is the TRUSPEAK process, which combines HDEHP, the TALSPEAK ligand with CMPO, the TRUEX ligand into a single organic phase.³⁴ As a solvating extractant, CMPO requires a high anion concentration for metal extraction. Conversely, HDEHP must extract from a higher pH aqueous phase in order to deprotonate and complex metals. These opposing aqueous conditions provide the potential for multiple separations in a single process.

The TRUSPEAK process was designed to treat PUREX raffinates in order to partition trivalent minor actinides from lanthanides. The PUREX process operates with a moderate concentration nitric acid aqueous phase, meaning that both the minor actinides and lanthanides can be coextracted from the raffinate without significant adjustment using CMPO. Following extraction, the remaining fission products are carried away in the TRUSPEAK raffinate, while a TALSPEAK aqueous phase is contacted with the loaded organic phase. This aqueous phase strips the trivalent minor actinides through DTPA complexation, while the lanthanides are retained in the organic phase by HDEHP in a reverse-TALSPEAK style step. Following partitioning, the lanthanides can then be stripped to the aqueous phase using a higher concentration of DTPA or an alternate, stronger aqueous phase complexant. The TRUSPEAK process promised to greatly reduce the chemical waste burden and complexity inherent to using the individual stages separately.

Unfortunately, the TRUSPEAK process suffered from several process problems, leading to lower-than-anticipated actinide lanthanide separations.³⁴ In both 1M HDEHP + 0.1M CMPO and 0.3M HDEHP + 0.2M CMPO organic phases, the extraction of fission

produced lanthanides and americium are seen to decrease with an increase in acidity.^{35,36} This is not anticipated, as the presence of a solvating extractant should lead to an increase in extraction at higher acidities. Furthermore, when extracting from pH 1.0 nitric acid into 0.1M HDEHP with varying concentration of CMPO, increasing the concentration of CMPO leads to a decrease in extraction.³⁷ This was accompanied by a relative increase in extractability of metals using 1M HDEHP + 0.1M CMPO at lower pH compared to 1M HDEHP in a typical TALSPEAK extraction, and a subsequent decrease in separation factors.³⁴

These process problems were determined to be caused by the formation of interligand adducts between the two extractant molecules in the organic phase.³⁸ The mechanism of adduct formation can be modelled as a competition between dimer formation in the organic phase. Dimerization was defined by Equations 1.4A and 1.4B, while the equilibrium of adduct formation is shown in Equation 1.7A with the equilibrium constant defined in Equation 1.7B.



$$K_{add} = \frac{[\overline{HDEHP \cdot CMPO}]}{[\overline{HDEHP}][\overline{CMPO}]} \quad (1.7B)$$

In Equations 1.7A and 1.7B, “K_{add}” is the constant for adduct formation. In aliphatic diluents, the base-10 logarithmic dimerization constant of HDEHP has been determined to be 4.43, and the adduct formation constant competing with dimerization has been determined to be 3.07 by ³¹P NMR spectroscopy and 3.4 by infrared spectroscopy.³⁸⁻⁴⁰ For an organic phase with 1M HDEHP and 0.1M CMPO, consistent with the extractant formulation for most proposed TRUSPEAK operations, these constants would mean that 83% or 91% (based on the constant applied) of the available CMPO would be bound in an adduct to an HDEHP molecule.

Further investigation of the system reveals that the HDEHP-CMPO adduct is a powerful metal complexant, and primarily behaves in the fashion of a cation exchange ligand. When HDEHP is present in a greater concentration than CMPO, complexes at low acidity extract metals as a combination of M(H(DEHP)₂)₃ and M(NO₃)(DEHP)₂(CMPO)₂, and at high acidities M(NO₃)₂(DEHP)(CMPO), although other complexes are likely present in the

organic phase.³⁸ These possible complexes further complicate the chemistry of TRUSPEAK-like systems, making the generation of a chemical model for predictive operations a nearly impossible task. For this reason, as well as the decreased trivalent minor actinide and lanthanide separation factors, the TRUSPEAK process was largely abandoned in the hopes of developing an alternative process which displays more predictable chemical behavior and favorable extraction characteristics.

1.6 Advanced TALSPEAK Processes

While the TALSPEAK process provides an efficient means of isolating trivalent actinides from bulk lanthanides, extraction ability is highly dependent on maintaining pH in the proposed operating range. This lack of pH stability is contrary to thermodynamically derived data at higher pH values and leads to a system which would be very difficult to predictably control from an engineering standpoint.⁴¹ This has led to investigations as to the cause of the deviation between expected and experienced process behavior, as well as the use of alternate reagents to mitigate these effects.⁴²

One of the major reasons thought to contribute to the lack of pH stability in TALSPEAK systems is the partitioning of the lactic acid buffer to the organic phase.⁴² Typical TALSPEAK aqueous phases call for lactic acid concentrations between 0.5M and 2M to hold the pH constant following the release of protons from the organic extractant to the aqueous phase. Using radiolabeled lactate, the effects of lactate partitioning under a variety of conditions was investigated.³⁰ It was revealed that lactic acid is the species primarily extracted into HDEHP in 1,3-diisopropylbenzene and is completely unconnected to the extraction of lanthanides at low metal loading. This indicates that lactic acid is the extracted species as opposed to some lactate-metal complex.³⁰ At higher metal loading however, lactate metal complexes can be extracted with differing stoichiometry.⁴³ Furthermore, lactate extraction increases with an increase in pH and with an increase in HDEHP concentration with a suggested 1:2 Lactic Acid:HDEHP ratio.³⁰

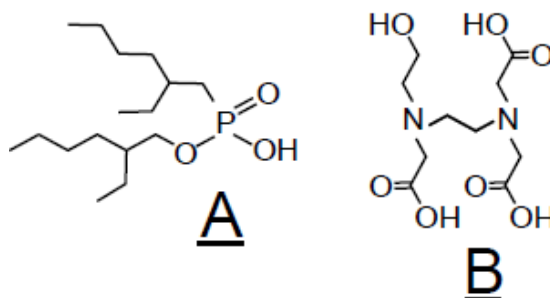
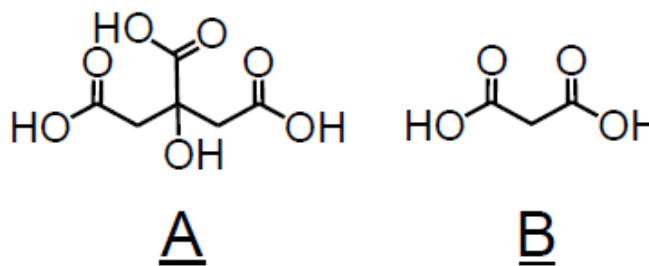


Figure 1.9 – Proposed Advanced TALSPEAK Molecules: HEH[EHP] (A) and HEDTA (B)

The occupation of potential metal extraction sites by organic phase lactate can help to explain the poor pH stability and extraction suppression at higher pH.

To address the difficulties of alternate aqueous species extraction, several new molecules have been proposed which have been shown to greatly improve process operations. 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEH[EHP], Figure 1.9A), the phosphonic acid analogue of HDEHP, has been used tested an alternative organic phase complexant for advanced TALSPEAK.⁴⁴ HEH[EHP] is a slightly weaker acid than HDEHP, and therefore a slightly weaker extractant, but still produces high An/Ln separation factors when used in conjunction with a weaker aqueous phase complexant, such as N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid (HEDTA, Figure 1.9B). In n-dodecane, HEH[EHP] exhibits a much flatter pH extraction profile, as well as reduced lactic acid extraction.⁴⁴ Kinetics of extraction are slower than HDEHP extraction however, meaning that an increased residence contactor time may be necessary for use in an industrial scale process.⁴⁵

Another area of interest for addressing problems with the TALSPEAK process is the exploration of alternate aqueous phase buffer molecules and metal complexants.⁴⁶ Citric acid (Figure 1.10A) has been proposed as a possible alternative to lactic acid for several reasons. Given its multiple functional groups, citric acid has a much higher potential buffer capacity. Also, issues of third phase formation, precipitation, and lowered lanthanide-actinide separation factors in the presence of zirconium are significantly reduced.⁴⁷ Other pathways for buffer development come from the observation that the TALSPEAK process exhibits improved kinetics at lower aqueous phase pH. Therefore, new buffer molecules which provide a higher buffer capacity at lower pH values could reduce the time required to reach equilibrium. Malonic acid (Figure 1.10B) has a pKa of 2.58 at I=1.0M as opposed to lactic acid, which has a pKa of 3.64 at I=1.0M, suggesting the possibility of stable aqueous phase acidity at a lower pH, and was therefore tested as a buffer. Lower pH extraction was demonstrated in this system, and malonate concentration was found to have little effect on extraction, however separation factors for light lanthanides and americium were



*Figure 1.10 – Proposed Advanced TALSPEAK Buffers:
Citric Acid (A) and Malonic Acid (B)*

slightly lower than with other buffers.⁴⁸ Other aqueous phase holdback reagents have also been proposed, such as dipicolinate ligands, although the aqueous phase solubility of the ligands is low, and more polar derivatives are currently being synthesized and investigated.⁴⁹

Further advancements of the advanced TALSPEAK process are attempts to develop combined extractant processes using newly introduced ligands. A TRUSPEAK-like system using CMPO in conjunction with HEH[EHP] in an aliphatic organic diluent was attempted. Promising separation factors were observed, however similar complications to the TRUSPEAK process were seen, notably depression of metal extraction at high acidities, suggesting significant interligand interactions in the organic phase.⁵⁰ Additionally, the TALSPEAK-MME (Mixed Monofunctional Extractant) process was tested, combining HEH[EHP] into solution with a mixed, monofunctional phosphine oxide extractant blend referred to as Cyanex-923. While metal stripping produced suitable separation factors using HEDTA as an aqueous complexant, americium extraction was seen to be depressed at high acidities in the presence of HEH[EHP]. Further developments of this process may yield more optimized results however, and the investigation into this system is ongoing.⁵¹

1.7 Complexation of f-Elements with Organophosphorus Acid Extractants

Despite extensive research into the nature of metal coordination in organic phases of cation exchange ligands such as HDEHP and HEH[EHP], gaps still exist in the understanding of what types of complexes form. One research group found that the complexation of neodymium in HDEHP organic phases changed based on the metal loading as a percentage of the extractant concentration. At low metal loading, species of the type $\text{Nd}(\text{H}(\text{DEHP})_2)_3$ were proposed, while at high metal loading, polynuclear species of the type $\text{Nd}_2(\text{DEHP})_6$ were proposed.⁵² These species produced different UV-Vis spectra, appearing to show an increase in the coordination number with a decreased metal loading percentage.^{52,53} The same research group found that the complexation of other f-elements, such as americium and curium change based on which cation exchange ligand is used.⁵⁴

Another research group later found that, in HDEHP organic phases, the metal loading percentage does not affect the UV-Vis speciation, and that a species of $\text{Nd}(\text{DEHP})_3$ is the most likely species present as compared to the spectral properties of a solid crystal prepared through methyl analogues of HDEHP. The differences in spectra were attributed to diacid impurities that were not completely removed from the HDEHP during reported purification

steps.⁵⁵ It was argued that these impurities would complex extracted metals more strongly than HDEHP, and produce a UV-Vis spectrum shift that resembled an increase in the coordination number of the metal.^{53,55} These explanations do not fully resolve the complexation questions

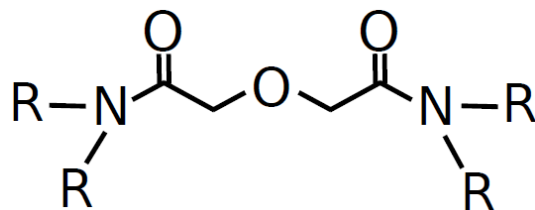


Figure 1.11 – Diglycolamide (DGA) Functional Group

present in cation exchange ligand organic phases however, and further investigation could provide valuable insights into the extractions performed in TALSPEAK-like systems.

1.8 Diglycolamide Complexants

A new group of diamide solvating ligands called diglycolamides has been studied over the last 15 years, and has been found to have several promising characteristics for coextraction of trivalent actinides and lanthanides from PUREX raffinates.^{56,57} Diglycolamides, or collectively DGAs, feature two amide groups separated by a methyl ether bridge, as shown in Figure 1.11. The nature of the R-group determines both ligand solubility and metal complexation ability. For tetraalkyl DGAs, with an increase in alkyl chain length, the molecule shifts from aqueous phase solubility to organic phase solubility, with tetraamyl- and tetrahexyl-DGA showing slight solubility in both phases. Furthermore, with an increase in alkyl chain length, the extraction distribution ratios of americium and europium decrease, most likely due to the steric hindrance of coordination with a more bulky ligand.⁵⁶

As DGAs are solvating ligands, the charge of the metals complexed must be counterbalanced by anions, typically coming from the aqueous phase mineral acid medium. The nature of such complexation has been investigated by x-ray crystallography. For low-R, aqueous phases DGAs (e.g., propyl- and butyl-), when crystalized with lanthanum, alternating LaDGA_3^{3+} and $\text{La}(\text{NO}_3)_6^{3-}$ sites were observed which indicate that the counterbalancing nitrate was outside of the inner metal coordination sphere.⁵⁸ Comparative studies of plutonium complexes with methyl-, ethyl-, and octyl- DGA in polar diluents suggest that, for the high R-chain DGAs, inner coordination sphere nitrate is possible.⁵⁹

While shorter-R chain DGAs have the potential to be used as aqueous phase holdback reagents, longer-R chain DGAs have attracted widespread interest as organic phase extractant molecules. The most commonly investigated organic phase DGA is tetraoctyldiglycolamide,

or TODGA (Figure 1.12A), where four, straight chain octyl- groups branch from the two amide sites. 0.1M TODGA in n-dodecane complexes metals as a 1:4 metal:ligand ratio at lower acidities, however reverse micellar aggregation and third phase formation occurs when extracting from higher acidities. In metal-free extraction studies with 0.1M TODGA in n-dodecane, a critical micellar concentration (CMC) of 0.7M HNO₃

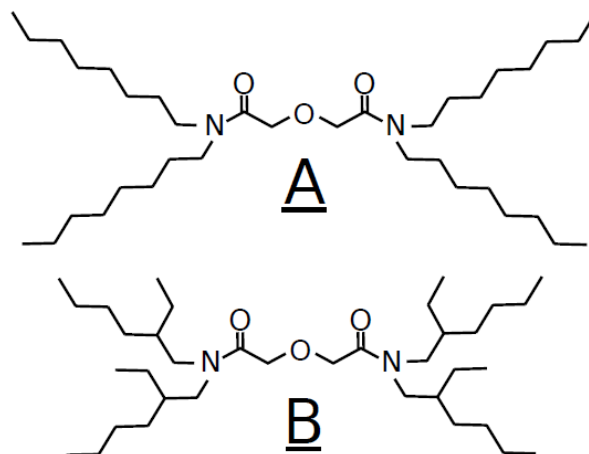


Figure 1.12 – Commonly Investigated Organic Phase DGAs: TODGA (A) and T2EHDGA (B)

was observed, and a value was not obtained in HCl systems due to the poor extractability of HCl.^{60,61} Interfacial tension measurements taken at the interface of a 2.0M HNO₃ aqueous phase and varying concentration TODGA in n-dodecane show that 0.1M TODGA is the CMC for this acidity meaning that this concentration may be the CMC for a range of acidities.⁶² When the organic diluent used was a branched hydrocarbon (hydrogenated tetrapropene), third phase formation was not seen until higher acidity aqueous phases (4-6M HNO₃) were used, indicating that phase modification could lead to expanded parameters of applicability for ligand use.⁶³

Several batch contactor tests were performed to test the ability of TODGA to separate trivalent actinides from lanthanides, revealing several aspects about the use of TODGA in engineering scale processes. Use of DTPA in the aqueous phase does not significantly change the extractability of light lanthanides, and can increase the separation factors of trivalent actinides and lanthanides to around 60.⁶⁴ For a 0.2M TODGA in n-dodecane or TPH organic phase, oxalic acid added to the aqueous phase both suppresses the extraction of zirconium and the formation of a third phase, and was seen to have little effect on the extraction of most metals in a PUREX raffinate simulant. Furthermore, TODGA was seen to show excellent radiolytic and hydrolytic stability.⁶³ Engineering scale centrifugal contactor studies were performed using fuel simulant and actual spent fuel and showed very high recovery of both americium and curium, with a minor contamination of yttrium and ruthenium in the final product.^{65,66}

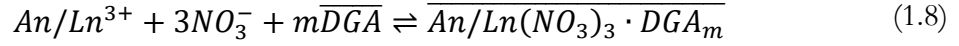
Another organic phase DGA receiving attention is tetra-2-ethylhexyldiglycolamide, or T2EHDGA (Figure 1.12B), which has the same alkyl chain length as TODGA, but contains branching at the β -position to the amide. T2EHDGA has been observed to form aggregates less readily in aliphatic diluents, which could prove beneficial for reduction of third phase formation.⁶⁷ It is also observed to be a less powerful extractant of americium, neodymium, and nitric acid than TODGA, but still possesses D-values approaching 100 at and above 3M HNO₃.⁶⁸ Similar to TODGA, T2EHDGA extraction systems in aliphatic hydrocarbon diluents require a phase modifier, such as N,N-di-n-hexyl octanamide (DHOA), isodecanol, or n-decanol to prevent the formation of interfacial phases when extracting from high acidities.^{69,70} Furthermore, the presence of phase modifiers was seen to reduce the radiolytic degradation of T2EHDGA (which results in reduced metal extraction) in gamma irradiation doses up to 1.0 MGy.⁷¹

Engineering scale tests of a T2EHDGA system for reprocessing were performed for optimization, revealing the effects of several process conditions. The metal limiting organic content (the point at which a third phase forms) increases using TBP over DHOA and isodecanol, and also increases when the concentration of T2EHDGA increases. When extracting from 3M HNO₃, D-values were seen to be effective enough to produce complete extraction in four stages and complete stripping in two stages.⁷² A mixer-settler contactor bank, using 12 stages for each extraction, scrubbing, and stripping showed complete separation of americium and several lanthanides (La, Ce, Pr, Nd, Sm, Eu, and the lanthanide analogue Y) from several common fission products and likely processing contaminants (Sr, Fe, Cs, Ru, Mo, Pd, Zr, Na, K, Cr, Mn, and Ba).⁷³

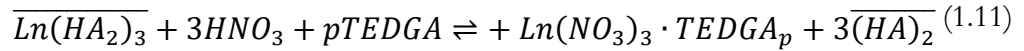
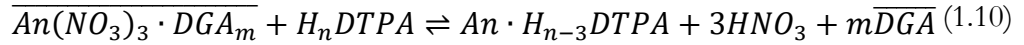
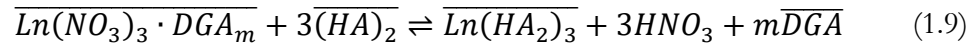
1.9 The ALSEP Process

One method developed to alleviate the process difficulties encountered in the TRUSPEAK Process is the proposed Actinide Lanthanide Separation (ALSEP) Process. The ALSEP Process uses organic phase extractants developed in the Advanced TALSPEAK process and other recent ligand design.⁷⁴ Proposed ALSEP Process organic phases combine either HDEHP or HEH[EHP] in conjunction with either TODGA or T2EHDGA to coextract both trivalent minor actinides and lanthanides, followed by a selective strip of actinides. Bench scale trials have shown extraction and stripping qualities suitable to warrant engineering scale evaluation.

The group extraction of metals in the ALSEP Process is performed through the mechanism proposed in Equation 1.8.



In this extraction scheme, the bulk trivalent actinides and lanthanides are coextracted to the organic phase from a high concentration nitric acid aqueous phase. Partitioning is then achieved through a selective strip of the actinides with the lanthanides held back in the organic phase. The proposed mechanism is shown in Equations 1.9 and 1.10. Finally, the lanthanides are stripped from the organic phase using an aqueous phase diglycolamide, such as tetraethyldiglycolamide (TEDGA), with the proposed mechanism shown in Equation 1.11



On the extraction side of the ALSEP Process, organic phases possessing 1M HDEHP + 20mM TODGA, 0.75M HEH[EHP] + 50mM T2EHDGA, and 0.75M HEH[EHP] + 50mM TODGA all show an increase in extraction with an increase in the aqueous phase nitric acid concentration, with the D-values increasing above ~0.5 M HNO₃ for the HEH[EHP] systems and above ~1M HNO₃ for the HDEHP system.⁷⁵ This D-value increase is the result of metal solvate complexation and is promising for development of a group extraction of trivalent f-elements with these extractant combinations. Furthermore, it was seen that the extraction of light lanthanides is not as powerful as that of heavier lanthanides, with the D-values of lanthanum into 0.75M HEH[EHP] + 50mM T2EHDGA being ~1 at ~5M HNO₃.⁷⁶ This lack of extraction is not especially problematic however, as light lanthanides are an ultimate waste product, so any residual lanthanides being carried away in the extraction raffinate will simply go to waste.

The first bench scale tests on the stripping side of the ALSEP Process displays the processes effectiveness, as the minimum separation factor of neodymium and americium from

a 0.75M HEH[EHP] + 50mM TODGA organic phase into a 0.25M citrate +25mM DTPA aqueous phase at pH 4.15 is 39, which is believed to be adequate to account for any anomalies experienced at an engineering scale. The separation factors in HDEHP systems are not as high, with the limiting separation factor in a 1M HDEHP + 75mM TODGA system as low as 9, precluding its use as a potential solvent mixture in the ALSEP system. For a 0.75M HEH[EHP] + 50mM TODGA system, there is excellent pH stability, with nearly flat extraction and separation factor profile from pH 3.4 to 4.2.⁷⁵ For a 0.75M HEH[EHP] + 50mM T2EHDGA system, stripping into 0.2M citrate with 10 and 15mM DTPA, the stripping of americium is less effective below pH~3, dropping the separation factors below 10. This suggests that attempts to increase kinetics by dropping the pH may not be effective due to reduced separations.⁷⁶ For a 0.75M HDEHP + 50mM T2EHDGA system, the pH stability is not flat, indicating that this system suffers the similar drawbacks to the TALSPEAK system. Finally, slight evidence of inter-molecular adducts in the organic phase is seen, as extraction of americium and europium into a 1M HEH[EHP] organic phase with varying TODGA concentration reveals that the extraction distribution ratios are dependent on TODGA concentration, and the separation factor drops by half of an order of magnitude from 0 to 150mM TODGA.

The kinetics of potential ALSEP systems has also been investigated to determine process feasibility. It was found that, in HEDTA containing aqueous phases, kinetics of extraction into HEH[EHP] are quite slow, with the system not coming to equilibrium until well after 20 seconds, the average phase contact time of centrifugal contactors. In general, these kinetics are slowed at higher pH values and for heavier lanthanides. Alternate aqueous phase complexants show mixed result. Most importantly, DTPA containing aqueous phases show much faster kinetics than those with HEDTA.⁷⁷ Furthermore, during ALSEP Processing, a scrub phase containing acetohydroxamic acid and citrate at around pH 3.75 was added to strip molybdenum from the extraction organic phase. This also effectively strips nitrate from the organic phase, promoting metal complexation with the cation exchange ligand throughout the entire strip stage.⁷⁸ These investigations were all performed from an extraction standpoint, so similar investigations while stripping metals may be more relevant to the ALSEP process.

While the ALSEP process has been shown to be an effective means of partitioning trivalent minor actinides and lanthanides, the slight evidence of adduct formation when

extracting metals could be problematic, and must be investigated. Determining the nature of these adducts and quantifying their equilibrium constants is crucial for the development of a predictive chemical model for engineering scale operations of the process. The purpose of this investigation is to develop a means of modeling the interligand interactions of mixtures of either HDEHP or HEH[EHP] with either TODGA or T2EHDGA. This investigation will be performed both with and without extracted metals in the organic phase, hopefully revealing trend behavior across the systems. Furthermore, this investigation will assist in the selection of the final extractant blend to be used in the ALSEP Process.

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II. Research Methods

2.1 Proposed Research Aims

Interligand interactions in the organic phase of previously studied mixed extractant solvent extraction systems have shown to cause lowered metal extraction yields and reduced separation factors of bulk lanthanides from the trivalent actinides, as well as complicating predictive operations through chemical modelling.¹ Determining the nature and extent to which these interligand interactions form is of great importance for modelling the process chemistry. This plays a crucial role in predictive process operations and allows for real-time correction of process transients at an industrial level. While the ALSEP Process has not shown the same general peculiarities that predecessor mixed extractant processes had shown, there is some evidence that there is some degree of interaction between the organic phase molecules.^{1,2} The work performed herein is intended to investigate these interligand interactions, in both metal-free and metal-loaded solutions. This may help to explain any deviations from typical TALSPEAK separations during ALSEP metal stripping.

The first objective of this research was to clarify the role of water coextracted with metal into the organophosphorus extractants HDEHP and HEH[EHP]. Anomalous effects reported in the organic phase spectrophotometric behavior of f-elements following extraction into HDEHP and HEH[EHP]. This investigation served as a means of resolving a scientific disagreement as the nature of perceived increases in coordination when extraction conditions vary. Determination of the influence of several factors, such as the cation exchange ligand investigated, the concentration of metal extracted, the concentration of extractant in the organic phase, and the position of the metal along the lanthanide series were probed. The techniques used to perform these determinations were UV-Visible spectroscopy and organic phase water determination by Karl Fischer titrations.

The second objective of this research is to investigate any inter-extractant complexes formed in the bulk organic phases of potential ALSEP combinations, and their effect on metal complexations and extraction. Four possible organic phase formulations will be investigated, using either HDEHP or HEH[EHP] as a cation exchange ligand in conjunction with either TODGA or T2EHDGA as a solvating ligand. The interactions between the two ligands prior to extraction have been characterized and quantified, and their ability to form metal complexes with f-elements have been probed. The techniques to perform this analysis are IR

spectroscopy, UV-Visible Spectroscopy, radiometric distribution analysis, and data modelling by non-linear least squares regression fitting.

The third objective of this research is to determine the speciation of metals in mixed extractant organic phases in the presence of variable organic phase nitric acid concentrations. HEH[EHP] and either TODGA or T2EHDGA combinations were analyzed to reveal the nature of metal coordination changes with incremental increases in organic phase nitric acid. This is intended to display the preferential complexation of nitrate – DGA species across the lanthanide series and with either DGA. The experimental techniques used in this investigation are IR spectroscopy and UV-Visible spectroscopy.

2.2 Instrumentation Methods

2.2.1 Metal Distribution and Solvent Extraction Technique

The objective of the following investigations is to identify the stoichiometry and stability constants of the extracted metal complexes in organic phases. Solvent extraction methods allow for the determination of distribution ratios, equilibrium constants of metal complexes with ligands in either aqueous phases or organic phases, and the stoichiometry of ternary complexes extracted to the organic phase. Distribution of metal between two immiscible phases is a chemical reaction when the metal, usually dissolved in an aqueous mineral acid is extracted into an organic solvent containing molecules of a metal complexing ligand. Quantification of the distribution ratios D can be performed radioanalytically or by a chemical analytical method, such as spectrophotometry, ICP-MS, or by volumetric titration with complexometric dye. Radiotracer techniques allow for the analysis of much lower metal concentrations than most analytical techniques. Additionally, they use smaller volumes and are measured directly as they do not require stripping of metal from organic phase (like in ICP-MS) making the probability of dilution errors is much smaller.³

Radiolanthanides can be purchased, however most of them have relatively high neutron capture cross sections, meaning that they can be easily activated by thermal-neutron capture in a nuclear reactor. Following irradiation, the lanthanide tracers can be dissolved in an appropriate aqueous phase and their stock solution used to spike extraction samples. Prior to extraction of the analyzed metals, preequilibration with an identical, metal-free aqueous phase can be performed to achieve distribution equilibrium of water, mineral acid and other components present in the aqueous extraction phase that could eventually affect the

distribution of the studied metal. The organic solvent is then contacted with a fresh portion of the aqueous phase spiked with the studied metal. Typically, a 1:1 volume phase ratio is used in distribution equilibrium experiments. Aliquots of each extraction phase are measured for concentration of metal. When measuring the activity of the samples, care can be taken to ensure that the sample and detector geometry remain consistent so as to maintain the same proportionality between the count rate of the sample and the chemical concentration of the radiotracer in the sample. A direct ratio of the count rates is thusly appropriate for determination of the metal distribution.

2.2.2 Radiometric Determination of Metal Concentration

Analysis of the metal concentration was determined through radiometry as the activity concentration of radiotracers is a linear function of the chemical concentration of chemical elements. The first type of detector is a sodium iodide (NaI(Tl)) scintillation counter for gamma spectroscopy. NaI(Tl) detectors use large, nearly completely uniform crystals containing a dopant material (typically thallium). Once a gamma ray interaction takes place with the crystal, it electronically excites an electron from the valence band of the NaI crystal to the conduction band, which then travels along the crystal until it deexcites. The dopant material has a slightly lower deexcitation energy than the crystal lattice, which prevents immediate reabsorption of the energy emitted from its deexcitation. When the energy is transferred from the conduction band of the crystal lattice to the dopant material, another photon which cannot be reabsorbed by the lattice is produced. These photons are then absorbed by a photocathode at the edge of the crystal, converting the photon into an electron. The produced electrons are then multiplied by the dynodes in a photomultiplier tube until there are enough electrons to produce a measurable voltage signal.⁴ This process is shown in Figure 2.1.

The iodine in sodium iodide detectors are high-Z atoms, which have large electron clouds, making the detection of gamma rays more efficient than in other gamma detectors which have lower-Z materials. As a tradeoff, however is the larger energetic bandgap of deexcitation than other gamma detectors, such as high purity germanium detectors, leading to a lower energetic resolution. This makes these detectors better for quantifying the activity of a sample of known composition, but not as powerful as identifying the composition of unknown samples.⁴

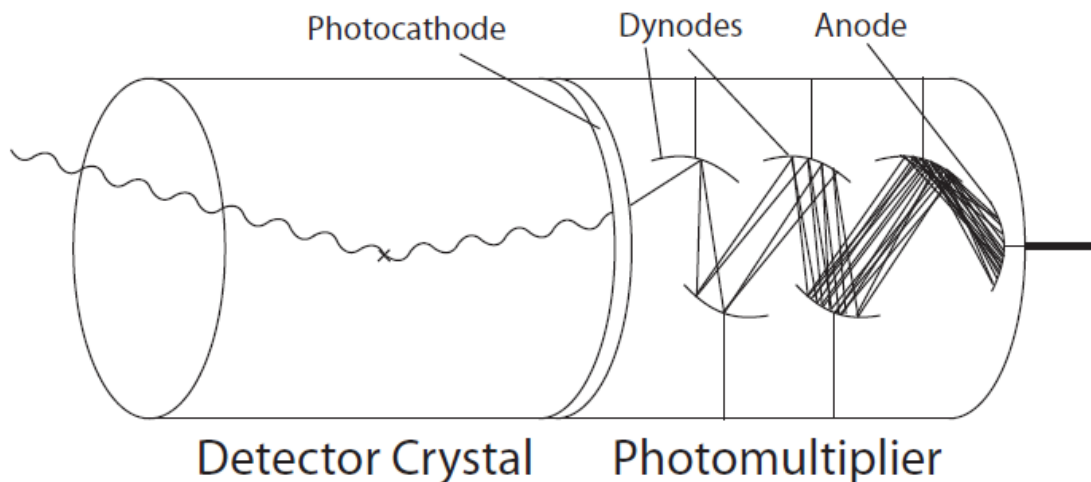


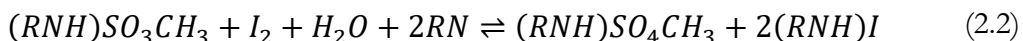
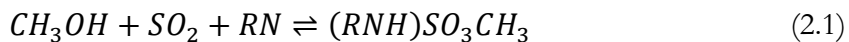
Figure 2.1 – Sodium Iodide Detector Crystal

For gross alpha and beta activity determination, the Liquid Scintillation Counting (LSC) method was used. For LSC detection, a radioactive sample is dissolved into an LSC cocktail, which contains an aromatic diluent and a small amount of “fluor,” or fluorescent material. The aromatic diluent is susceptible to energetic excitation due to its π -orbital structure, which can then transfer this absorbed energy through the solution to the fluor, which deexcites at a lower energy following rotational and vibrational deexcitation. The final deexcitation is then unlikely to reabsorb in the solution, and can be detected as light by a detector outside of the sample. This detector type can be used to measure α - and β -particles as opposed to γ -rays, but can detect them at very high efficiency (nearly 100% for α -particles and low energy β -particles). This technique can also be used to discriminate between α - and β -particles in a mixed nuclide sample due to the temporal differences in the deexcitation of the radiation types, although energetic spectroscopy is not possible. LSC detection and NaI(Tl) scintillation detection can be combined to perform the determination of distribution ratios for these stoichiometric and equilibrium analyses.⁴

2.2.3 Titration Determination of Coextracted Water and Nitric Acid

Karl Fischer (KF) titrations are a standard technique used to determine the water concentration of organic solutions. Such titrations involve preparing a sample and adding a solution which reacts on a stoichiometric basis with water, producing different voltage signals when the reaction is occurring and once all water has been consumed. KF titrants contain I_2 , SO_2 , an amine base (in this investigation, imidazole was used over the historically used

pyridine), and an alcohol (typically methanol). Two reactions occur when the titrant is added to a water containing solution, as shown in Equations 2.1 and 2.2.⁵



In Equation 2.1, the methanol, SO₂, and amine base (abbreviated RN) form a conjugate complex with the base deprotonating the methanol, and the sulfur dioxide bonding to the methanol. In Equation 2.2, the iodine deprotonates the water present in the sample to form hydroiodic acid, which is then consumed by unreacted amine base. The resulting oxygen is then bound to the conjugate complex formed in Equation 2.1, becoming a sulfate species. In these reactions, water and iodine are consumed in equimolar amounts, presenting an opportunity to accurately quantify the concentration of water in a sample.⁵

The two main methods of performing this analysis are coulombic and volumetric KF titrations. Coulombic titrations involve an anode in a solution containing the unknown material along with the KF titrant solution separated from a cathode by an ion-permeable membrane. Current run across the cell generates iodine ions, propelling the reaction. Coulombic titrations are useful for samples with very low concentrations of water. Volumetric KF titrations, which were used in the analysis herein, are more useful for solutions with larger concentrations of water. Volumetric KF titrations involve placing a sample with an unknown concentration of water into an alcohol solution with an immersed platinum electrode. A constant current is applied across the electrode, with the voltage required to maintain this current measured as an output. KF titrant is then volumetrically added to the sample chamber, stepwise consuming the water in the sample. In the presence of excess iodine, iodide ions form about the electrode, which greatly reduces the voltage required to maintain the current applied. Thus, once the measured voltage drops below a user-defined set point, the water in the solution is determined to have been fully consumed, and the concentration of water in the unknown solution can be determined.⁵

Organic phase nitric acid concentrations were determined as the difference in the concentration of nitric acid between an aqueous phase before and after contacting with the organic phase. The concentration of nitric acid in the aqueous phase was determined by acid-

base titration using a standardized base solution and a pH electrode to determine the equivalence point.

2.2.4 Infrared (IR) Spectroscopy

In order to investigate interligand interactions in metal-free organic phases, techniques which are able to observe changes in the bond energetics of interacting functional groups in an organic phase must be utilized. One of the methods that can be utilized is infrared (IR) spectroscopy; a form of vibrational spectroscopy. The principles of spectrophotometry rely on the relationship between the wavelength of electromagnetic radiation and its energy, as defined in Equation 2.3.⁵

$$E = h\nu = \frac{hc}{\lambda} \quad (2.3)$$

In Equation 2.3, “E” is the energy of the photon, “h” is Planck’s constant, “c” is the speed of light, “ν” is the frequency of the light, and “λ” is its wavelength. The energy of a photon is therefore inversely proportional to its wavelength. When light is absorbed by a molecule, its energy promotes the molecule to a higher energy excited state through various means based on the energy of the incident photon. Absorbed microwave radiation (100 mm – 1 mm, 12.3 μeV – 1.23 meV) promotes molecular rotation producing heat through by the kinetic energy generated. Absorbed infrared radiation (1 mm – 780 nm, 1.23 meV – 1.6 eV) promotes intramolecular bond vibrations, while absorbed visible (780 nm – 380 nm, 1.6 eV – 3.3 eV) and ultraviolet radiation (380 nm – 10 nm, 3.3 eV – 132 eV) both promote the excitation of electrons to higher energy states. Finally, X-rays (<10 nm, >132 eV) induce bond breakage and molecular ionization.⁵

In infrared spectroscopy, the light which is passed through a chemical sample can promote bond vibrations through a number of means. The number of vibrational modes which can occur in a molecule is equal to the number of degrees of freedom present for its individual atoms. For a molecule of N atoms, the degrees of freedom of a linear molecule is $3N - 5$, while a non-linear molecule has $3N - 6$ degrees of freedom. Stretching frequencies which produce no change in the dipole moment of the molecule are inactive in IR spectra, but are observable with Raman spectroscopy, whereas stretching frequencies which produce a change in the dipole moment are observable in IR spectra. For non-linear molecules, there are six vibrational types possible (shown in Figure 2.2), all which preserve the overall momentum of the molecule. These vibrational modes all absorb at independent wavelengths, however similar bond types can produce overlapping absorbance signals.⁶

Most IR spectra are recorded in units of wavenumber, or the inverse of the wavelength of light. The primary region of interest for IR spectra is in the $650 - 4000 \text{ cm}^{-1}$ range, which can further be divided into two sections. Above $\sim 1500 \text{ cm}^{-1}$, there are several characteristic absorbance bands, such as those for hydroxyl, hydrocarbon, aromatic, carboxyl, and other representative groups. Below this region, a molecule specific characteristic region known as the fingerprint region contains absorbances specific to the individual bonds observed. Since the extractant molecules proposed for the ALSEP process contain multiple functional groups

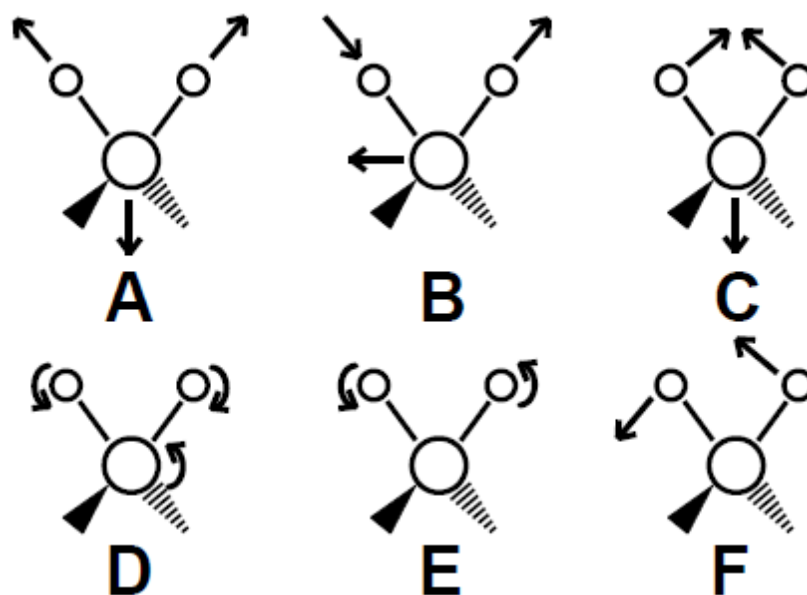


Figure 2.2— Non-Linear Molecule IR Vibrational Modes: Symmetrical Stretching (A), Asymmetrical Stretching (B), Scissoring (C), Wagging (D), Twisting (E), and Rocking (F)

which are IR-active, investigating inter-ligand bond formation should be possible through the collection of IR spectra.⁶ Furthermore, the location of absorbance regions for individual functional groups can be approximated through documented absorbance regions of similar functional groups which can help to identify which functional groups of the two molecules are interacting.⁷ Finally, bonds formed between the two molecules should be observable, which should allow the qualification and quantification of interligand interactions between the extractant molecules.

2.2.5 Ultraviolet-Visible (UV-Vis) Spectroscopy

One of the purposes of this investigation is to clarify the nature of metal complexation in cation exchange ligand containing organic phases following extraction. One method of investigating organic phase metal complexes is through UV-Visible (or UV-Vis) spectroscopy. UV-Vis follows the same general principles as IR spectroscopy, where light intensity is measured before and after it has passed through a sample to measure its wavelength-dependent absorbance. The difference primarily lies in the type of excitation that occurs, as well as the kinds of materials which can be investigated. UV-Vis light absorbs through an excitation of an electron from one orbital to another, as opposed to bond vibrations. This allows changes in the electronic configuration of a sample to be investigated, such as those related to changes in coordination.⁵

When light of a certain wavelength is passed through a sample, the amount of light which is absorbed in the sample can be defined as unitless absorbance units, as defined in Equation 2.4.⁵

$$A_{\lambda} = \log_{10} \left(\frac{P_{0,\lambda}}{P_{\lambda}} \right) \quad (2.4)$$

In Equation 2.4, “ $P_{0,\lambda}$ ” and “ P_{λ} ” are the incident and final light intensity respectively at a particular wavelength, while “ A_{λ} ” is the sample absorbance at that wavelength. In most samples, absorbance is proportional to the concentration of an absorbing species in solution. This relationship is known as the Beer-Lambert Law, as defined in Equation 2.5.⁵

$$A_{\lambda} = \epsilon_{\lambda} \ell c \quad (2.5)$$

In this law, “ c ” is the concentration of the absorbing species, “ l ” is the pathlength of the light through the sample, and “ ϵ_λ ” is what is referred to as the molar absorptivity constant, or extinction coefficient, a species and wavelength dependent property. The Beer-Lambert Law is applicable in most instances, however certain criteria, known as selection rules must be satisfied.⁵ Selection rules primarily govern which electronic transitions can occur to absorb incident radiation. The first selection rule is called the Spin Selection Rule. This rule states that the light passed through a sample cannot change the relative orientation of the electrons in which it is incident. This means the spin of the electrons cannot be reversed without alternate pathways, such as spin-orbit coupling. The second selection rule is the Laporte Selection Rule which states that, in centrosymmetric molecules, electronic transitions must be accompanied by a change in parity. This means that transitions in d - and f -elements in symmetrical molecules can lead to suppressed absorption, however disruptions in the symmetry can improve the absorption.⁸ The selection criteria can lead to identifications of spectral effects in chemical systems.

f -Elements show particularly sharp, narrow, low intensity absorption peaks with respect to other metals in the d -block. This is due to the relatively minimal f - d transitions, while f - f transitions are Laporte forbidden. There are a high number of microstates of transition, however, meaning that there are a large number of peaks present in an absorption spectra. Since f -orbitals are well shielded from ligand interactions, the absorption spectra typically do not show significant changes based on the coordination environment.⁸ Certain f -elements however, such as neodymium, holmium, and erbium, possess absorption regions called hypersensitive regions, a result of inhomogeneity in the electrical field about the metals, which allow fine structure to be classified.⁹

Typically, UV-Vis spectrometers contain several components designed to pass specific wavelengths through a sample for measurement. First, a broadband light source is used to generate all wavelengths of light required in the spectrogram. Next, the light is passed through a slit to generate a beam of light. The beam impacts a diffraction grating which separates the light into a spectrum of monochromatic light. This grating is rotated such that individual light wavelengths pass through a second slit and on to the sample. This configuration is shown in Figure 2.3. Prior to passing through a sample, the light can be partially reflected through a polarized mirror and through a reference cell to correct for changes in the light intensity from

the source. Both light beams are then collected in photomultiplier tubes to generate a measureable signal.⁵

In order to utilize UV-Vis spectrometry, a chemical species must absorb in either the visible or UV light regions. Many organic and inorganic molecules can absorb at very low wavelengths (<200nm), but do not absorb particularly well in the high-UV or visible regions, providing minimal interferences.⁵ On the other hand, several metals exhibit the ability to absorb in the visible region, with their absorbance dependent on the electronic configuration of the metal. Of the lanthanides, praseodymium, neodymium, holmium, and erbium absorb in the visible region with all but praseodymium absorbing with a so-called hypersensitive region where changes in the absorption can represent structural or coordination changes.⁹ Americium also absorbs in the visible region as a representative trivalent actinide.⁸

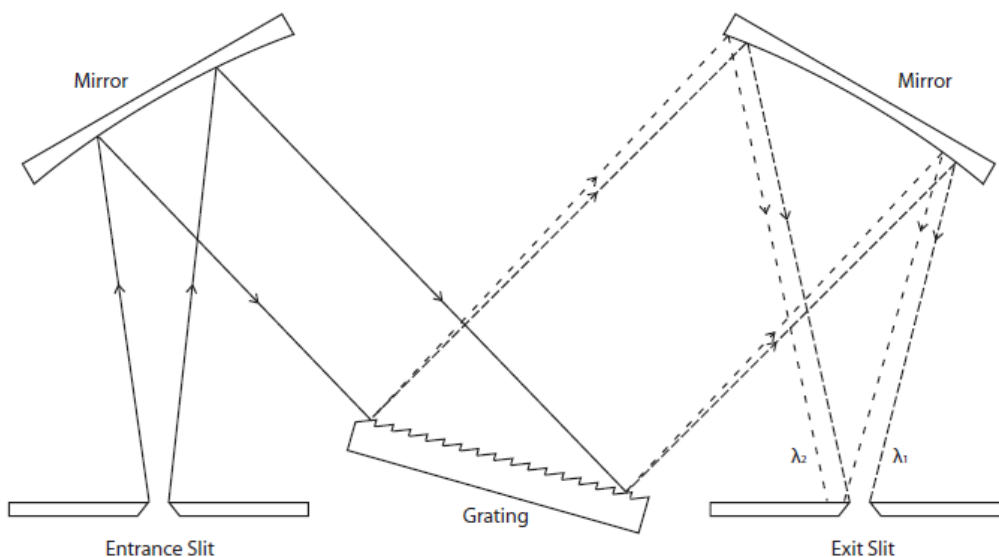


Figure 2.3 – UV-Vis Spectrometer Light Diffraction Configuration

2.3 Procedures for Organic Phase Characterization

2.3.1 Slope Analysis Method

For determining the number of the solvating ligand molecules in the extracted metal complex, the method of slope analysis was applied. Using a uniform aqueous phase which allows for metal extraction into one of the extractant type but not by the other extractant type, the effects of interligand species can be seen. Using a buffered, high pH aqueous phase, for example, would allow for the extraction of metals with a cation exchange ligand, however

would not allow for metal extraction by a solvating ligand alone. This presumption would mean that any effect on distribution in the presence of a constant concentration of a cation exchange ligand while increasing the solvating ligand concentration would solely be caused by interligand adduct formation around the metal. This can be used to determine both the partial stoichiometry as well as the equilibrium constant of interaction.³

The mathematical justification behind this method comes from the definition of the distribution ratio, given that the solvating ligand cannot extract metals on its own. This relationship is shown in Equation 2.6.³

$$D_{total} = \frac{[\overline{MA}] + [\overline{MAE}] + [\overline{MAE_2}] + [\overline{MAE_3}] + \dots}{[M]} \quad (2.6)$$

In Equation 2.6, “D” represents the distribution ratio of metal “M”, “A” is the ligand of constant concentration (in this case, a cation exchange ligand), and “E” represents an individual solvating ligand with increasing concentration across the sample set. Coupled with the definition of equilibria in terms of distribution ratios (Equation 2.7A and 2.7B with all other possible stiochiometries following thusly), Equation 2.6 can be manipulated to form Equation 2.8A, or alternately Equation 2.8B, where “D₀” is the distribution ratio of the metal prior to the addition of any solvating ligand.³

$$K_0 = \frac{[\overline{MA}]}{[M][\overline{A}]} = \frac{D_0}{[\overline{A}]} \quad (2.7A)$$

$$K_1 = \frac{[\overline{MAE}]}{[\overline{MA}][\overline{E}]} = \frac{[\overline{MAE}]}{D_0[M][\overline{E}]} \quad (2.7B)$$

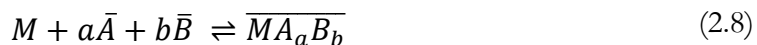
$$D_{total} = D_0 + D_0K_1[\overline{E}] + D_0K_2[\overline{E}]^2 + D_0K_3[\overline{E}]^3 + \dots \quad (2.8A)$$

$$\frac{D}{D_0} - 1 = K_1[\overline{E}] + K_2[\overline{E}]^2 + K_3[\overline{E}]^3 + \dots \quad (2.8B)$$

From the relationship in Equation 2.8b, it can be shown that a plot of D/D₀ – 1 vs. varying solvating extractant concentrations can reveal both the stoichiometry of the adducts with respect to the solvating extractant (via the trendline shape), as well as the ability of these adducts to form (via the polynomial trendline coefficients).³

2.3.2 Job's Method Procedure

A second method for the determination of the stoichiometry of the extracted species is with the method of continuous variation, or Job's Plot method. With Job's Plot method, a physical property of solution is measured in a two component system. The concentrations of the two components are changed, but their total, additive concentration is held constant. For these purposes, the physical property measured is the distribution ratio of a metal into an organic phase with a varying extractant concentration ratio. The mathematical basis behind this type of analysis comes from the equilibrium relationship of the extraction, as shown in Equation 16.⁸



From the equilibrium in Equation 16, a specific ratio (say, "R") of "b" to "a" will lead to a maximum possible concentration of " $\overline{MA_aB_b}$," the metal containing organic phase complex. If there is a higher concentration of "a," leading to a ratio lower than "R," the "B" component will be the limiting reagent in the extraction. Likewise with a higher concentration of "b" producing a ratio higher than "R," "A" will become the limiting reagent to the equilibrium. Using the Job's Method, the stoichiometry of the system can be fully identified by the ratio "R."³

2.3.3 Spectrophotometric Titrations

Spectrophotometric titration involves preparing a solution for UV-Vis analysis, followed by stepwise additions of a secondary solution and similar UV-Vis spectral collection. This technique can be used to determine the concentration of an unknown analyte through titration of a known concentration complexant with known stoichiometric interaction, as well as to determine the equilibrium constant of interaction between two species. For these investigations, one of the absorbing lanthanides or actinides can be extracted from a non-extracting aqueous phase (such as dilute HCl) into an organic phase containing only the cation exchange extractant. Then, the organic phase can be titrated with a solution containing the same concentration of the cation exchange extractant (to keep its concentration constant) and a known concentration of one of the solvating extractants. Any change in the electronic configuration of the metal following titration can be solely attributed to the formation of

interligand adducts, as there is no other pathway for the solvating extractant to complex the metals in the organic phase. After this, a second titration can be performed following a similar extraction, but with a titrant that has been preequilibrated with an aqueous phase which could allow for metal complexation with the solvating extractant, such as higher concentration nitric acid. This titration can reveal the competition between the complexation of metals with a cation exchange ligand, an interligand adduct, and the solvating ligand.⁵

2.4 Data Analysis and Equilibrium Constant Determination

Many of the techniques detailed above can be used to show the qualitative, as well as the quantitative nature of molecular interactions in solution. In order to determine equilibrium constants for the interactions of DGAs with organophosphorus acid extractants, appropriate data fitting of the collected spectra must be applied. Non-linear least squares regression data fitting is a common technique used to perform these types of quantifications. Least squares regression fitting seeks to calculate a predicted data set from a provided chemical model based on the minimization of the squared error between the observed and the calculated data. For example, if “ $y_{i, \text{obs}}$ ” is an experimentally observed value in a data set of size “ m ,” and “ $y_{i, \text{calc}}$ ” is a mathematically calculated value in the same data set, then the minimum error obtained would be at a position defined by Equation 2.10.¹⁰

$$S = \sum_{i=1,m} r_i^2 = \sum_{i=1,m} (y_i^{\text{obs}} - y_i^{\text{calc}})^2 \quad (2.10)$$

In Equation 2.10, “ r_i ” is referred to as the residual, or the error between the observed and calculated value, and “ S ” is the sum of squared residuals. Typically, the most accurate calculated system is one in which this sum of squared residuals is at a minimum. The calculated values in this system are dependent on the parameters of the experiment, as well as the independent variables which are defined by the model applied to the system, such that the calculated value at any point along the data set is defined in Equation 2.11.¹⁰

$$y_i^{\text{calc}} = f(p, x_i) \quad (2.11)$$

For non-linear least squares regression fitting, it is assumed that the parameters and the coefficient variables are not independent on each other. In these presumed non-linear

systems, a Taylor Series approximation is typically applied to approximate the partial derivative of the independent variable function by the parameters under the assumption that small, incremental changes in the parameters are approximately linear. In the case of linear systems, this approximation becomes zero, meaning that non-linear techniques can be used for both linear and non-linear systems.¹⁰

The minimum of the sum of the residuals is the point at which its partial derivative of the calculated value with respect to each of its parameters is equal to zero. This can be derived through a step-wise calculation of a Jacobian matrix of the calculated values to the system parameters. An initial guess of the parameters must be applied in non-linear systems, with each solution iteratively approaching the observed values arrived experimentally. Once the sum of residuals has reached a minimum, the parameters which have been arrived upon can be presented as the parameters of the actual chemical system.¹⁰

For the data collected in the IR and UV-Vis experiments, the experimentally observed values are the spectra which have been collected. For the UV-Vis and the IR spectra, the observed values are vectors of the absorbances observed across the wavelength range. The modeled systems are the chemical interaction models proposed from the systems, while the parameters to be derived are the system equilibrium constants. Using non-linear least squares regression fitting, the chemical equilibria can be determined by observing the step-wise changes in the spectra following changes in chemical concentration. This provides a system with potentially several hundred data points with which to calculate the system parameters, making for determinations with minimal calculation error. Several commercial programs exist for performing this type of chemical analysis. The software which will be used in this work will be part of the HyperQuad suite of programs, most notably HypSpec and HySS.¹⁰

The investigation proposed herein represent a means of clarifying the organic phase nature of the mixed extractant solvent extraction processes using either HDEHP or HEH[EHP] with either TODGA or T2EHDGA. Furthermore, this investigation looked to clarify the nature of how metals exist in cation exchange extractant organic phases. These studies will help to resolve any potential processing issues or model establishment difficulties, as well as to inform the final extractant combination for continued process development. The results of this dissertation is separated into three chapters representing adaptations of three publications which were produced from the research. The first section details the metal coordination environment of f-elements in HDEHP and HEH[EHP] organic phases with

respect to organic phase metal, extractant and water concentration. This serves as a method of determining inner-sphere metal interactions and clarifying the resultant spectroscopic effects. The next section details the competition in ALSEP organic phases for the formation of interligand adduct species, both in the bulk organic and in coordination with metals. This section serves to quantify the interactions and determine which extractant formulation is most appropriate for engineering and industrial scale operations. The final section details the competition of organic phase extractant molecules following the extraction of nitrate to the organic phase. This reveals the nature of metal coordination across a range of nitric acid concentrations which could help to advise the bounding process conditions for engineering and industrial applications.

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III. Extraction of Water and Speciation of Trivalent Lanthanides and Americium in Organophosphorous Extractants

This text is a modified version of an accepted publication in Inorganic Chemistry.

3.1 Introduction

Organophosphoric cation-exchange extractants have been widely employed as a means of partitioning metals in solvent extraction processes and analytical chromatographic techniques. Di-2-ethylhexylphosphoric acid (HDEHP) in particular has been used in separation of uranium, lanthanides, and transition metals in post-leaching extraction and in separation of transuranics in the nuclear fuel cycle.¹⁻³ HDEHP is used in the TALSPEAK process as a means of separating trivalent minor actinides from fission produced lanthanides in Used Nuclear Fuel (UNF).^{4,5} In recent years, advances have focused on combining TALSPEAK with other process steps to simplify separations or through the use of analogous extractants, such as 2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) to improve process operations.⁶⁻⁸

Metal complexation in the HDEHP organic phases remains a subject of investigation, with multiple interpretations as to the nature of organophosphoric extractant coordination to the metal center. The traditional interpretation of trivalent actinide and lanthanide speciation following extraction has been metal coordination with three mono-deprotonated dimers of HDEHP in the form $M(HA_2)_3$, where “A” represents the DEHP anion and “H” represents the acid proton; however, several alternate species have been proposed.^{9,10} Pseudo-octahedral coordination of the metal in highly symmetrical systems has been suggested through investigations with time-resolved laser fluorescence spectroscopy (TRLFS) and Extended X-ray Absorption Fine Structure (EXAFS) of similar systems, however differences in experimental conditions prompt further studies.^{11,12}

UV-Vis-NIR spectroscopy of f-elements has been used to identify the types of complexes that these metals form with various ligands.^{13,14} Certain electronic transitions are hypersensitive to symmetry and electronic field strength of the metals, such as the $^4I_{9/2} \rightarrow ^4G_{5/2}$, $^2G_{7/2}$ transition of neodymium, the $^4I_{9/2} \rightarrow ^2H_{9/2}$, $^4F_{5/2}$ transition of holmium, and the $^4I_{15/2} \rightarrow ^2H_{11/2}$ transition of erbium. Several other trivalent f-elements, such as praseodymium ($^3H_4 \rightarrow ^3P_2$, 1I_6 , 3P_1 , 3P_0) and americium ($^7F_0 \rightarrow ^5L_6$), have absorption bands in the visible

region.¹⁴ Jensen, *et. al.* reported multiple means of organic Nd complexation in HDEHP using Small Angle Neutron Scattering (SANS) coupled with UV-Vis-NIR spectroscopy, with Nd(HA₂)₃ present at high HDEHP concentration and low metal loading, and a bridged, two metal species of the type Nd₂(DEHP)₆ reported at low HDEHP concentration and high metal loading.¹⁵ Alternately, using single-crystal X-ray scattering of Nd dimethylphosphate compounds and UV-Vis spectroscopic results, the coordination of Nd in HDEHP organic phases has been found to exist as a pseudo-octahedral coordination environment independent of metal loading percentage, and the changes in speciation at low HDEHP concentration were a result of impurities in the cation exchange extractant.¹⁶

In particular, a recent study pointed out that the differences in 570 nm to 583 nm absorption ratio was due to the impurity in HDEHP and left no question as to other causes that effect this ratio. Indeed, we recently found that the 570 nm to 583 nm absorption ratio did change, even with the lack of impurity.¹⁷ It has been noted that aqueous species such as water and lactate can co-extract with metals into the organic phase.¹⁰ These co-extracted species, if bound to the inner coordination sphere of the metal could produce an effect on the hyperfine regions of Nd UV-Vis spectrum. This would also have an effect on process monitoring which relies on these electronic transitions.¹⁸ This investigation seeks to identify the source of metal coordination changes in different concentration HDEHP containing organic phases in order to improve understanding of how metals coordinate to HDEHP and HEH[EHP] under different organic phase conditions.

3.2 Experimental Methods

Organic solution were prepared on a mass basis from purified cation exchange ligand stocks. HDEHP (J.T. Baker, 98%) was purified by the copper precipitation purification technique to >99% purity as confirmed by acid base titration.¹⁹ HEH[EHP] (Yick-Vic Chemicals & Pharmaceuticals, 97%) was purified using the copper precipitation purification technique to >99% purity as confirmed by ³¹P NMR spectroscopy.¹⁹ Each extractant was dissolved in n-dodecane (Acros Organics 99+%), used as delivered. Lanthanide chlorides were individually prepared by dissolving Nd₂O₃ (Sigma Aldrich, 99.9%), Pr(NO₃)₃ (Alfa Aesar, 99.9%), Sm(NO₃)₃ (Sigma Aldrich, 99.9%), Er₂O₃ (Sigma Aldrich, >99.9%) and Ho₂O₃ (Sigma Aldrich, >99.9%) in concentrated HCl (Macron, ACS grade) and evaporated. Aqueous solutions were then prepared by dissolving in pH 2.80 HCl (Macron, ACS grade) with the final

solution measured to be pH 2.80 +/- 0.05 as checked with an Orion 8165 BNWP pH electrode. Metal concentrations were determined by EDTA titrations with xylenol orange as an indicator.²⁰ Americium chloride was prepared similarly through conversion of an in-house ²⁴³Am stock solution purified using a DGA column (Eichrom) by dissolution in concentrated HCl and subsequent evaporation, followed by dissolution in pH 2.80 HCl. Concentration was determined through LSC counting on a Perkin Elmer Tricarb 3180 with alpha/beta discrimination. All aqueous solutions were prepared with deionized water (Millipore, 18.1 MΩ-cm).

Solvent extraction was performed by contacting 1 mL of the extracting organic phase with 1 mL of the metal loaded aqueous phases via vigorous shaking for 10 minutes using a vortex mixer. Extraction was performed in 4.5 mL polyvials followed by centrifugation at 3000rpm for 5 minutes or until phase disengagement. Phases were separated using a fine tipped transfer pipet.

UV-Vis-NIR spectra of the post extraction organic phases were collected on a Cary 6000i UV-Vis-NIR spectrometer with a jacketed cell held at 20 °C. Water concentration in the organic phases was determined by volumetric Karl Fischer titrations on a Mettler Toledo DL58 auto titrator with each sample measured in duplicate.²⁰ Distribution ratios of the lanthanides were determined using a colorimetric technique with Arsenazo III at pH 9 buffered by triethanolamine and compared to a calibration curve.²¹ Distribution ratios of ²⁴³Am were determined through LSC alpha counting using an alpha-beta discriminator to prevent the interference from the beta-emitting ²³⁹Np daughter radioisotope. Water was removed from post-metal extraction organic phases with 3Å molecular sieves baked for at least 5 hours at 225 °C at 15 kPa.

3.3 Experimental Results

3.3.1 Neodymium Speciation in HDEHP Organic Phases

Aqueous phase neodymium solutions between 1.3 mM Nd and 29.3 mM Nd were extracted into 0.2 M - 2.0 M HDEHP solutions in n-dodecane. UV-Vis spectra were taken for each post-extraction organic phase with the absorption bands of the ⁴I_{9/2} → ⁴G_{5/2}, ²G_{7/2} electronic transition shown in Figure 3.1.

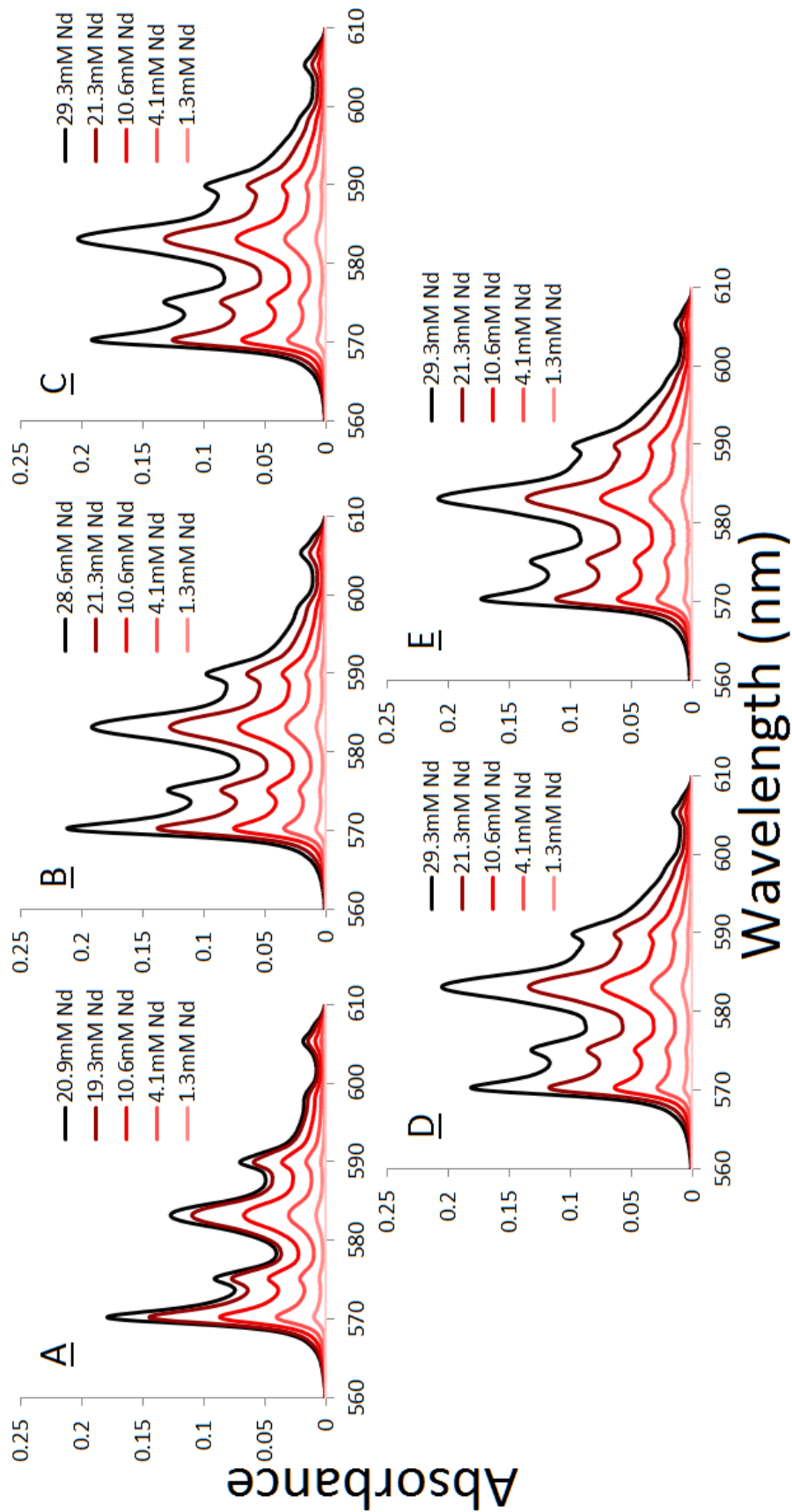


Figure 3.1 – Neodymium UV-Vis Spectra of Varying Metal Concentrations in (A) 0.2M HDEHP, (B) 0.5M HDEHP, (C) 1.0M HDEHP, (D) 1.5M HDEHP, and (E) 2.0M HDEHP

The spectral characteristics remain constant with changes in metal concentration, but shift with respect to HDEHP concentration. Spectra normalized to the metal spectra are shown in Figure 3.2. At low HDEHP concentrations, the spectra resemble those of a pseudo-octahedron, containing the characteristic 6 absorption bands of such structures with a prominent absorption band at 570 nm (A_{570}).¹⁶ This type of absorbance has been previously identified as representative of polymeric speciation in the organic phase.^{15,16} With an increase in HDEHP concentration however, A_{570} is seen to decrease while the absorption band at 583 nm (A_{583}) is seen to increase. This is consistent with an increase in the coordination number of the metal complex to a seven coordinate species.¹³

Dilution of Nd loaded organic phases of higher HDEHP concentration with non-preequilibrated solutions of the same HDEHP concentration resulted in a substantial shift of the UV-Vis spectra, whereas dilution with pre-equilibrated organic phases resulted in no spectrum change (Figure 3.3). In particular, upon dilution, A_{570} was seen to increase and A_{583} was seen to decrease, suggesting a decrease in the coordination number.¹³ Furthermore, when Nd is extracted into a 0.5 M HDEHP organic phase and the HDEHP concentration is increased via titration of a higher HDEHP concentration organic phase, no shifting of the spectrum is seen, as shown in Figure 3.4. This behavior also alludes to the presence of an alternate extracted species may be causing changes in the metal complexation in these organic

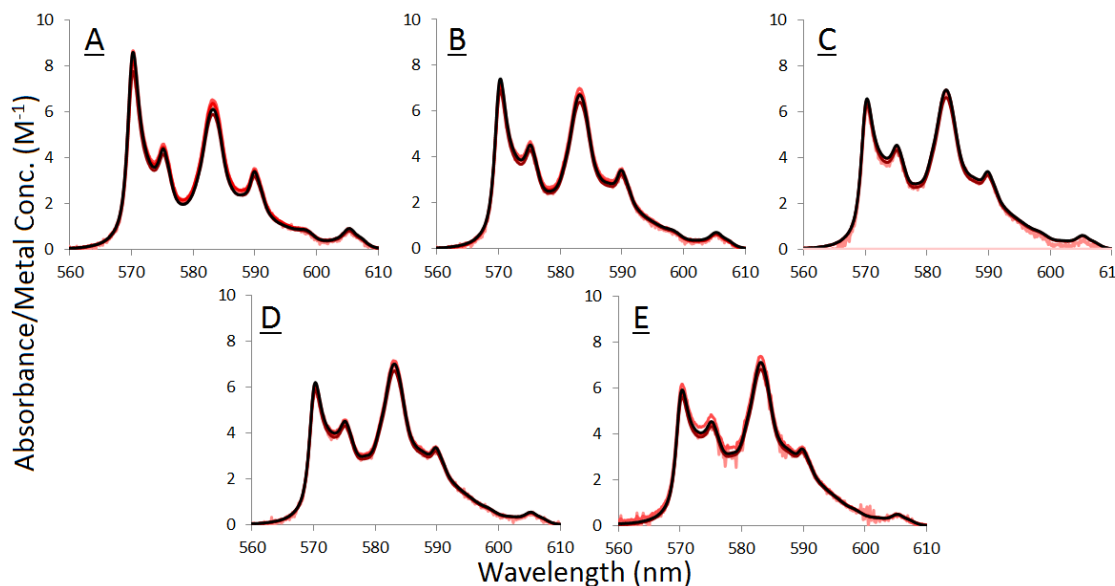


Figure 3.2 – Metal Concentration Corrected Spectra of Nd in (A) 0.2 M HDEHP, (B) 0.5 M HDEHP, (C) 1.0 M HDEHP, (D) 1.5 M HDEHP, and (E) 2.0 M HDEHP

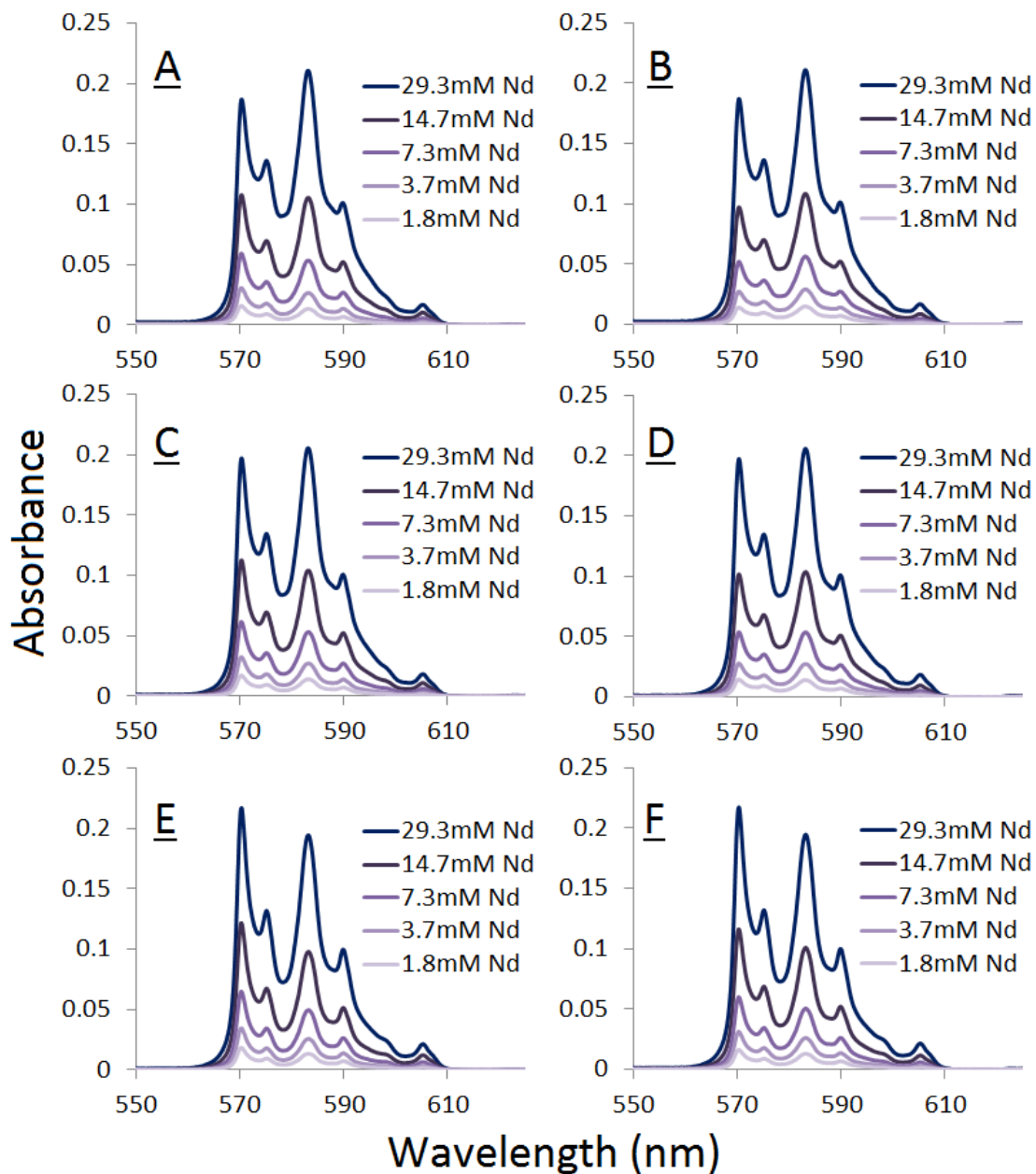


Figure 3.3 – UV-Vis Spectra of Nd Extracted into 1.5 M HDEHP and Diluted with Non-preequilibrated (A) and Preequilibrated (B) 1.5 M HDEHP, 1 M HDEHP and Diluted with Non-preequilibrated (C) and Preequilibrated (D) 1 M HDEHP, and 0.5 M HDEHP and Diluted with Non-preequilibrated (E) and Preequilibrated (F) 0.5 M HDEHP

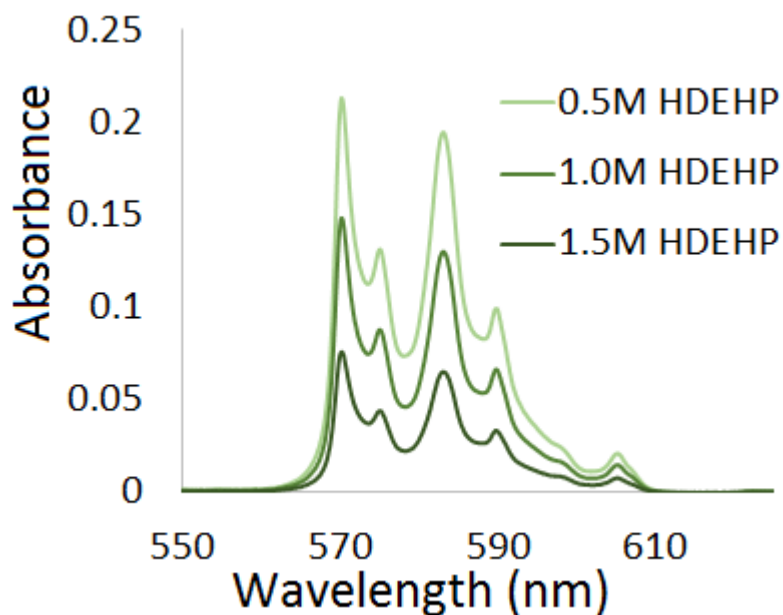


Figure 3.4 – Nd Extraction into 0.5M HDEHP Followed By Titration With 2.0M HDEHP, Increasing HDEHP Concentration

phases. The water concentration in post-extraction organic phases were determined by Karl Fischer titrations, as shown in Figure 3.5 as a function of preextraction aqueous phase metal concentration for each HDEHP concentration. Increasing the organic phase HDEHP concentration result in appreciable increases in the extracted water concentration, however metal concentration in the ranges studies have little to no effect on the extraction of water. Given the significant excess of ligand relative to metal concentration, these results suggest that the ligand is the primary vehicle for loading the significant quantities of water into the organic phase.

In an attempt to relate organic phase water content to metal speciation, 29.3mM Nd was extracted into a 2 M HDEHP organic phase and was then dried over 3 Å molecular sieves for two, 3 day periods. UV-Vis spectra were collected and water concentration was determined using Karl Fischer titrations after extraction and each drying step. The UV-Vis spectra are shown in Figure 3.6. As seen, the spectra shift significantly upon removal of water with A_{570} increasing and A_{583} decreasing, similar to the spectra of lower HDEHP concentration organic phases. This suggests that the speciation changes of neodymium in HDEHP organic phases are largely a result of water coextracted to the organic phase. Furthermore, the nature of spectral shift indicates that the coordination number of the metal in the organic phase could be decreasing as water is removed.¹³

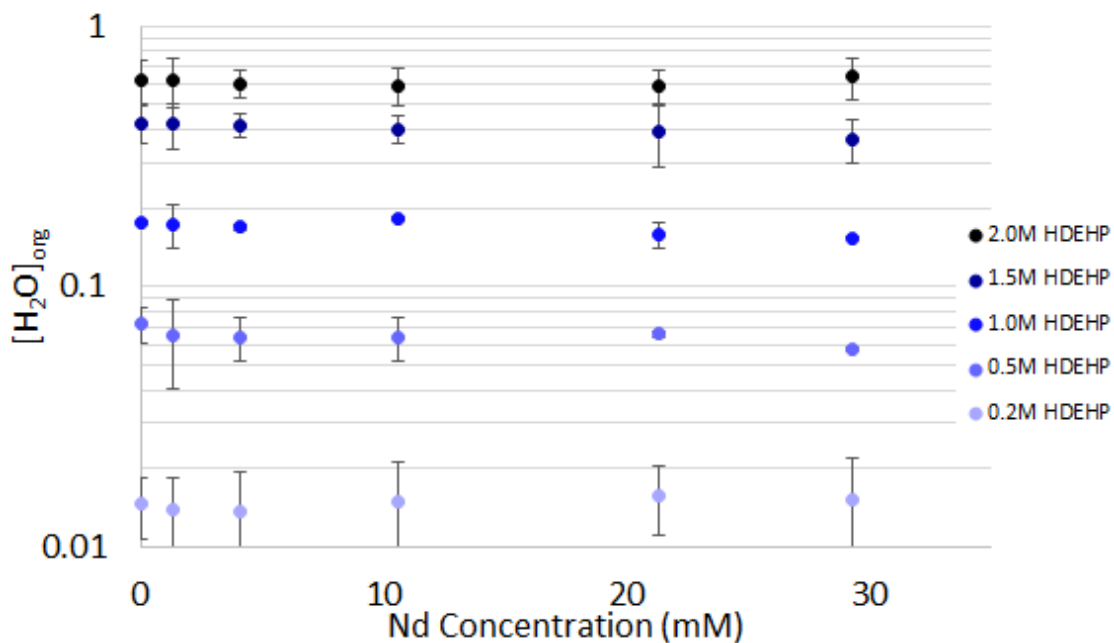


Figure 3.5 – Water Concentration of HDEHP Organic Phases Following Extraction of Neodymium

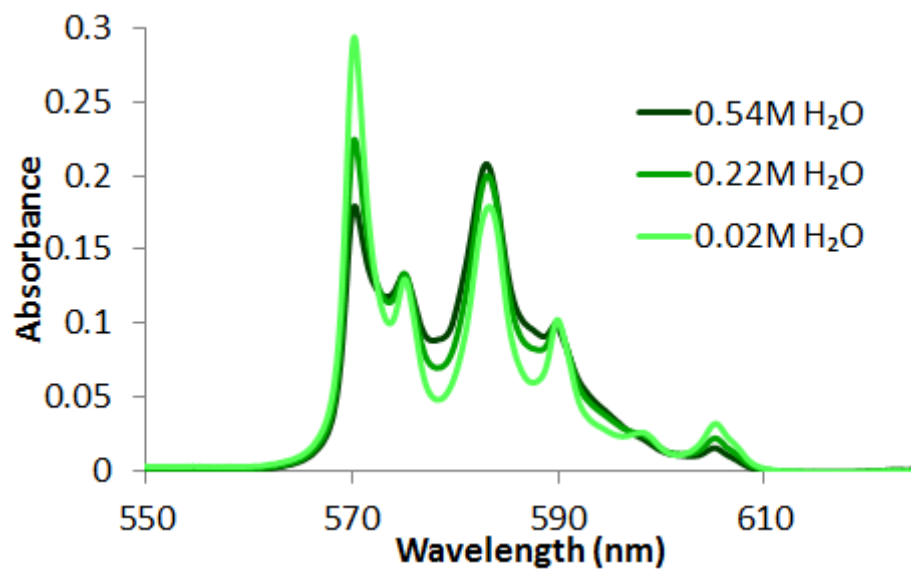


Figure 3.6 – UV-Vis Spectrum of 29.3 mM Nd in 2.0 M HDEHP Following Extraction and Subsequent Desiccation

Table 3.2 – Water Concentration in Post-Extraction Organic Phases of Various f-Elements

	Pr	Sm	Ho	Er
2.0 M HDEHP	0.590 +/- 0.021	0.521 +/- 0.116	0.569 +/- 0.054	0.539 +/- 0.022
0.2 M HDEHP	0.020 +/- 0.001	0.013 +/- 0.002	0.011 +/- 0.001	0.009 +/- 0.001
2.0 M HEH[EHP]	0.319 +/- 0.007	0.308 +/- 0.028	0.322 +/- 0.011	0.318 +/- 0.007

3.3.2 Other f-Elements in HDEHP Organic Phases

In order to understand the effects of water extraction into HDEHP organic phases on other f-elements and as a function of radii, UV-Vis spectra were collected at low (0.2 M) and high (2.0 M) HDEHP concentration after extraction of 17.7 mM Pr, 0.3mM Am, 29.8 mM Sm, 12.9 mM Ho, and 14.4 mM Er. The water concentration in the post-extraction organic phases as determined by Karl Fischer titration for Pr, Sm, Ho, and Er are comparable to that of Nd as shown in Table 3.2. Because Karl Fischer is a destructive technique, water extraction testing was not performed for the americium extraction. The spectra of the $^3H_4 \rightarrow ^3P_2$, 1I_6 , 3P_1 , 3P_0 transitions of praseodymium, the $^7F_0 \rightarrow ^5L_6$ transition of americium, the $^4I_{9/2} \rightarrow ^2H_{9/2}$, $^4F_{5/2}$ transition of holmium, $^6H_{5/2} \rightarrow ^6P_{7/2}$, $^4D_{1/2}$, $^4F_{9/2}$ transition of samarium, and the $^4I_{15/2} \rightarrow ^4H_{11/2}$ transition of erbium are shown in Figure 3.7, and corrected for metal concentration.²²⁻²⁴

When varying the HDEHP concentration, the spectra shifts significantly for Pr and Am, while the spectral shift of Sm is present but is much more subtle. However, the spectra remain constant for Ho and Er. Furthermore, the absorbances of Pr, Am, and Sm increased with an increase in HDEHP concentration and the resulting increase in water concentration. This suggests that, with an increase in water concentration, the symmetry of the metal complexes is perturbed allowing for parity changes not otherwise allowed by the Laporte selection rule.²⁵ These changes in the light lanthanide spectra indicate metal speciation changes, however the constant spectra for the hypersensitive regions of holmium and erbium suggest that water might be less able to coordinate with metal center due to lanthanide contraction.

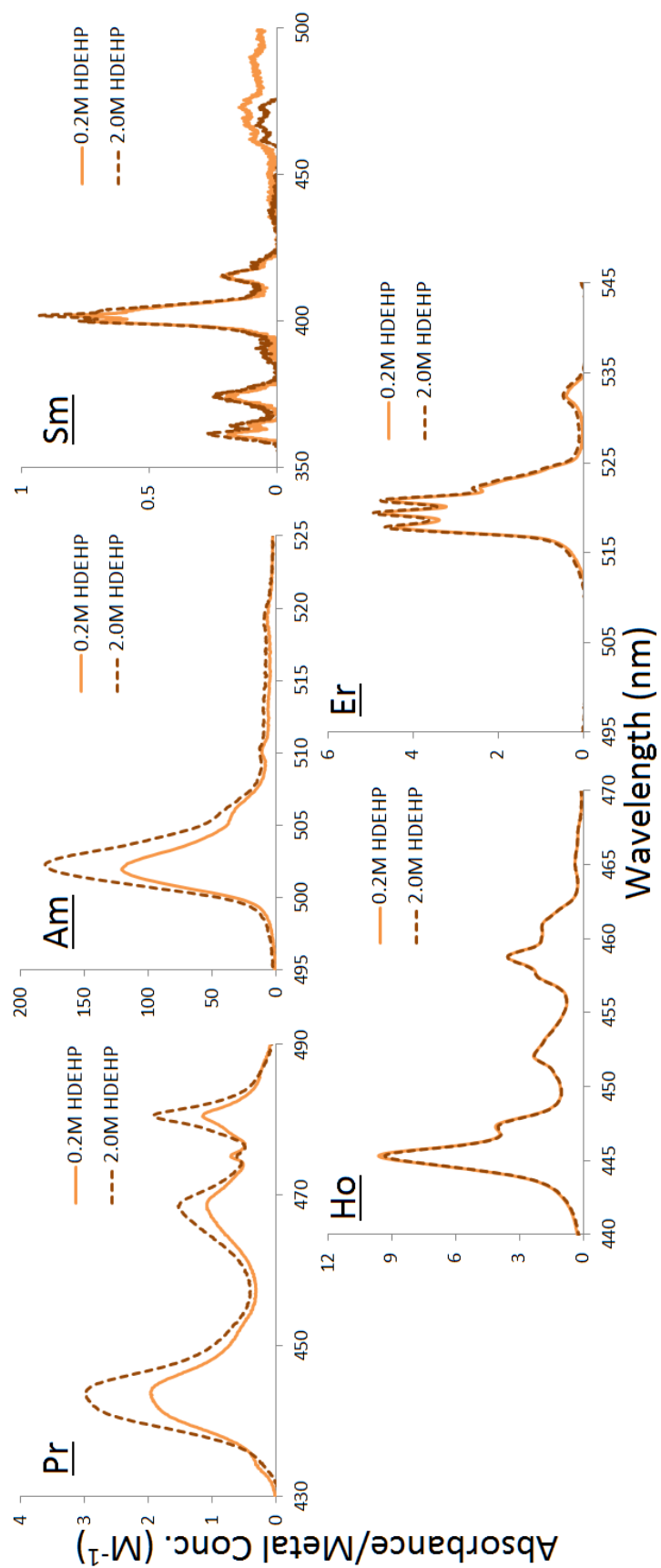


Figure 3.7 – UV-Vis Spectra of Praseodymium, Americium, Samarium, Holmium, and Erbium following extraction into 0.2 M HDEHP (solid line) and 2.0 M HDEHP (dashed line)

3.3.3 f-Element Speciation in HEH[EHP] Organic Phases

The spectra of Nd between 1.4 mM and 29.3 mM in 2.0 M HEH[EHP] and 0.5 M HEH[EHP] are shown in Figure 3.8, while Karl Fischer determination of organic phase water are shown in Figure 3.9. The concentration of water extracted to HEH[EHP] organic phases is similarly flat across the range of metals extracted, however the water extraction ability of HEH[EHP] is significantly lower. The UV-Vis spectra of Nd in HEH[EHP] organic phases is constant with differing concentrations of HEH[EHP] however, indicating that water does not coordinate with Nd in HEH[EHP] organic phases.

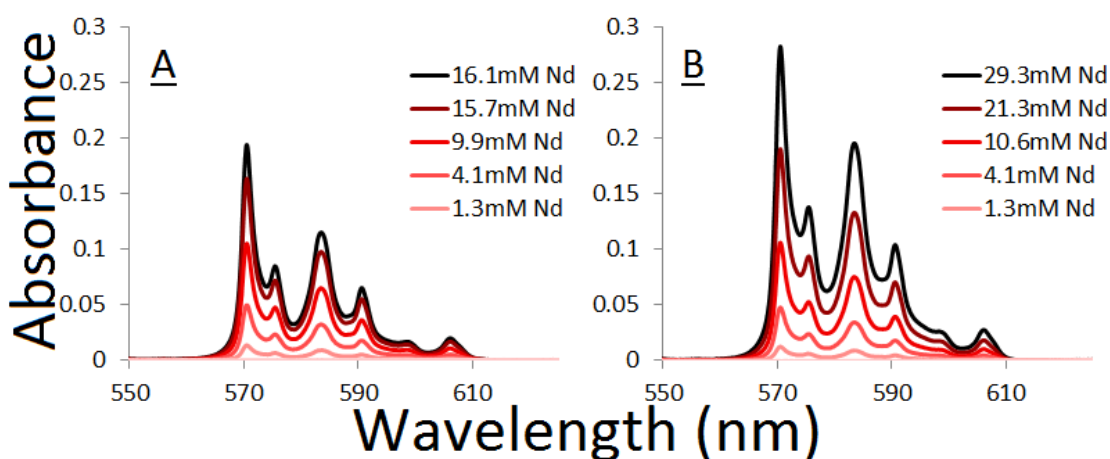


Figure 3.8 – Neodymium UV-Vis Spectra of Varying Metal Concentrations in (A) 0.5 M HEH[EHP] and (B) 2.0 M HEH[EHP]

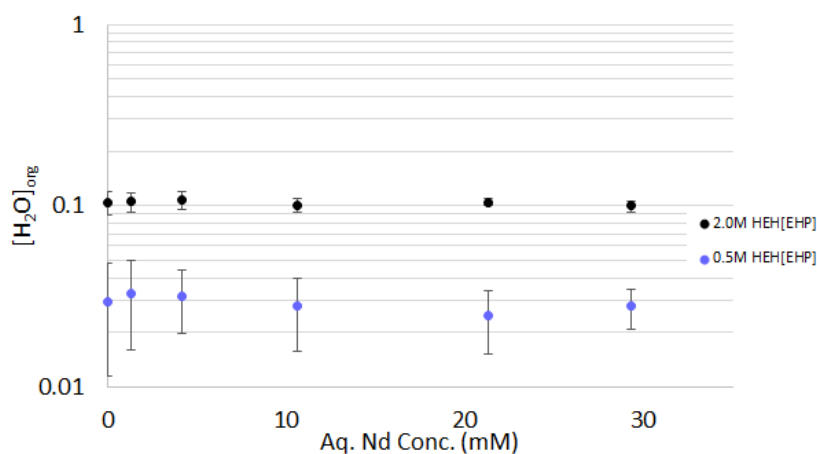


Figure 3.9 – Water Concentration of HEH[EHP] Organic Phases Following Extraction of Neodymium

Similar to the HDEHP investigation, 17.7 mM Pr, 0.3 mM Am, 13.6mM Sm, 12.9 mM Ho, and 14.4mM Er were extracted into 0.2 M and 2.0 M HEH[EHP] with UV-Vis spectra collected of the post-extraction organic phases, shown in Figure 3.10. The water concentration in 2.0M HEH[EHP] is shown in Table 3.2, while the water concentration in 0.2M HEH[EHP] was too low to be accurately quantified. Praseodymium showed a similar increase in absorbance intensity, possibly indicating a change in the metal complex symmetry. All other metals however show the same metal corrected spectra, regardless of HEH[EHP] concentration. Furthermore, americium shows much lower absorbance intensity when bound with HEH[EHP] than when bound with HDEHP, possibly indicating greater complex symmetry. This data suggests that while the lightest lanthanides may have different metal complexation environments based on HEH[EHP] concentration, lanthanides above neodymium (as well as americium) are not affected by the extractant concentration, and subsequent differences in the water concentration.

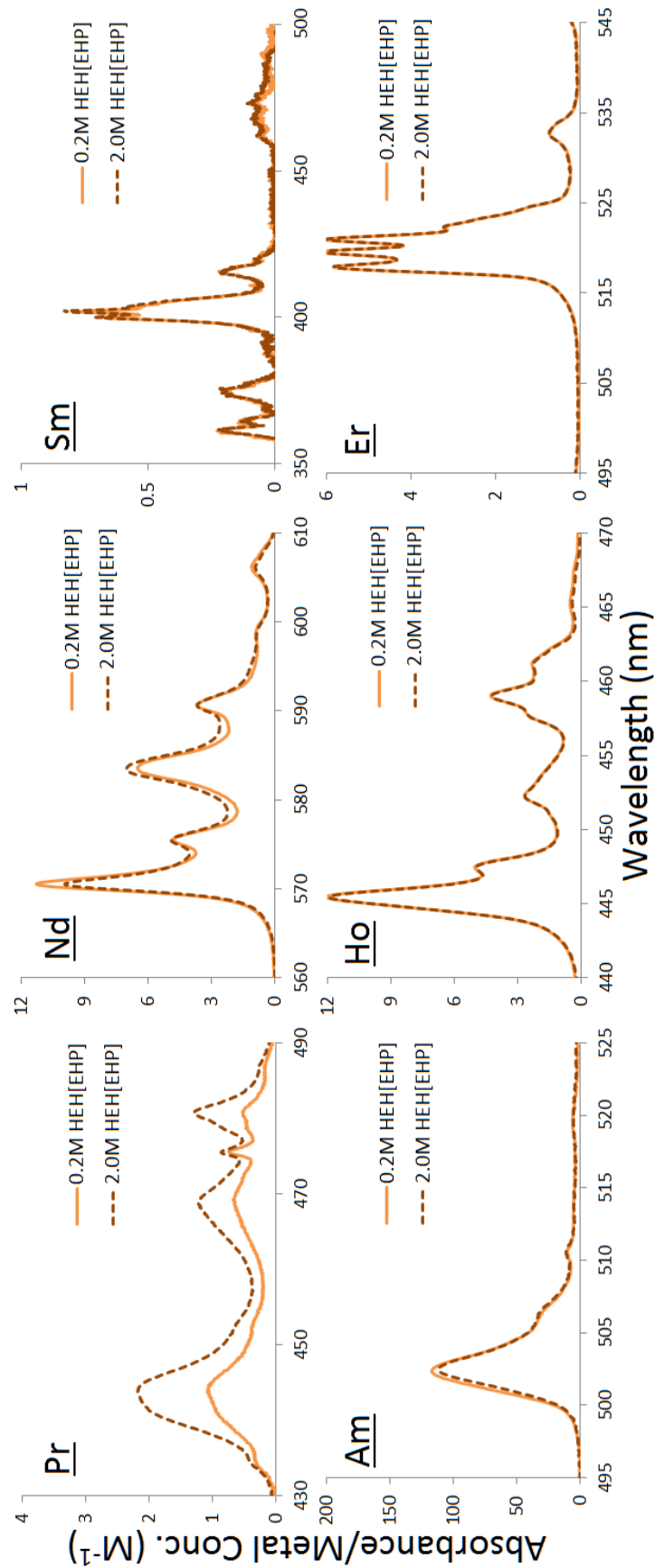


Figure 3.10 – UV-Vis Spectra of Praseodymium, Neodymium, Americium, Samarium, Holmium, and Erbium following extraction into 0.2 M HEH[EHP] (solid line) and 2.0 M HEH[EHP] (dashed line)

3.4 Conclusions

UV-Vis Spectroscopy and Karl Fischer Titrations of various lanthanides and americium extracted by HDEHP in n-dodecane led to insight into changes in metal coordination with HDEHP concentrations ranging from 0.2 M HDEHP to 2.0 M HDEHP. It was found that water was concomitant to metal extraction by the ligand which resulted in a change in the electronic spectrum. Due to the size of the f-element radius, the effect that water had on the spectrum was due to the equilibrium for forming the 7-coordinate species which included water in the inner coordination sphere of the extracted metal. This equilibrium is entirely dominated by the radii as smaller radii lanthanides did not show the same propensity for changes in the hyperfine region UV-Vis spectra. Thus it is suggested that for Am and larger Ln as the first Ln tetrad, water forms a 7-coordinate species of $\text{Ln}(\text{H}(\text{EDHP})_2)_3(\text{H}_2\text{O})$. In comparison, metals extracted into HEH[EHP] in n-dodecane showed lowered ability for the extraction of water to the organic phase, and for the ability to form the inner coordination sphere water complex except with the lightest lanthanides.

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IV. Ligand-Ligand and Metal-Ligand Interactions in Proposed ALSEP Organic Phases

This text is a modified version of a paper draft to be submitted to Industrial and Engineering Chemistry Research and a conference proceedings paper at Global 2015

4.1 Introduction

Used Nuclear Fuel (UNF) is a complicated chemical system consisting of nearly half of the periodic table.¹ Plutonium and the minor actinides (MA), bred through neutron capture of the fuel material and subsequent decay are one of the most significant sources of long-lived radioactivity in UNF, making alternate forms of disposal attractive.^{1,2} Transmutation through neutron bombardment in nuclear reactors has been proposed as a means of actinide waste treatment, but separation from the strongly neutron absorbing, fission produced lanthanides (Ln) must first be performed in order to transmute efficiently. This remains one of the primary concerns of closing the nuclear fuel cycle. Of particular concern amongst the MAs are the typically trivalent americium and curium (An(III)) which have the same oxidation state and similar ionic radii to several of the more abundantly produced lanthanides, making them very chemically similar.³ Separations of these elements has been a major concern of UNF reprocessing process development and repository planning since the origins of nuclear power generation.

The most globally employed method of UNF reprocessing is solvent extraction, where metals dissolved in an aqueous phase are extracted to an organic phase using an extractant molecule. These extracted metals are then typically stripped back into an aqueous phase for further processing or conversion to a final waste form.⁴ The traditional approach toward partitioning An(III)s and Ln is to first isolate them from a PUREX raffinate from other fission products (in processes such as TRUEX or DIAMEX), followed by partitioning using a more sensitive process (such as TALSPEAK or SANEX).^{3,5-8} Recently, mixed extractant solvent extraction processes have been explored which perform both the isolation and partitioning of An(III) and Ln in a single processing step, decreasing the chemical waste generated and simplifying the process flowsheet.⁹ In these efforts, two extractants are combined in a single organic solvent to perform a group extraction of trivalent f-elements followed by an actinide/lanthanide partition through a selective strip. Typically, a cation exchange ligand

which extracts from higher pH aqueous phases due to its required deprotonation is employed along with a solvating ligands which require metal charge balancing through coextraction with aqueous phase anions. Since these extractants complex metals under different aqueous phase conditions, one ligand type can be used for coextraction with the other ligand type used as a holdback reagent in a selective stripping stage. Unfortunately, in previously proposed mixed extractant systems, interactions between the two extractant molecules, both in pre-extraction organic phases and in organic phase metal complexes led to non-ideal extraction behavior and lowered separation factors.^{10,11} This makes process operations difficult to predict and scale.

Recently, several extractant molecules have been identified as potential candidates for An(III)/Ln separations that show more favorable processing characteristics than those of their predecessors. The organophosphorus acidic extractant 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) has been measured to have a flatter pH dependence for metal partitioning, as well as a lower tendency to extract other aqueous species than the chemically analogous di-2-ethylhexylphosphoric acid (HDEHP) traditionally used in the TALSPEAK process.¹² HEH[EHP] has been selected for use in other mixed combined solvent extractant processes such as the TALSPEAK-MME Process.¹³ Furthermore, the diglycolamides (collectively, DGAs) tetraoctyldiglycolamide (TODGA) and tetra-2-ethylhexyldiglycolamide (T2EHDGA) have been identified as viable solvating extractants due to their preferential extraction of trivalent metals from aqueous phases of high nitric acid concentration.¹⁴ In the Actinide Lanthanide Separation Process (ALSEP), a mixed solvent extraction system under current development, combinations of HEH[EHP] with either TODGA or T2EHDGA have shown more ideal extraction behavior, as well as more efficient An(III)/Ln separations compared to previous attempts at mixed extractant system development. A mixture of HDEHP with T2EHDGA provided sufficient An/Ln selectivity for the application, however it possessed a similar pH dependent extraction profile observed in TALSPEAK separations. On the other hand, a combination of HDEHP and TODGA did not provide adequate selectivity for process consideration.¹⁵

In order to better understand and to possibly predict the extraction and stripping behavior of An/Ln in mixtures of solvating and cation exchange extractants, any possible interligand interactions must be investigated. Quantification of the ability of extractants to form interligand adducts and complex with f-elements is crucial for modeling mixed extractant systems. Determination of the stoichiometry of these complexes in the organic phase is further

necessary for accurate chemical modelling of these systems. This research investigates these aspects with an aim to predict the behavior of mixed extractant solvent extraction processes.

4.2 Experimental Methods

4.2.1 Chemical Preparation

The HDEHP in this study was obtained from Alfa Aesar at 97% purity and was purified to >99% purity using the copper precipitation technique as confirmed by ^{31}P NMR.¹⁶ The HEH[EHP] in this study was obtained from Yick-Vic Chemicals & Pharmaceuticals at 95% purity and was purified to 99% purity using either the third phase formation purification technique as confirmed by acid-base titration in methanol-water mixture (70/30% v/v) or by the copper precipitation technique as confirmed by ^{31}P NMR spectroscopy.^{16,17} The diglycolamides TODGA and T2EHDGA were obtained from Eichrom Technologies at >99% purity and used as delivered. The n-dodecane was purchased from Acros Organics at 99% purity and used as delivered. In the aqueous phases used, citric acid was received from Sigma Aldrich (ACS reagent grade, >99.5%), while DTPA was obtained from Fluka ($\geq 99.0\%$) and TCI (98%) and used as delivered. Concentrated NH_4OH (Sigma Aldrich, ACS reagent grade) was used to dissolve the polyaminocarboxylates and adjust pH as checked by a pH electrode (Orion). All solutions were diluted to the desired volume with deionized water (Millipore, $18.2\text{M}\Omega\text{-cm}$).

Organic phase preequilibration and metal extraction was performed by contacting the extracting organic phase with the aqueous phases via vigorous shaking for 10 minutes using a vortex mixer. Extraction was performed in 4.5 mL polyvials followed by centrifugation at 3000rpm for 5 minutes or until phase disengagement. Phases were separated using a fine tipped transfer pipet.

4.2.2 Infrared (IR) Spectra Procedure

IR spectroscopy was used to probe the bonding nature of the organic phase ligands prior to metal extraction to determine how intermolecular adducts form in these organic phases. Solutions of constant cation exchange ligand concentration (0.3 M) and varying DGA concentration (0 M – 0.5 M) produced through dilutions of the highest concentration DGA solution. IR spectra were collected on a Nicolet 6700 FTIR Spectrometer using an attenuated total reflectance (ATR) diamond plate attachment. Approximately 50uL of the combined

extraction organic phase were placed atop the crystal with air used as a reference spectrum, with a new reference spectrum collected prior to each solution. Following collection of the spectra, the data was modeled using the non-linear least squares regression fitting software HypSpec with error reported as two standard deviations of the model fit.¹⁸

IR spectroscopy was further used to probe the nature of ligand coordination with metals at high metal concentrations. 1 mL of solutions of 1 M HDEHP + 200 mM T2EHDGA, 1 M HEH[EHP] + 200 mM TODGA, and 1 M HEH[EHP] + 200 mM T2EHDGA in n-dodecane were metal loaded from 1 mL of a 25.2 mM Nd in pH 3 HCl aqueous phase. The HDEHP + T2EHDGA solution performed extraction three times sequentially and organic phases containing HEH[EHP] performed extraction four times sequentially to adequately load the organic phase for observation via IR spectroscopy. Organic phase metal concentration was quantified by collecting UV-Vis spectra of the post-extraction aqueous phase.

4.2.3 Job's Method Procedure

Job's method was employed to elucidate the stoichiometry of ternary complexes through varying the ligand ratio used for extraction while keeping constant the total extractant concentration. Europium nitrate (Alfa Aesar, 99.9%) was irradiated in the Oregon State TRIGA reactor for 7 hours, followed by conversion to a chloride salt by dissolution in concentrated HCl and evaporated followed by dissolution in the appropriate aqueous phases. ²⁴¹Am was also converted to a chloride salt in a similar technique and dissolved in the appropriate aqueous phase. Organic phases of 0.2 M total extractant concentration were prepared from 0.2 M solutions of the individual extractants in the appropriate volumetric ratios to achieve the desired mole fractions of the ligands. For extraction into HDEHP solutions, 0.5M HDEHP + 50mM DTPA at pH = 3.36 +/- 0.05 was used for Eu extraction and 0.5M (H⁺/NH⁺) citrate + 10mM DTPA at pH = 3.36 +/- 0.05 was used for Am extraction. For extraction in HEH[EHP] solutions, 0.5M (H⁺/NH⁺) citrate at pH = 3.17 +/- 0.05 was used for both nuclides. Organic phases were preequilibrated 3 times by vortexing a 3:1 aq:org ratio prior to metal extraction by vortexing a 1:1 aq org ratio. Distribution ratios were determined through gamma spectroscopy of aliquots of each liquid phase, using a NaI(Tl) scintillation counter (Packard COBRA II).

4.2.4 UV-Vis Spectra Collection Procedure

UV-Vis spectra of f-elements were used to determine and further quantify the mechanism of intermolecular interaction with metals in post-extraction organic phases. Neodymium and holmium chloride were prepared by dissolving either Nd_2O_3 (Sigma Aldrich, 99.9%) or Ho_2O_3 (Sigma Aldrich, 99.9%) in concentrated HCl (Macron, ACS grade) and evaporated. An ^{243}Am stock was prepared similarly by dissolution in concentrated HCl and evaporation twice. Both were then dissolved in pH3 HCl prepared by dissolution of concentrated HCl with deionized water (Millipore, 18.1M Ω -cm). Extraction into 0.2 M HDEHP for Nd and Am, 1.0 M HDEHP for Ho, or 1.0 M HEH[EHP] for all metals in n-dodecane was performed by vortexing a 1 mL of the metal loaded aqueous phase with 1 mL of the extracting organic phase. Nd and Ho distribution ratios were determined using an A(III) colorimetric technique, while the Am organic phase concentration was determined using LSC counting.¹⁹ Each metal extraction was found to be quantitative however, such that the concentration of metal in the organic phase is equivalent to the initial aqueous phase metal concentration. When Nd was extracted into HDEHP, the extraction organic phase was dried over 3Å molecular sieves for 3 days to alleviate the effects of water in the organic phase.²⁰ This was not done for americium to prevent excessive waste generation.

UV-Vis spectra of the organic phase were collected from a 1cm quartz cuvette with an n-dodecane background solvent on a Cary 6000i UV-Vis-NIR spectrometer with a temperature jacket held at 20°C. Spectra were collected of the $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2}$, $^2\text{G}_{7/2}$ hypersensitive transition of Nd, the $^4\text{I}_{9/2} \rightarrow ^2\text{H}_{9/2}$, $^4\text{F}_{5/2}$ hypersensitive transition of holmium, and the $^7\text{F}_0 \rightarrow ^5\text{L}_6$ transition of americium.^{21,22} The first UV-Vis spectra were collected immediately following extraction followed by titration of an organic phase containing the same concentration of the cation exchange ligand used in extraction as well as either TODGA or T2EHDGA into the metal loaded organic phase. The solution was vortexed for 30 seconds, and a new spectrum was collected. At least 20 spectra were collected for each system, and non-linear least squares regression fitting using HypSpec was then performed on the spectra to quantify interactions with error reported as two standard deviations of the model fit.¹⁸

4.3 Experimental Results

4.3.1 IR Spectroscopy Organic Extractant Interaction Results

The IR spectra of several ligand ratios of HDEHP and T2EHDGA, HEH[EHP] and TODGA, and HEH[EHP] and T2EHDGA are shown in Figure 4.1. The peak assignments for the cation exchange ligands and the two DGAs are shown in Table 4.1. For all three ligand combinations, the phosphoryl group of the cation exchange ligand is seen to shift, with slight absorbance changes noticed in the carbonyl and ether groups of the DGAs. This indicates that interactions between the two molecules likely occur between the phosphoric acid group of HDEHP or the phosphonic acid group of HEH[EHP] and in the diglycol- group of the DGAs. HEH[EHP] mixtures with DGAs also show a shift in the P-C band in HEH[EHP] becoming more intense with an increase in DGA concentration, potentially indicating greater electron density donated to this bond in the adduct form.

Table 4.1 – IR Peak Assignments for ALSEP Ligands

Molecule	Absorbance Band (cm ⁻¹)	Bond
HDEHP/HEH[EHP]	1300 – 1150	P=O
	1100 – 900	P-O-C, P-C
TO/2EHDGA	1450 – 1400	P=O
	1700 – 1600	C=O
	1150 - 1100 cm ⁻¹	C-O-C

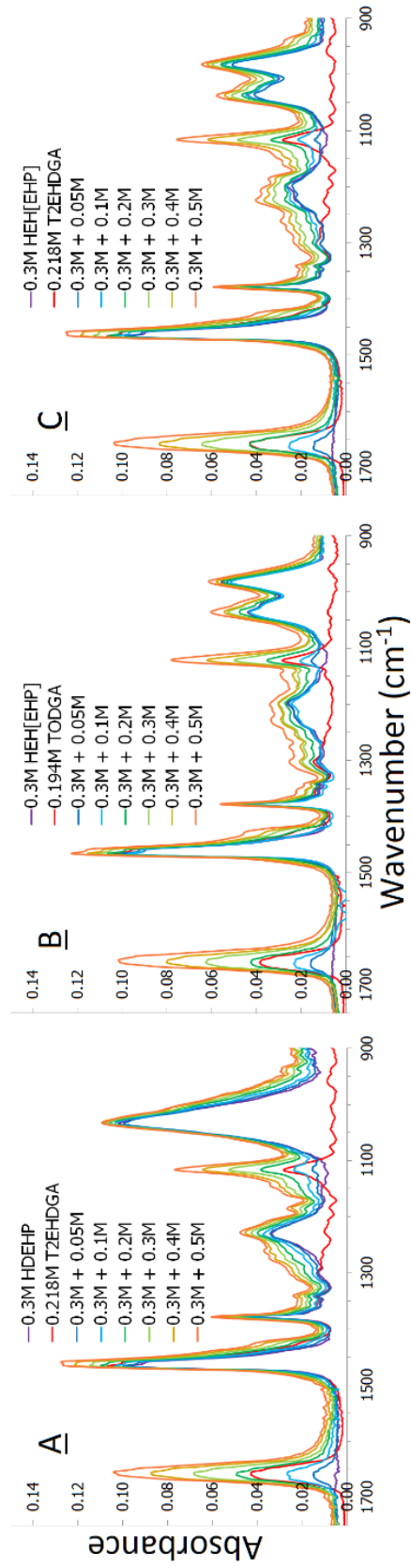
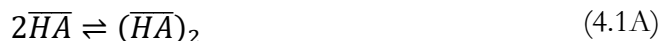


Figure 26 – IR Spectra of a Constant Concentration of a Cation Exchange Extractant and Variable DGA for the Mixtures of (A) HDEHP and T2EHDGA, (B) HEH[EHP] and TODGA, and (C) HEH[EHP] and T2EHDGA

At least 19 spectra of 0.3 M cation exchange extractant with varying DGA concentration were used to generate a chemical model. Previously, it has been shown that cation exchange ligands primarily form 1:1 complexes with neutral ligands, so the model established is a competition between adduct formation of the cation exchange ligand with the formation of an interligand adduct.^{11,23} This is defined by the equilibria in Equations 4.1A and 4.1B and the equilibrium constants in Equations 4.2A and 4.2B.



$$K_{dim} = \frac{[(\overline{HA})_2]}{[\overline{HA}]^2} \quad (4.2A)$$

$$K_{add} = \frac{[\overline{HA - DGA}]}{[\overline{HA}][\overline{DGA}]} \quad (4.2B)$$

The dimerization constants of the cation exchange ligands applied to the chemical model were found in literature to be 4.82 and 4.23 for HDEHP and HEH[EHP] respectively.²⁴ The adduct formation constant for each combination of cation exchange and solvating ligands are shown in Table 4.2. The combination which interacts the most strongly is the HEH[EHP] – TODGA mixture, although each ligand combination had adduct formation constants within an order of magnitude of each other. Overall however, all combinations have a much lower capacity for adduct formation than the proposed HDEHP – CMPO combination for the TRUSPEAK process.¹¹

IR spectra of organic phases in the presence of metal were also collected. Neodymium was loaded from pH 0.001 M HCl into organic phases of 1 M cation exchange ligand and 200 mM DGA are shown in Figure 4.2. The neodymium concentration in each organic phase was determined to be 75+/- 3 mM Nd in each organic phase. Under the studied aqueous extraction phase conditions, no changes in the DGA bond environment are

Table 4.2 – Log(K) Values of Adduct Formation Between Cation Exchange and Solvating Ligands

HDEHP – T2EHDGA	2.42 ± 0.01
HEH[EHP] – TODGA	2.62 ± 0.01
HEH[EHP] – T2EHDGA	2.31 ± 0.01

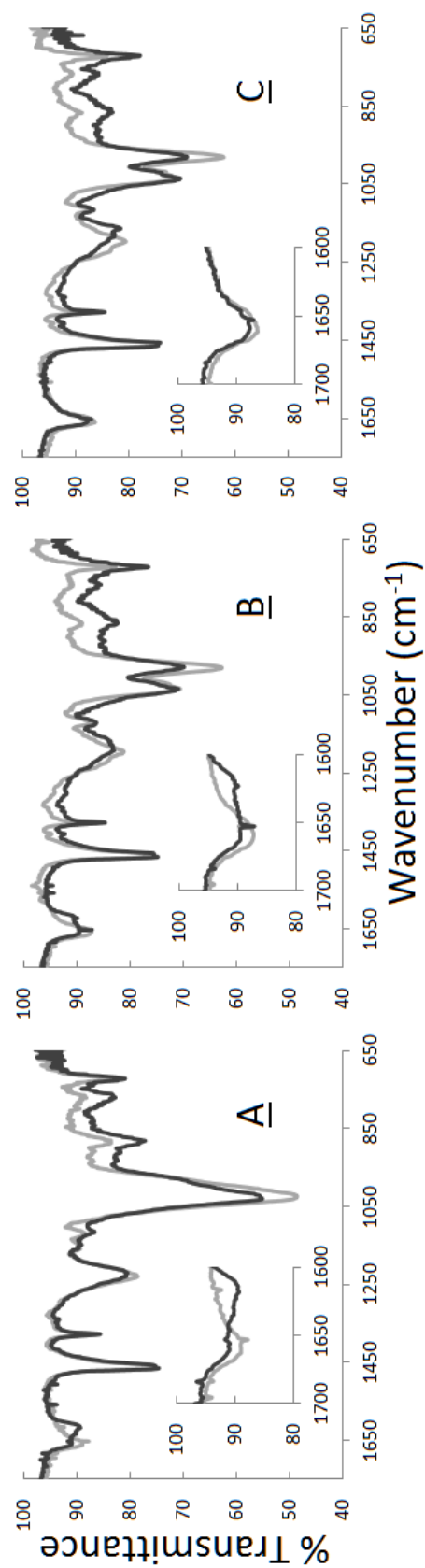


Figure 4.2 – IR Spectra of the ALSEP Organic Solutions Prior to Extraction of Metal (Light Lines) and Following Metal Loading from a pH 2.8 HCl aqueous phase (Dark Lines). Combination are (A) 1 M HDEHP + 200 mM T2EHDGA, (B) 1 M HEH[EHP] + 200 mM TODGA, (C) 1 M HEH[EHP] + 200 mM T2EHDGA

expected, as the binding of metal cation with a neutral ligand should not be favored in the absence of the extractable nitrate ion, which could balance the metal cationic charge. However, as shown in the Figure 4.2 inset, this is not the case in either the HDEHP - T2EHDGA or HEH[EHP] - TODGA systems, where the carbonyl group of the DGA is strongly affected by the presence of metal, confirming presence of DGA in the metal complex. On the contrary, in the HEH[EHP] - T2EHDGA organic solution, the carbonyl absorption band is not affected by the presence of organic phase metal.

Overall, the infrared spectroscopy data shows that, even in the absence of metal-charge compensating nitrate, both the neutral and acidic ligand may be present in the metal complex. This is true for both HDEHP - T2EHDGA and HEH[EHP] - TODGA, but does not appear to be the case for HEH[EHP] - T2EHDGA.

4.3.2 Stoichiometric Analysis by Job's Method

Job's method, or the method of continuous variation is a fundamental method in organometallic chemistry for the elucidation of the stoichiometry of metal complexes.²⁵ Applied to solvent extraction systems, the monitored value is the distribution ratio of the metal studies while varying the concentration ratio of the extractant molecules. Job's Method uses utilizes the simplified chemical equilibrium in Equation 4.3.



In this equation, “A” and “B” are the individual organic extractant species, while “MA_aB_b,” is the resulting extracted ternary species. When the intermolecular species complex metals stronger than the individual metals, there will be a ratio of “a” to “b” which represents the stoichiometry of the ligands complexing the metal. Job's Method utilizes a constant total extractant concentration with a varying ligand ratio to determine the maximum possible extraction and thus the complex stoichiometry.

Job's Method plots of americium and europium into 0.2M total extractant are shown in Figure 4.3 and 4.4 respectively, plotted as metal distribution ratio values against the 0.2 M total ligand concentration. It can be seen that, for the HDEHP – T2EHDGA combination, as well as HEH[EHP] – TODGA complexes for americium, the stoichiometry of the metal ligand complexes is 6:1 HA:DGA molecule per metal center. This suggests that the metal

complex contains three cation exchange ligand dimers with a single solvating DGA molecule. For europium extraction into HEH[EHP] – TODGA, and with either metal into HEH[EHP] – T2EHDGA systems, the ability of the ligands to complex with intermolecular adducts is not strong enough to determine the stoichiometry via Job's Method. From these Job's Plots, it appears that the primary mode of adduct complexation with metals is a single DGA joining the metal complex.

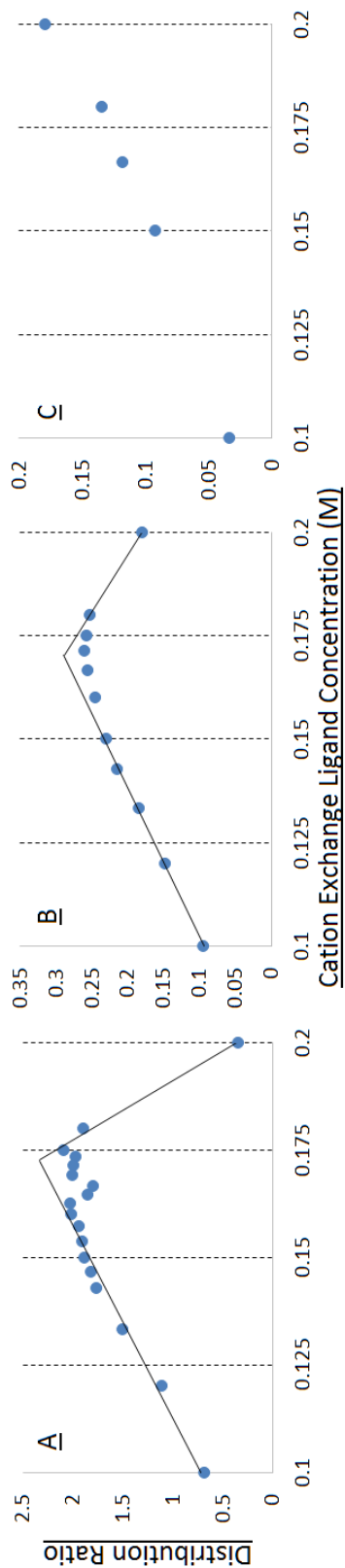


Figure 4.3 – Job's Method Plots of Americium Distribution Ratios into 0.2M Total Extractant Organic Phases of HDEHP and T2EHDGA (A), HEH[EHP] and TODGA (B), and HEH[EHP] and T2EHDGA (C)

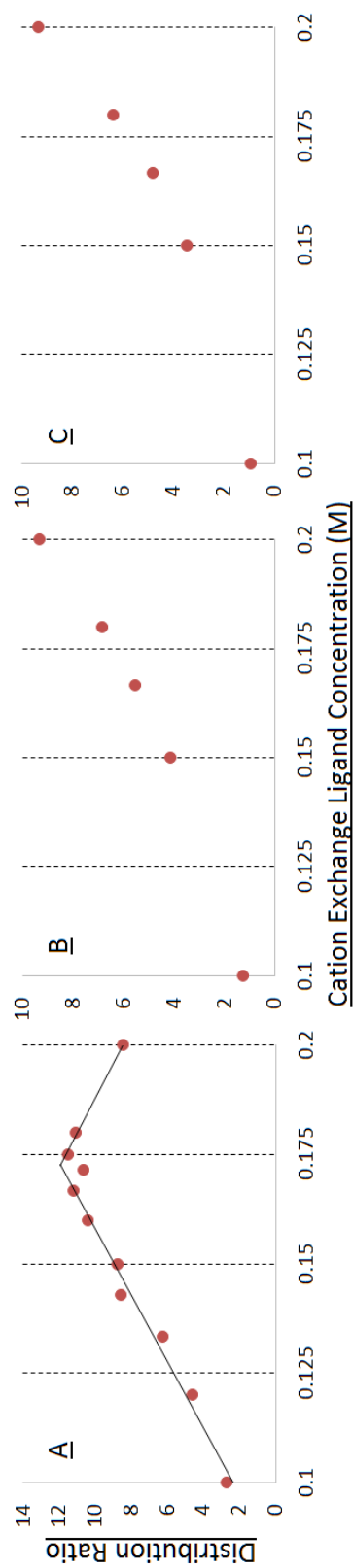


Figure 4.4 – Job's Method Plots of Europium Distribution Ratios into 0.2M Total Extractant Organic Phases of HDEHP and T2EHDGA (A), HEH[EHP] and TODGA (B), and HEH[EHP] and T2EHDGA (C)

4.3.3 UV-Vis Spectroscopic Titrations

The UV-Vis spectra of Nd, Am, and Ho extracted into each ligand combination are shown in Figures 4.5, 4.6, and 4.7 respectively. In the Nd spectra, with the addition of T2EHDGA to the HDEHP systems and the addition of TODGA to the HEH[EHP] system, the absorbance peak at 570nm appears to diminish while the absorbance peak at 583nm absorbs with greater intensity. This shifting behavior resembles that of an increase in the coordination number of the metal in the organic phase as previously reported.²¹ Nd in the HEH[EHP] – T2EHDGA system show very little effect on the spectra based on the DGA concentration, suggesting minimal ability for ternary complexes to form with neodymium. In the Am systems, an increase in absorbance intensity is seen for all ligand combinations, however the increase is not as prominent in the HEH[EHP] – T2EHDGA system. While this transition is not hypersensitive, an increase in the absorbance intensity is suggestive of a decrease in the metal coordination symmetry.

The holmium spectra collected also contains a hypersensitive transition which are able to reveal structural information. In the HDEHP – T2EHDGA organic phase, a similar peak shift behavior is seen as is seen with the neodymium spectra, where it appears that there is an increase in the coordination number with an increase in the DGA concentration. In both HEH[EHP] systems however, there is no spectrum change with the titration addition of DGAs. This indicates that, in HEH[EHP] systems, intermolecular adducts are largely unable to complex with holmium in the organic phase. The trans-lanthanide effect observed in the slope analysis is further confirmed in this system, as Ho is heavier lanthanide than Nd, and therefore has a smaller ionic radius than either Nd or Am. The fact that intermolecular adducts cannot form even in HEH[EHP] – TODGA systems serves to reinforce that adduct formation with metals is largely dependent on the metal ion size, with greater adduct formation ability seen in the lighter, larger ionic radii f-elements.

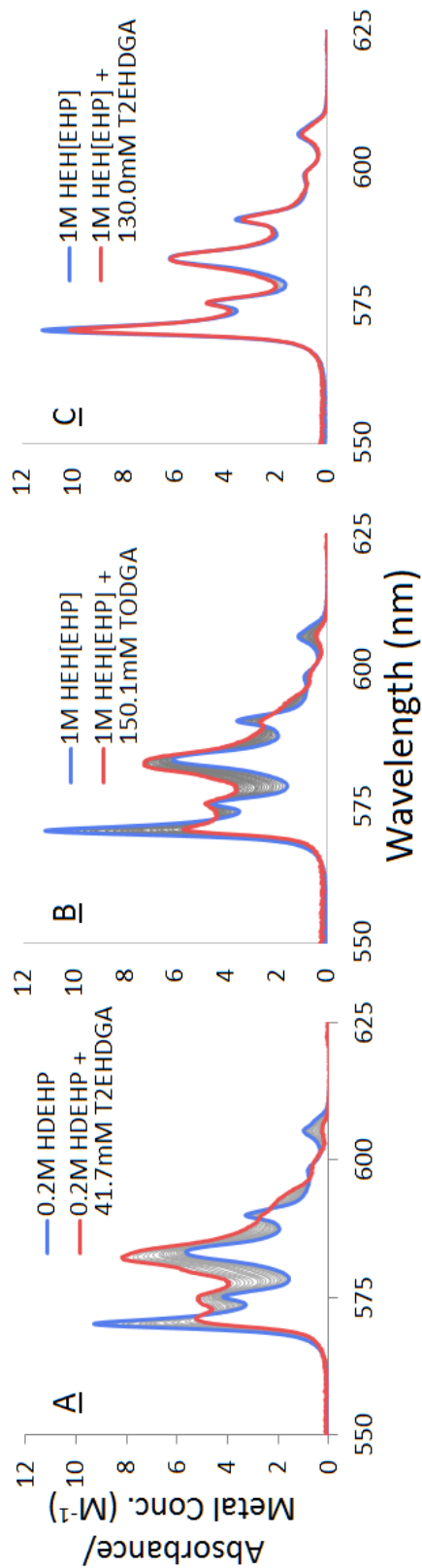


Figure 4.5 – UV-Vis Spectra of Nd in Organic Phases of Varying DGGA Concentration with Constant Cation Exchange Ligand Concentration for (A) HDEHP – T2EHDGA, (B) HEH[EHP] – TODGA, and (C) HEH[EHP] – T2EHDGA Combinations

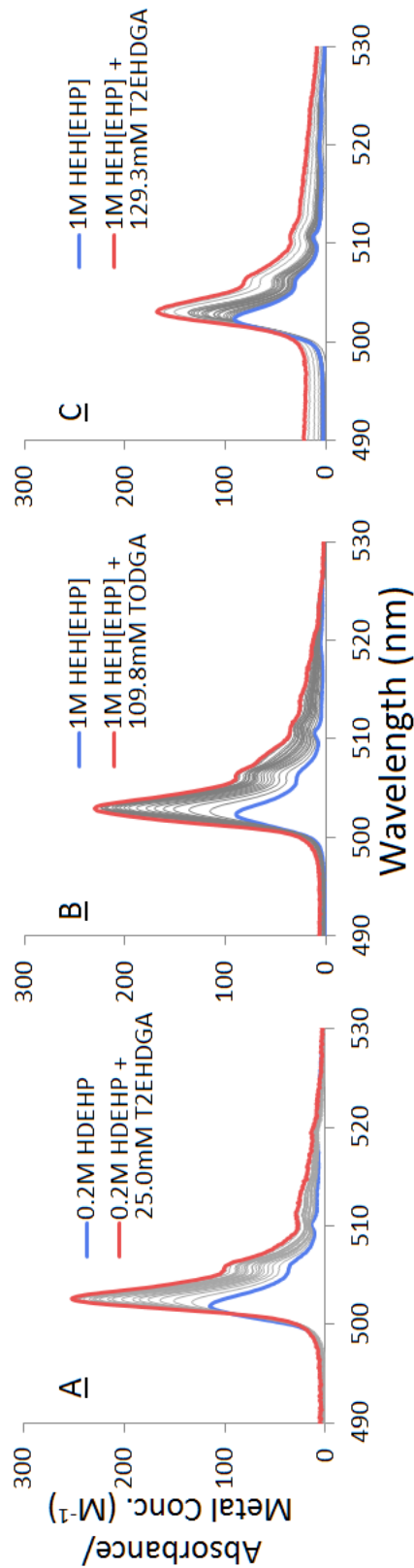


Figure 4.6 – UV-Vis Spectra of Am in Organic Phases of Varying DGGA Concentration with Constant Cation Exchange Ligand Concentration for (A) HDEHP – T2EHDGA, (B) HEH[EHP] – TODGA, and (C) HEH[EHP] – T2EHDGA combinations

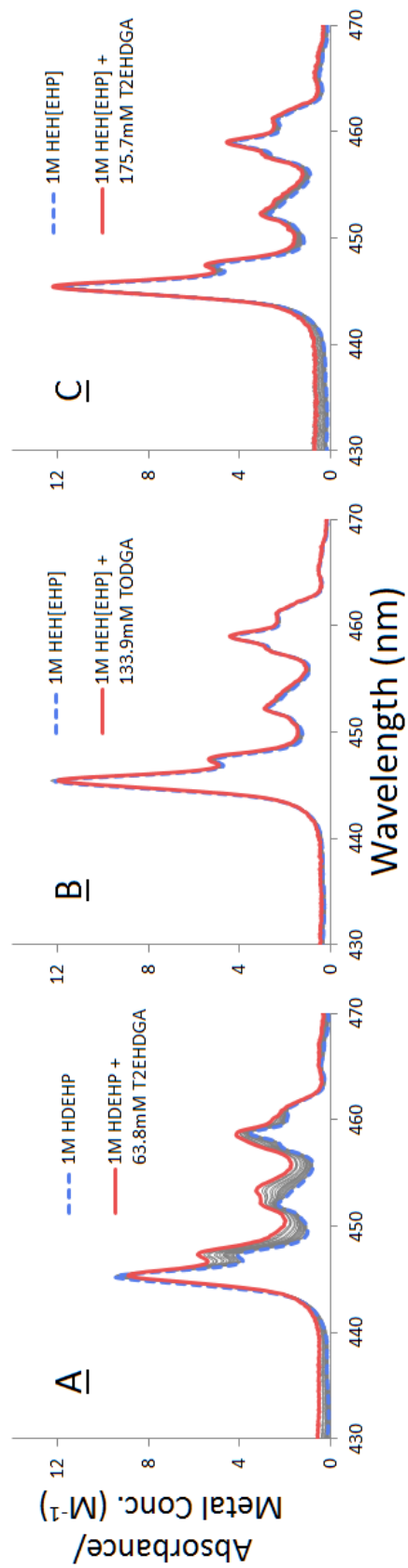
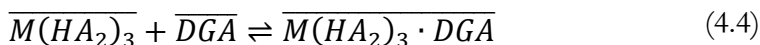


Figure 4.7 – UV-Vis Spectra of Ho in Organic Phases of Varying DGA Concentration with Constant Cation Exchange Ligand Concentration for (A) HDEHP – T2EHDGA, (B) HEH[EHP] – TODGA, and (C) HEH[EHP] – T2EHDGA combinations

The UV-Vis spectra data were modeled using the non-linear least-squares regression fitting software HYPSpec. The model which was generated to interpret the data, as advised by the Job's method plot is shown in Equation 4.4.



Values of the conditional stability constant in the absence of nitric acid are shown in Table 4.3. HDEHP – T2EHDGA possesses the greatest ability to form ternary complexes with metals in the organic phase. The HEH[EHP] – TODGA combination has a slightly lesser ability to form ternary complexes with americium and neodymium, but no discernable ability to form intermolecular complexes with holmium. The HEH[EHP] – T2EHDGA combination however shows very little ability to form ternary complexes with americium, and shows almost no ability to form adduct complexes with neodymium or holmium. In general, ternary form metal complexes with americium stronger than with neodymium and holmium, and there appears to be a translanthanide trend where intermolecular adducts do not complex

with heavier lanthanides as effectively as with light lanthanides. *Table 4.3 – Log₁₀K Values of Ternary Complex Formation as Determined by UV-Vis Spectroscopy*

	Neodymium	Americium	Holmium
HDEHP - T2EHDGA	1.98 ± 0.01	2.73 ± 0.01	1.62 ± 0.01
HEH[EHP] - TODGA	1.20 ± 0.01	2.25 ± 0.01	--
HEH[EHP] - T2EHDGA	--	1.53 ± 0.01	--

4.4 Conclusions

From this work, several conclusions can be drawn about the ability of proposed ALSEP ligands to form intermolecular species in preextraction organic phases and how these adducts can complex with f-elements. First, HDEHP – T2EHDGA and HEH[EHP] – TODGA combinations form intermolecular adducts in metal-free organic phases with relatively similar ability, however HDEHP – T2EHDGA adducts appear to complex f-elements slightly better than HEH[EHP] – TODGA adducts. HEH[EHP] – T2EHDGA appeared to have the least ability to form intermolecular adducts in metal-free organic phases and was the least able to complex metals. From the Job's Method plot it appears that metal complexation for each extractant combination it is likely that 6:1 HA:DGA ratio complexes

are the most common inter-ligand species in the organic phase, while HEH[EHP] – T2EHDGA systems do not generally favor inter-ligand species forming with metals.

The UV-Vis spectra prepared for Nd, Am, and Ho in the organic phase lend further insight into the nature of metal complexation in mixed ligand systems. With an increase in the DGA concentration, an increase in the metal coordination number appears to occur, resulting in a decrease in the complex symmetry. Data fitting suggests a similar trend of the ability of adducts to form metal complexes however, as HDEHP – T2EHDGA shows the greatest ability to form intermolecular adduct complexes with extracted metals, while HEH[EHP] – T2EHDGA shows the least ability to form such complexes. Furthermore, a trans-lanthanide trend is suggested showing that intermolecular adducts do not complex metals as effectively with heavier lanthanides than with light lanthanides.

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V. Ligand-Ligand and Metal-Ligand Interactions in Proposed ALSEP Organic Phases

This text is a modified version of a paper draft to be submitted to Separation Science and Technology

5.1 Introduction

Separations of trivalent minor actinides and lanthanides represent a significant technical challenge in Used Nuclear Fuel (UNF) reprocessing.¹ Americium poses one of the greatest sources of thermal loading to planned geologic repositories which could result in an exceedance of temperature limits.² Treatment of americium and other actinides has been proposed as part of partitioning and transmutation disposal options. This strategy requires that they be subject to high neutron fluxes, such as those in fast spectrum nuclear reactors for reduction of waste decay time by transmutation.³ To achieve this goal, actinides must be first separated from lanthanides, which are produced by fission and represent a significant fraction of UNF. Lanthanides fission products are strong neutron absorbers, and hence their separation is key to a successful actinide transmutation strategy.³

Several solvent extraction methods which address this goal have been developed in recent years for performing these separations from the aqueous raffinate streams resultant from the PUREX process. Typical solvent extraction methods of partitioning the two species are to first isolate trivalent minor actinides and lanthanides from the remaining fission products, followed by their separation.^{4,5} Performing this separation in two stages generates significant chemical waste and increases the complexity of process flowsheets.

In recent years, mixed extractant solvent extraction processes have been developed to address these concerns.⁶ Typically, a solvating ligand requiring charge balancing anions and a cation exchange ligand are combined in a single organic phase to perform a group extraction of trivalent f-elements followed by an actinide-lanthanide partition in a single process. Both the trivalent actinides and lanthanides are coextracted from a highly acidic aqueous phase via complexation with the solvating ligand, followed by a selective strip of one metal type using a buffered aqueous phase and a holdback of the other metal type in the organic phase utilizing the cation exchange ligand. Development of processes such as the TRUSPEAK process, combining HDEHP and CMPO in a single organic phase, has revealed some anomalous processing behavior however, such as reduced extraction at higher acidities and lower overall

separation factors than anticipated.⁷ These effects are largely attributed to intermolecular interactions between the two extractants in the organic phase, creating alternate pathways for metal complexation.

Several studies have been performed to characterize the complex type formed upon extraction from varying aqueous phases. When neodymium and europium were extracted from lactate media, the interactions between HDEHP and CMPO with metals were confirmed using metal distribution, FTIR and UV-Vis spectroscopies, further showing that extracted lactate ternary species were not present in the organic phase.⁸ Modelling of extraction behaviour in the presence of nitrate has revealed several mixed ligand species with organic phase nitrate as well.⁹ Investigations into other processes, such as the TALSPEAK-MME system have revealed the competition between ligands with the introduction of nitrate to the organic phase. This showed the relative competition of nitrate species across the lanthanide series.¹⁰

Another important factor to be considered in the determining of chemical speciation are the non-idealities of these systems and formation of micellar structures of the organic extraction solutions. Recently, the metal complexes of europium in HDEHP and TODGA organic phases were studied using synchrotron small angle X-ray scattering (SAXS) and X-ray absorption fine structure spectroscopy (EXAFS).¹¹ In this system, varying the nitric acid concentration of the aqueous phase had negligible impact on the size and structure of the organic phase reverse-micelles structures, but caused a change in the dominant coordination mode from HDEHP complexes at low acidity to TODGA complexes at high nitric acid concentrations.¹¹

Recent developments have shown that 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) in conjunction with either tetraoctyldiglycolamide (TODGA) or tetra-2-ethylhexyldiglycolamide (T2EHDGA) in n-dodecane allows for extraction of trivalent actinides and lanthanides from high nitric acid concentration aqueous phases and possess the ability to selectively retain lanthanides over actinides with HEH[EHP] when contacted with an aqueous stripping solution of a polyaminocarboxylate and a buffer.¹² Furthermore, the stripping stage displays the favourable pH stability present in HEH[EHP] extraction processes.¹³

The different interaction mechanisms of these ligands with metals suggests the ability of extractant molecules to coordinate with metals independently of each other. While previous

investigations have suggested that inter-ligand interactions without the presence of mineral acid anions are not prominent, the nature of ligand competition for the metal as an effect of organic phase nitrate concentration is as of yet uncharacterized.¹⁴ This prompted an investigation into the shift from metal complexation with the cation exchange ligand to the solvating ligand as the charge balancing nitrate anion is introduced. This could assist in the determination of process boundary conditions for industrial scale operations.

5.2 Experimental Methods

The HEH[EHP] used in this study was obtained from Yick-Vic Chemicals & Pharmaceuticals at 95% purity and was purified to 99% purity using the third phase formation purification technique as confirmed by acid-base titration in methanol-water mixture (70/30% v/v).¹⁵ The diglycolamides TODGA and T2EHDGA were obtained from Marshallton Technologies at >98% purity and used as delivered. The n-dodecane was purchased from Acros Organics at 99% purity and used as delivered. Tetrachloroethylene (TCE) was obtained from J. T. Baker (>99.9%) and used as delivered. Organic solutions were prepared on a mass basis and diluted with n-dodecane except when extracting into just TODGA or T2EHDGA where TCE was used as a diluent to suppress third phase formation.

Aqueous phase metal solutions for HEH[EHP] extraction were prepared by dissolving Nd_2O_3 (Sigma Aldrich, 99.9%) or Ho_2O_3 (Sigma Aldrich, >99.9%) in concentrated HCl (Macron, ACS grade) and evaporated. Solutions were then prepared by dissolving the freshly prepared chloride salts into dilute HCl (pH 2.80) as checked with an Orion 8165 BNWP pH electrode. Aqueous phase metal solutions for TODGA and T2EHDGA extraction were prepared using $\text{Nd}(\text{NO}_3)_3$ (Alfa Aesar, 99.9%) and $\text{Ho}(\text{NO}_3)_3$ (Alfa Aesar, 99.9%) dissolved into 3M nitric acid (Mallinckrodt, ACS grade) as checked with NaOH titrations. All aqueous phases were prepared using 18.1 M Ω -cm deionized water generated using a Millipore system. Solvent extraction was performed by contacting 1 mL of the extracting organic phase with 1 mL of the metal loaded aqueous phases via vigorous shaking for 10 minutes using a vortex mixer. Extraction was performed in 4.5 mL polyvials followed by centrifugation at 3000rpm for 5 minutes or until phase disengagement. Phases were separated using a fine tipped transfer pipet.

For the IR spectroscopic investigation, two sets of solvent extraction organic phases were prepared by performing multiple, serial extraction to achieve adequate metal loading for

observation of ligand-metal bond interaction. 1 M HEH[EHP] solutions in n-dodecane were metal loaded by contacting with a 8.23mM Nd and a 12.9mM Ho in 0.001 M HCl solutions 5 times. 0.2 M solutions of either TODGA or T2EHDGA in tetrachloroethylene (TCE) were metal loaded by performing solvent extraction with a 13.8mM Nd and a 15.5mM Ho solution 4 times to achieve adequate metal loading. The metal-free, HNO₃ loaded organic phase was prepared by contacting the organic phase once with a 3 M HNO₃ solution. IR spectra were collected using a Nicolet 6700 FTIR Spectrometer using an attenuated total reflectance (ATR) diamond plate attachment. Approximately 50uL of each organic phase were placed atop the diamond crystal using air as a reference spectrum, with a new reference spectrum collected prior to each sample solution.

For the UV-Vis spectrophotometric titration, metals were extracted to the organic phase by performing solvent extraction once with either 10.6mM Nd, 12.9mM Ho in 0.001 M HCl, The titrant was prepared by contacting 1 M HEH[EHP] + 200 mM TODGA or T2EHDGA with 3 M HNO₃. The extracted metal concentration was determined by the pre- and post-extraction aqueous phase measured by UV-Vis while the concentration of HNO₃ extracted to the organic phase was determined by NaOH titration of the pre- and post-extraction aqueous phase. UV-Vis spectra of the organic phase were collected from a 1cm quartz cuvette with an n-dodecane background solvent on a Cary 6000i UV-Vis-NIR spectrometer with a temperature jacket held at 20°C. Spectroscopic data were modelled using the non-linear least squares regression fitting spectral analysis software Hypspec.¹⁶

5.3 Experimental Results

5.3.1 IR Spectroscopic Investigation

IR spectra of the organic phase combinations of HEH[EHP] and either TODGA or T2EHDGA can reveal the qualitative nature of metal-ligand bonds in these mixed extractant systems. Figure 5.1 shows the spectra of 200 mM DGA and 1 M HEH[EHP] +200 mM DGA prior to metal extraction, 200 mM DGA following neodymium and holmium extraction, and an organic phase of 1 M HEH[EHP] following extraction of neodymium and holmium and the addition of an equivalent volume of 1 M HEH[EHP] + 200 mM DGA preequilibrated

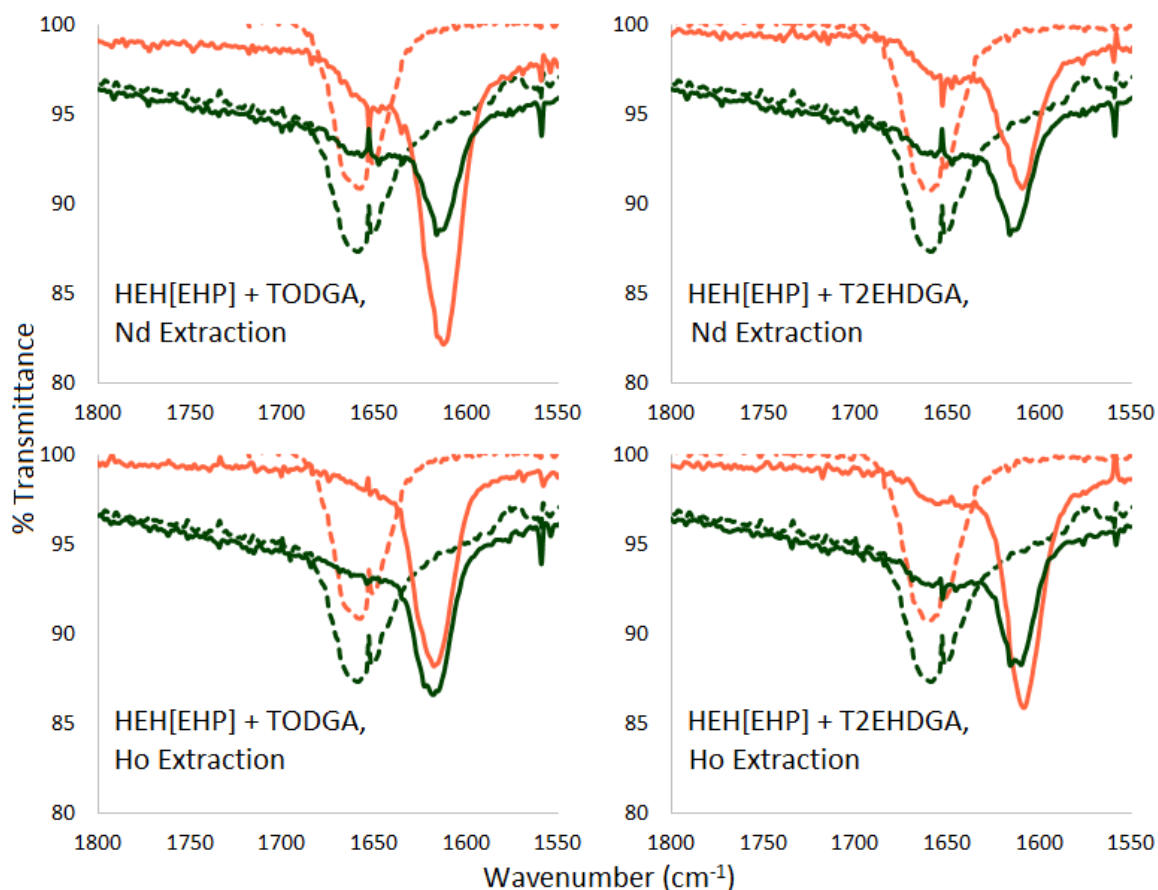


Figure 5.1 - IR Spectra of the Carbonyl Peak of TODGA in Solutions of 200 mM DGA Before Extraction (Light Dashes), 1 M HEH[EHP] + 200 mM DGA Before Extraction (Dark Dashes), 200 mM DGA Following Metal Extraction (Light Solid Line), and 1 M HEH[EHP] Metal Extraction with Preequilibrated DGA Addition (Dark Solid Line)

with 3M nitric acid. The absorbance band shown corresponds to the carbonyl group of the DGA molecule, one of the metal binding functional groups. Prior to extraction, the group absorbs at 1660 cm^{-1} , however following extraction of metal with only DGA, from a nitric acid solution, the absorbance band shifts to 1610 cm^{-1} . The same shift was observed when a solution of nitrate loaded DGA was added to a metal loaded organic phase. This result suggests that the dipole moment of the DGA carbonyl group is affected similarly both by extracted metals and by inclusion into a metal loaded organic phase in the presence of nitric acid.

The absorbance bands corresponding to the phosphoryl group of HEH[EHP] ($1300 - 1100\text{ cm}^{-1}$) and the P-O-C and P-C bonds of the HEH[EHP] functional group ($1100 - 900\text{ cm}^{-1}$) are shown in Figure 5.2. The spectra shown are of 1 M HEH[EHP] and 1 M HEH[EHP]

+ 200 mM DGA prior to extraction, as well 1 M HEH[EHP] following metal extraction and an organic phase of 1 M HEH[EHP] following metal extraction and the addition of an equivalent volume of 1 M HEH[EHP] + 200 mM DGA preequilibrated with 3 M nitric acid. Also shown is the ether peak of TODGA at 1140 cm⁻¹. In both solutions prior to extraction, the phosphoryl group shows a primary absorption band at 1200 cm⁻¹ and the P-C bond (980 cm⁻¹) absorbs slightly more strongly than the P-O-C bond (1040 cm⁻¹). Following extraction of metal, the primary phosphoryl absorbance band shifts to 1160 cm⁻¹, while the P-C and P-O-C bonds absorb with equal intensity confirming binding with the extracted metal cation. After addition of the organic phase containing DGA preequilibrated with nitric acid, the spectrum reverts to that of the preextraction HEH[EHP] spectrum. Furthermore, the DGA ether absorbance band is seen to broaden from the sharp peak present prior to extraction to the band present following addition of the nitrate containing solution to the metal loaded HEH[EHP] solution. These spectra indicate that the presence of nitric acid in an organic phase added to a HEH[EHP] organic phase loaded with a metal drives the complexation toward that of pure DGA-nitrate complexation. It further suggests that the proton released from the molecule of nitric acid is captured by the deprotonated dimer of the acidic extractant.

For combining of the cation exchange and solvating extractants, a general equation (Equation 5.1) can be written for equilibria of studied lanthanides with mixed extractants in the presence of nitrate.



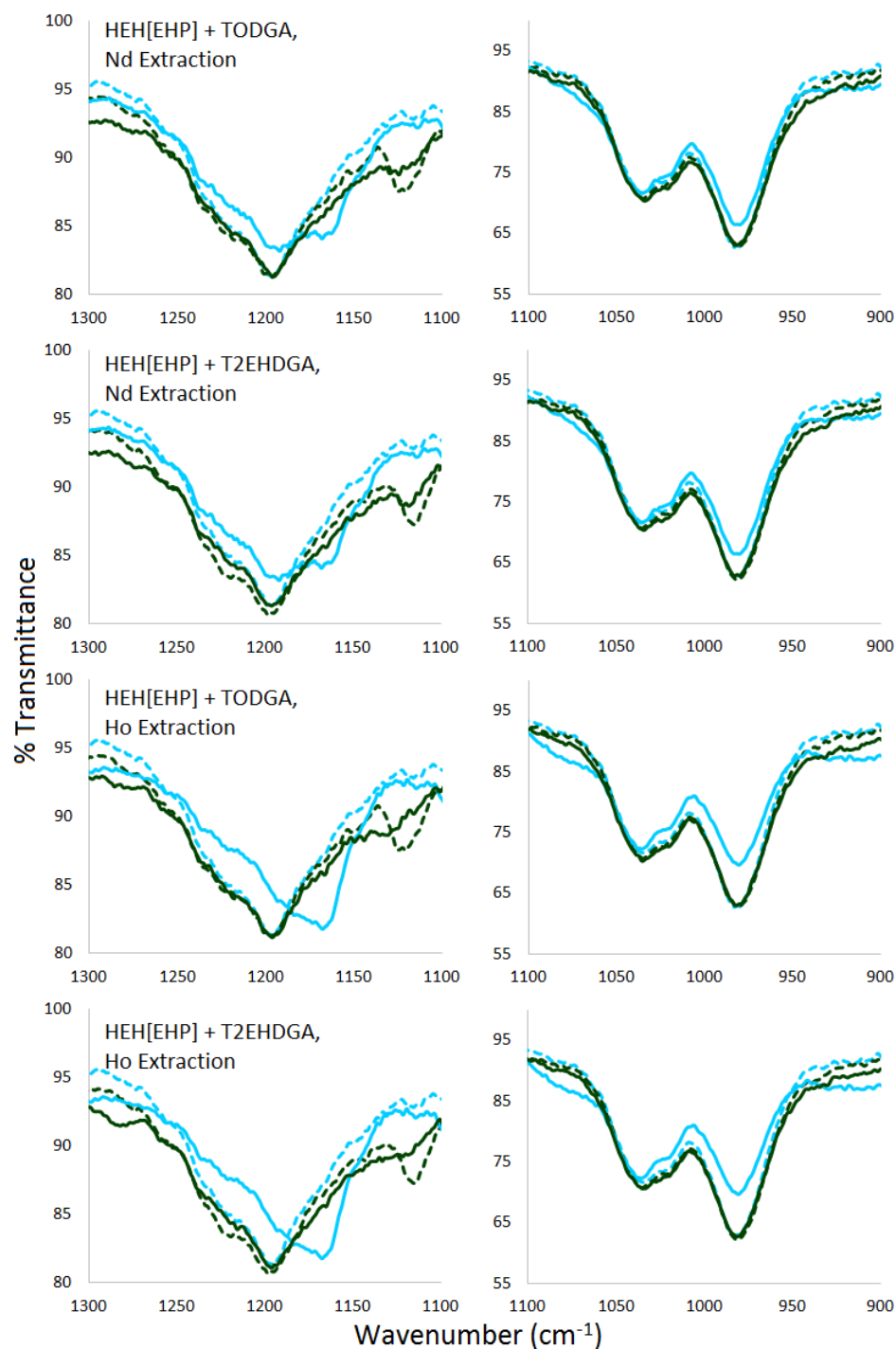


Figure 5.2 - IR Spectrum of the Phosphoryl Group and the P-O-C and P-C Group of HEH[EHP] in Solutions of 1 M HEH[EHP] Before Extraction (Light Dashes), 1 M HEH[EHP] + 200 mM DGA Before Extraction (Dark Dashes), 1 M HEH[EHP] Following Metal Extraction (Light Solid Line), and 1 M HEH[EHP] Following Metal Extraction with Preequilibrated DGA Addition (Dark Solid Line)

5.3.2 UV-Vis Spectroscopic Titration Results

UV-Visible spectroscopy was used to probe the metals in post-extraction organic phases as a function of nitric acid and DGA concentration. The neodymium $^4I_{9/2} \rightarrow ^4G_{5/2}$, $^2G_{7/2}$ electronic transition and the holmium $^4I_{9/2} \rightarrow ^2H_{9/2}$, $^4F_{5/2}$ electronic transition are hypersensitive, allowing for the fine metal coordination to be probed using UV-Vis spectroscopy.¹⁷ Our recent investigations have shown that the spectra of either neodymium or holmium extracted into 1 M HEH[EHP] and diluted with 1 M HEH[EHP] and either TODGA or T2EHDGA remain constant except for neodymium when introduced to high TODGA concentration.¹⁴ This slight Nd spectrum shift could be indicative of interligand interaction coordinating with the metal in n-dodecane solutions.

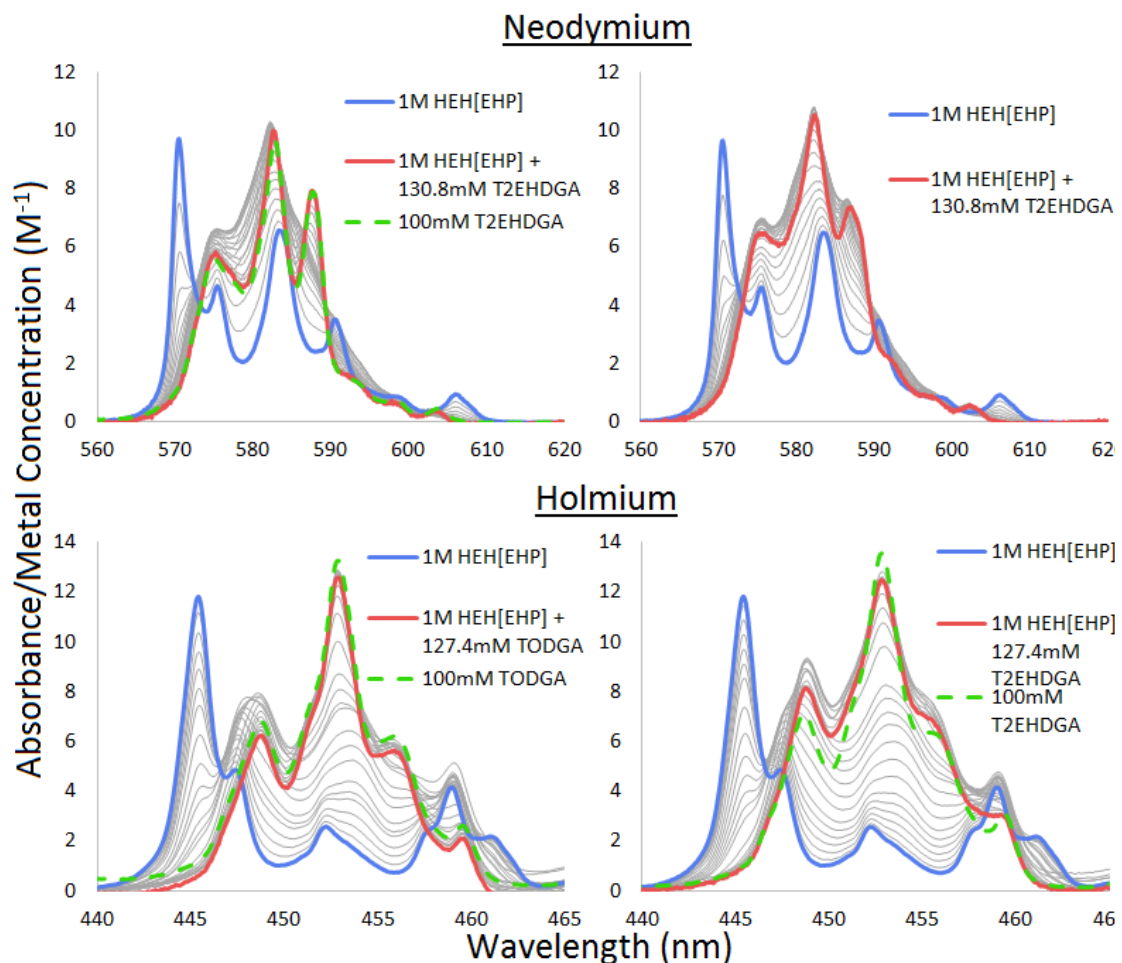
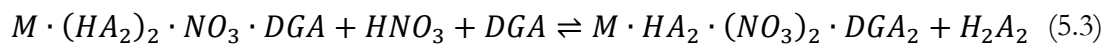
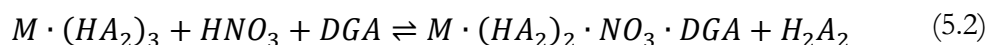


Figure 5.3 - UV-Vis Spectra of Organic Phase Holmium and Neodymium Extracted into 1M HEH[EHP] and Titrated with 1 M HEH[EHP] + 200 mM TO/T2EHDGA Preequilibrated with 3 M Nitric Acid

Figure 5.3 compares the spectra of neodymium and holmium extracted to a 1 M HEH[EHP] organic phase and titrated with 1 M HEH[EHP] + either TODGA or T2EHDGA which had been preequilibrated with 3 M nitric acid. The concentration of nitric acid in the titrants was determined to be 0.24 ± 0.02 M for HEH[EHP]+TODGA and 0.23 ± 0.02 M for HEH[EHP] +T2EHDGA. For both neodymium and holmium, the spectra exhibit a bathochromic shift, suggesting an increase in the coordination number of the complex.¹⁷ Nearing the end of the titration, the spectra resemble those seen when metal is extracted from 3 M HNO₃ to TODGA or T2EHDGA solutions in TCE, suggesting that coordination at this point is solely due to solvation with the DGA and charge balancing nitrate.

As was observed in the HDEHP and TODGA mixed solvent, the mode of complexation shifts with respect to the acidity of the extraction aqueous phase. At a low concentration of HNO₃ present in organic phase, the primary complexation mode is of chelate type with the cation exchange ligand, as its deprotonation is favoured by the aqueous conditions. Following extraction from the high acidity aqueous phase, the coordination is primarily dominated by the DGA, although the presence of the cation exchange ligand might still provide a solvating a micellar stabilizing effect.¹¹ Multiple intermediate spectral characteristics are seen, particularly the introduction and decrease of peaks at 577 nm and 449 nm for neodymium and holmium respectively. This could suggest that there are likely several species present which contribute to the metal coordination as the organic phase nitrate concentration increases.

For modelling the obtained spectrophotometric data, four species and three equilibria as adapted from Equation 5.1 and shown in Equations 5.2 – 5.4 were considered, where the species generated in Equation 5.4 was recently reported to be the species generated from extraction from high nitric acid concentration.¹¹ In these equations, M represents Nd³⁺ or Ho³⁺, and HA₂ and H₂A₂ are the deprotonated and protonated dimer of HEH[EHP], respectively.



These chemical equilibria are governed by equilibria as shown in the stability constants shown in Equations 5.5 – 5.7.

$$\beta_{121} = \frac{[M \cdot (HA_2)_2 \cdot NO_3 \cdot DGA][H_2A_2]}{[M \cdot (HA_2)_3][HNO_3][DGA]} \quad (5.5)$$

$$\beta_{112} = \frac{[M \cdot HA_2 \cdot (NO_3)_2 \cdot DGA_2][H_2A_2]^2}{[M \cdot (HA_2)_3][HNO_3]^2[DGA]^2} \quad (5.6)$$

$$\beta_{103} = \frac{[M \cdot (NO_3)_3 \cdot DGA_3][H_2A_2]^3}{[M \cdot (HA_2)_3][HNO_3]^3[DGA]^3} \quad (5.7)$$

The values of the conditional stability constants were calculated using the HypSpec software program using the spectrophotometric data and with arbitrary values for the stability constant of the HEH[EHP] bound species. The remaining stability constants were normalized to this constant to display the relative ability of these complexes to form in the presence of organic phase nitrate with the values for this model and their 2-sigma uncertainties are shown in Table 5.1. This method of chemical modelling has been used previously to compare the ability of metal-nitrate complexes to form across the f-element series in the TALSPEAK-MME Process.¹⁰

The obtained constants reveal that the relative ability of TODGA to form metal species is greater than with T2EHDGA. This is understandable as TODGA is a more powerful metal extractant than T2EHDGA. Furthermore, neodymium shows a greater ability to form DGA complexes than holmium. This likely indicates that the electrostatic interactions

Table 5.1 – Conditional Stability Constants for the Formation of Nitrated Metal Species

	HEH[EHP] - TODGA, Nd	HEH[EHP] - T2EHDGA, Nd	HEH[EHP] - TODGA, Ho	HEH[EHP] - T2EHDGA, Ho
β_{131}	1.00	1.00	1.00	1.00
β_{121}	3.28 +/- 0.07	2.37 +/- 0.05	2.17 +/- 0.07	1.89 +/- 0.01
β_{112}	5.36 +/- 0.12	3.33 +/- 0.07	3.11 +/- 0.09	2.68 +/- 0.01
β_{103}	6.16 +/- 0.13	3.90 +/- 0.08	3.52 +/- 0.11	3.06 +/- 0.01

of the HEH[EHP] dominates the interactions with the heavier, smaller lanthanides while DGA interactions are likely suffer from increased steric hindrance.

The speciation of holmium and neodymium as a function of the coextracted nitric acid concentration (0 – 0.25 M) were modelled with the calculated stability constants and shown in Figure 5.4. For the neodymium systems, the metal rapidly shifts to the DGA solvated species with the introduction of nitrate, with over 90% of the metal bound in a pure DGA-NO₃ complex by 0.2 M organic phase nitric acid concentration. For holmium species however, multiple species in the organic phase persists until high organic phase nitric acid concentrations are reached. At 0.25 M NO₃⁻ (roughly the concentration of nitrate extracted to the titrant solution from 3 M HNO₃), a combination of Ho(HA₂)(DGA-NO₃)₂ and Ho (DGA-NO₃)₃ are modelled to be the primary species present in solution. This illustrates the effect of

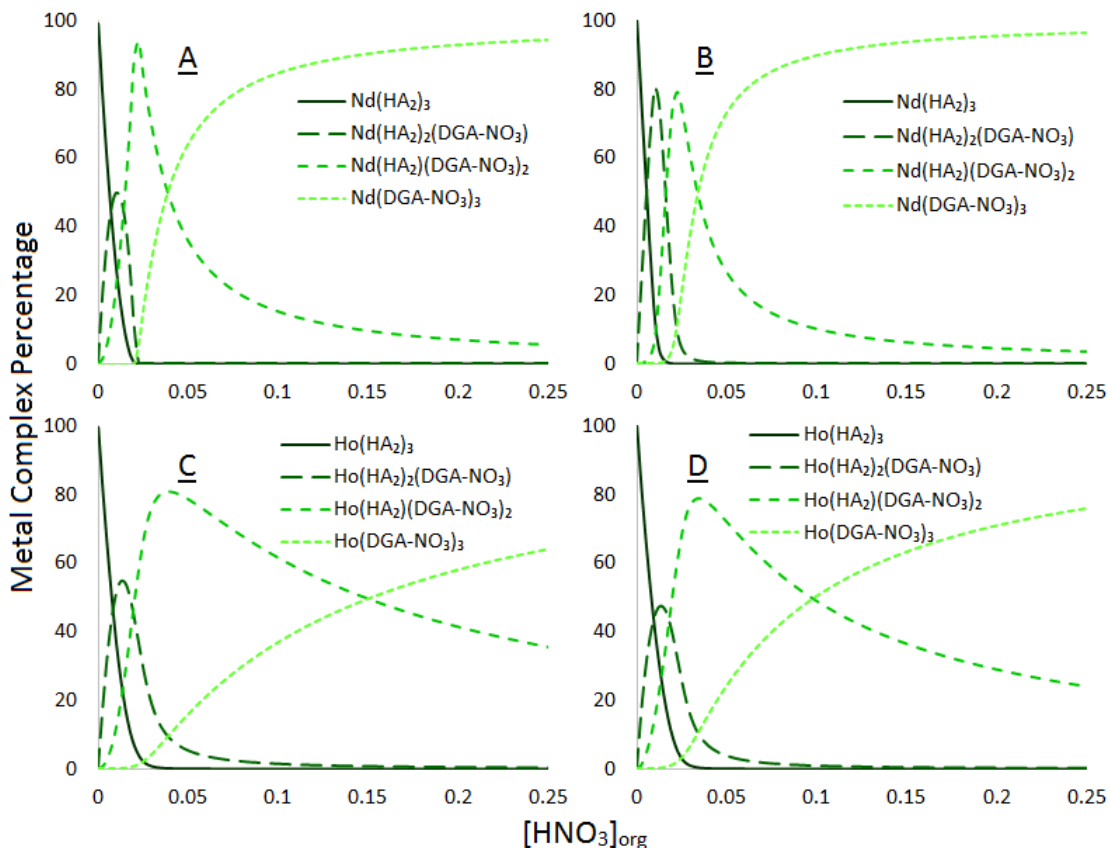


Figure 5.4 – Speciation Diagrams of Metal Complexation with Varying Organic Phase Nitrate Concentration for Neodymium in 1 M HEH[EHP] + 200 mM TODGA (A) and 1 M HEH[EHP] + 200 mM T2EHDGA (B) and Holmium in 1 M HEH[EHP] + 200 mM TODGA (C) and 1 M HEH[EHP] + 200 mM T2EHDGA (D)

a larger effective cationic radius of Nd, and consequently, a larger effective cationic charge for Ho which favors ion-exchange complexation and stronger binding with acidic organophosphorus extractants. This allows for speciation with both diglycoamide-nitrate solvates and cation exchange ligands while under the same high concentration nitric acid extraction conditions as the neodymium cation, which fully releases from the HEH[EHP] complex and exist almost exclusively as an diglycoamide-nitrate solvate.

5.4 Conclusions

Several explanations as to how HEH[EHP] – DGA interactions occur in the presence of organic phase nitrate can be concluded from this data. With the introduction of the charge balancing nitrate anion, metal speciation is seen to shift from that of a chelating mechanism with the cation exchange ligand HEH[EHP] to a solvating mechanism in a DGA-NO₃ species. Infrared spectroscopy confirmed that the means of DGA complexation of metals in the organic phase is the same when introducing organic phase nitrate by extraction or simply titration. UV-Vis spectrophotometric analysis was able to model the relative ability of DGAs to complex with neodymium and holmium. For both metals, TODGA was a more powerful metal complexant in the presence of NO₃ than T2EHDGA. Furthermore, neodymium is more able to form solvated species in the presence of nitrate than holmium. This work reveals the nature of metal complexation in the ALSEP system at intermediate acid concentrations, informing the conditions required for proper extraction and stripping for process scaling.

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VI. Additional Data

6.1 Introduction

Several other experiments pertaining to the characterization of intermolecular adduct formation in organic phases pertinent to the ALSEP system were conducted. These experiments produced results which provide qualitative information about the system, but indicate other complexities which will require additional investigations.

The first additional investigation is observing intermolecular adduct formation in HDEHP – TODGA organic phases. This ligand combination was not proposed for the ALSEP process as it did not provide adequate actinide – lanthanide separation factors for process scaling.¹ Investigation as to its ability to form organic phase complexes could provide an explanation for this behavior, and potentially draw trends for future process development. Secondly, a more conclusive trans-lanthanide investigation was undertaken to gain a better understanding of the relative ability for ALSEP ligands to form intermolecular adduct complexes with metals. This will help to understand fundamental process operations, as well as to advise limiting process conditions. Finally, the spectra of neodymium upon extraction in simulated ALSEP organic phases from various aqueous phase nitric acid concentrations are shown. This displays the difference in extraction mechanisms based on acid concentration. The procedures used and experimental results are detailed in the following sections.

6.2 HDEHP – TODGA Interactions Investigation

6.2.1 Chemical Preparation and Techniques

The HDEHP in this study was obtained from Alfa Aesar at 97% purity and was purified to >99% purity using the copper precipitation technique as confirmed by ³¹P NMR.² TODGA was obtained from Eichrom Technologies at >99% purity and used as delivered. The n-dodecane was purchased from Acros Organics at 99% purity and used as delivered. In the aqueous phases used, citric acid was received from Sigma Aldrich (ACS reagent grade, >99.5%), while DTPA was obtained from Fluka (≥99.0%) and TCI (98%) and used as delivered. Concentrated NH₄OH (Sigma Aldrich, ACS reagent grade) was used to dissolve the polyaminocarboxylates and adjust pH as checked by a pH electrode (Orion). All solutions were diluted to the desired volume with deionized water (Millipore, 18.2MΩ-cm).

For IR spectroscopy, solutions of constant cation exchange ligand concentration (0.3M) and varying DGA concentration (0M – 0.5M) produced through dilutions of the highest concentration DGA solution. IR spectra were collected on a Nicolet 6700 FTIR Spectrometer using an ATR diamond plate attachment. Approximately 50uL of the combined extraction organic phase were placed atop the crystal with air used as a reference spectrum, with a new reference spectrum collected prior to each solution. Following collection of the spectra, the data was modeled using the non-linear least squares regression fitting software HypSpec with error reported as two standard deviations of the model fit.³ Furthermore, IR spectroscopy was used to probe the nature of ligand coordination with metals at high metal concentrations. A solutions of 1 M HDEHP + 200 mM TODGA, was metal loaded from a 25.2 mM Nd in pH 3 HCl aqueous phase three times sequentially to adequately load the organic phase for observation via IR spectroscopy. Organic phase metal concentration was quantified by collecting UV-Vis spectra of the post-extraction aqueous phase.

For the Job's Method plots, europium nitrate (Alfa Aesar, 99.9%) was irradiated in the Oregon State TRIGA reactor for 7 hours, followed by conversion to a chloride salt by dissolution in concentrated HCl and evaporated followed by dissolution in the appropriate aqueous phases. ²⁴¹Am was also converted to a chloride salt in a similar technique and dissolved in the appropriate aqueous phase. Both metals were then dissolved into the aqueous phases used for extraction; 0.5M HDEHP + 50mM DTPA at pH = 3.36 +/- 0.05 was used for Eu extraction and 0.5M (H⁺/NH⁺) citrate + 10mM DTPA at pH = 3.36 +/- 0.05 was used for Am extraction. Organic phases of 0.2M total extractant concentration were prepared from 0.2M solutions of the individual extractants in the appropriate volumetric ratios. Organic phase preequilibration and metal extraction was performed by contacting the extracting organic phase with the aqueous phases via vigorous shaking for 10 minutes using a vortex mixer. Extraction was performed in 4.5 mL polyvials followed by centrifugation at 3000rpm for 5 minutes or until phase disengagement. Phases were separated using a fine tipped transfer pipet. Each were preequilibrated 3 times by vortexing a 3:1 aq:org ratio for 10 minutes followed by 5 minute centrifugation prior to metal extraction by vortexing a 1:1 aq org ratio, contacting for 10 minutes and centrifuging for 5 minutes. Distribution ratios were determined through gamma spectroscopy of aliquots of each liquid phase, using a NaI(Tl) scintillation counter (Packard COBRA II).

For UV-Vis spectra collection, neodymium and holmium chloride were prepared by dissolving either Nd_2O_3 (Sigma Aldrich, 99.9%) or Ho_2O_3 (Sigma Aldrich, 99.9%) in concentrated HCl (Macron, ACS grade) and evaporated. An ^{243}Am stock was prepared similarly by dissolution in concentrated HCl and evaporation twice. Both were then dissolved in pH3 HCl prepared by dissolution of concentrated HCl with deionized water (Millipore, 18.1M Ω -cm). Extraction into 0.2M HDEHP in n-dodecane was performed by vortexing a 1:1 aqueous to organic ratio for 10 minutes followed by centrifugation for 5 minutes or until phase disengagement. Nd and Ho distribution ratios were determined using an A(III) colorimetric technique, while the Am organic phase concentration was determined using LSC counting.⁴ Each metal extraction was found to be quantitative however, such that the concentration of the metal-extracted organic phase is equivalent to the preextraction aqueous phase concentration. For the Nd extraction, the extraction organic phase was dried over 3Å molecular sieves for 3 days to alleviate the effects of water in the organic phase.⁵ This was not done for americium to prevent excessive waste generation or holmium as the effects were not seen with holmium.

UV-Vis spectra of the organic phase were collected from a 1cm quartz cuvette with an n-dodecane background solvent on a Cary 6000i UV-Vis-NIR spectrometer with a temperature jacket held at 20°C. Spectra were collected of the $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2}$, $^2\text{G}_{7/2}$ hypersensitive transition of Nd, the $^4\text{I}_{9/2} \rightarrow ^2\text{H}_{9/2}$, $^4\text{F}_{5/2}$ hypersensitive transition of holmium, and the $^7\text{F}_0 \rightarrow ^5\text{L}_6$ transition of americium.^{6,7} Following spectra collection, an organic phase containing the same concentration of the cation exchange ligand used in extraction as well as either TODGA or T2EHDGA was titrated into the metal loaded organic phase. The solution was vortexed for 30 seconds, and a new spectrum was collected. Non-linear least squares regression fitting using HypSpec was then performed on the spectra to quantify interactions with error reported as two standard deviations of the model fit.³

6.2.2 Infrared Spectroscopic Results

The infrared spectra of HDEHP – TODGA combinations without metal are shown in Figure 6.1, while the spectra of neodymium loaded HDEHP – TODGA are shown in Figure 6.2. As seen in Figure 6.1, the changes in the IR spectra seen are similar to those seen in the HDEHP – T2EHDGA system, although with seemingly more intense shifting. The same chemical model applied to the previous investigation (Equations 4.1 and 4.2) was applied to

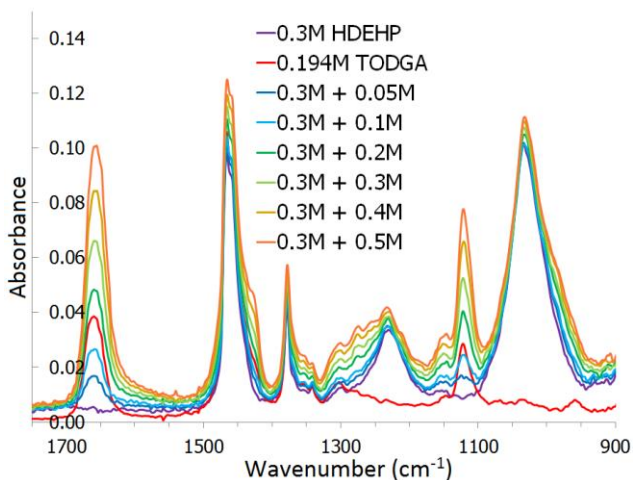


Figure 6.1 - IR Spectra of Constant 0.5 M HDEHP and Variable TODGA Concentrations

Figure 6.2 reveals the significant contribution of TODGA to the complexation of metals in post-extraction organic phases, as evidenced by the shift of the carbonyl peak from TODGA when extracting metals from an aqueous phase which should not allow for it to be a metal complexant. The shift of the carbonyl carbon is of a greater magnitude than that seen for any other ligand combination, suggesting that, not only does HDEHP and TODGA have a greater ability to form intermolecular adducts, but that these adducts also complex metals

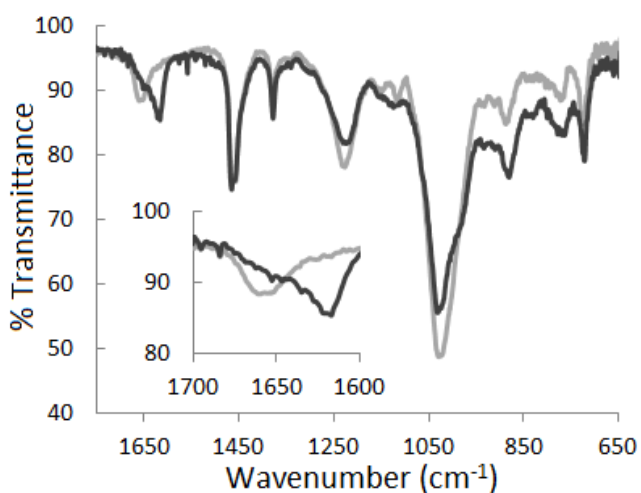


Figure 6.2 - IR Spectra of the 1 M HDEHP + 200 mM TODGA Prior to Extraction of Metal (Light Lines) and Following Metal Loading from a pH 2.8 HCl aqueous phase (Dark Lines)

this system, with the calculated adduct formation constant found to be 3.03 ± 0.02 . This value is almost half an order of magnitude larger than that for HEH[EHP] – TODGA, the next highest adduct formation constant. This suggests that HDEHP and TODGA possess a greater ability to form intermolecular adducts in n-dodecane than any other ligand combination studied.

more strongly.

6.2.3 Job's Method Results

Job's Method plots for both europium and americium were prepared for 0.2 M total extractant concentration with a combination of HDEHP and TODGA, as shown in Figure 6.3. The peak location for both americium and europium indicates that a 4:1 HDEHP:TODGA metal complex forms in both systems. This does not have as easy an explanation as the 6:1

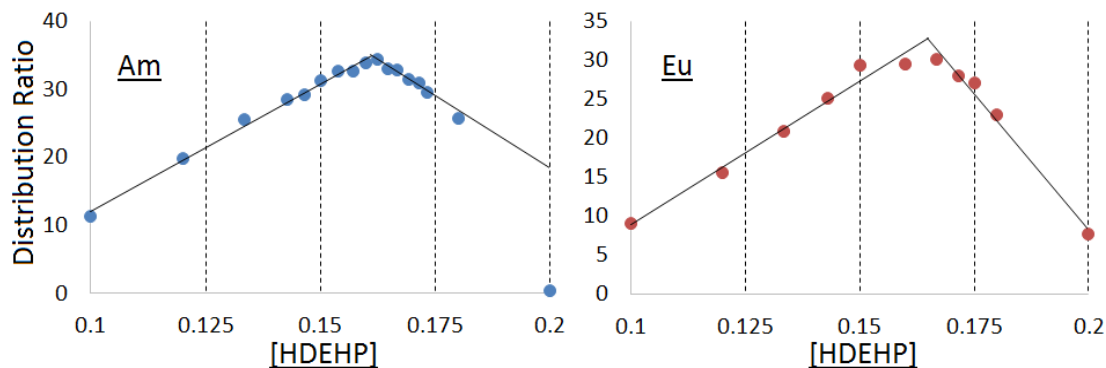


Figure 6.3 - Job's Method Plots of 0.2 M Total Extractant of HDEHP and TODGA for Americium and Europium

ratio seen for other ligand combinations, which indicates the formation of a simple intermolecular species based on the anticipated complex type for the pure cation exchange ligand. A 4:1 ligand ratio could indicate purely a 4:1 ligand ratio, or suggest the presence of multiple complex types in solution. If multiple complexes exist in solution, the Job's Method cannot be used to characterize the types of complexes which form, and as such this result should be considered qualitative. What can be seen however is the significant increase in the distribution ratios with the introduction of TODGA. For americium, the distribution ratio increases by several orders of magnitude, suggesting that adducts which form are much more powerful metal complexants than any other ligand combination.

6.2.4 UV-Vis Spectroscopic Titration Results

A similar spectroscopic titration investigation from HDEHP - TODGA to the one performed for HDEHP - T2EHDGA, HEH[EHP] - TODGA, and HEH[EHP] - T2EHDGA combinations was performed with neodymium, americium, and holmium. These spectra are shown in Figure 6.4. For all three metals, significant spectrum shifting is seen, similar to that seen with the introduction of T2EHDGA to the HDEHP system. The concentration of TODGA required to produce these shifts is much lower than the concentrations of DGA required to produce these types of shifts in any other system, indicating that HDEHP and TODGA possess a significantly greater ability to form inter-ligand species with f-elements than the proposed ALSEP extractant combinations.

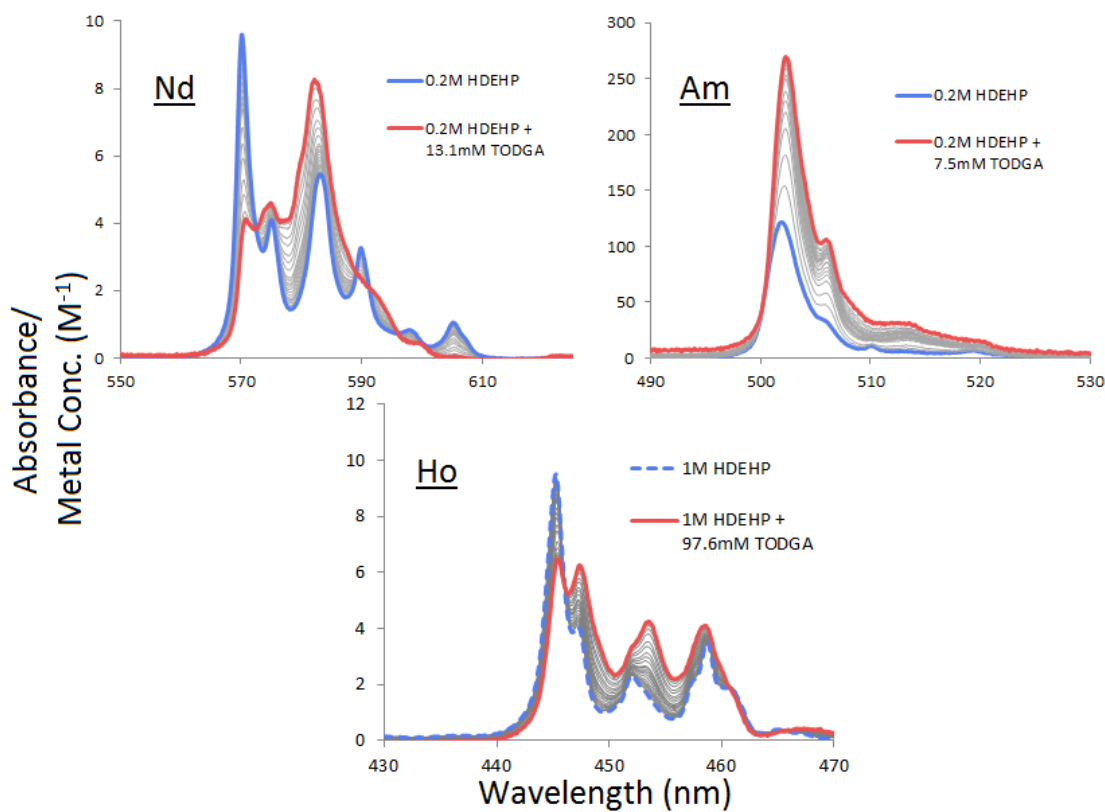


Figure 6.4 - UV-Vis Spectra of Nd, Am, and Ho in Organic Phases of Constant HDEHP Concentration and Increasing TODGA Concentration Through Titration

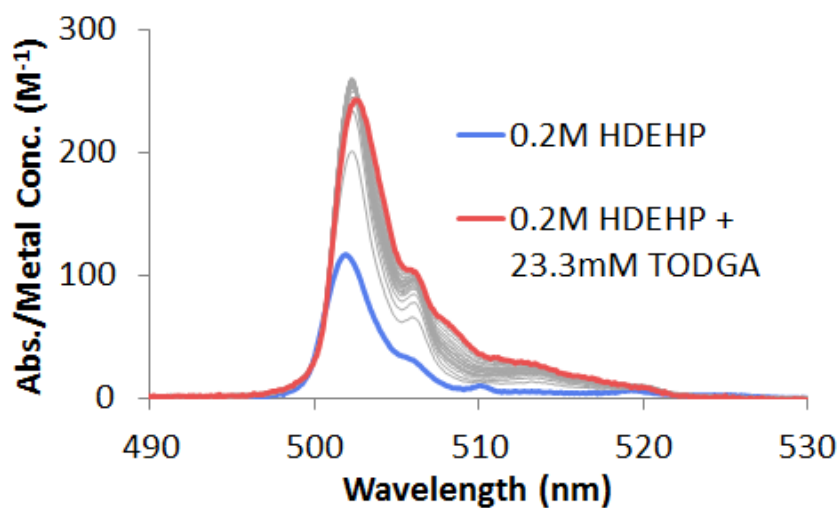


Figure 6.5 – UV-Vis Spectra of Am in Organic Phases of Constant 0.2M HDEHP with Varying TODGA Concentration, Potentially Revealing Complicated Speciation

A further observation is that, at higher DGA concentrations, a third species appears to begin forming as the spectrum begins shifting by an alternate means. This is seen most obviously in americium the americium spectra, such as the one shown in Figure 6.5. In this spectrum, the peak which becomes more prominent at 503 nm in the presence of TODGA begins to reduce in absorbance intensity and appears to undergo a slight redshift, indicating that there may be multiple modes of metal complexation which can exist in the HDEHP – TODGA containing organic phases. Despite the possibility of several species forming, the model defined in Equation 4.4 was applied to the UV-Vis spectra collected for each metal in the HDEHP – TODGA system. The adduct formation constants were determined to be 2.21 ± 0.01 for neodymium, 3.74 ± 0.01 for americium, and 1.26 ± 0.01 for holmium. These adduct formation constants are higher than those for adduct complexation with any other ligand combination studied. This is particularly the case with the americium system, where the adduct formation constant is determined to be an order of magnitude larger.

6.2.5 Conclusions

The investigations conducted on the HDEHP – TODGA ligand combination suggest that this ligand combination forms intermolecular adducts in metal-free organic phases, and that these adducts complex with metals more effectively than any ligand combination proposed for the ALSEP process. This improved ability is also coupled with a likely more complicated organic phase speciation than any of the other ligand combinations which would require further investigation if it were to be developed into an engineering UNF process. The poor separation factors for separating americium from the lighter lanthanides can partially be explained by this improved ability for intermolecular metal species however, particularly the improvement in the distribution ratios of americium with an increase in the TODGA concentration. This will likely preclude its use for mixed extractant solvent extraction systems in the future.

6.3 f-Element Complexation Trend

6.3.1 Chemical Preparation and Techniques

Solvent extraction of several lanthanides and americium was used to determine intermolecular adduct formation constants. Stable lanthanide nitrates (Pr, Nd, Eu, and Tb,

Alfa Aesar, 99%) were prepared as radiotracers through irradiation in the Oregon State TRIGA reactor for 7 hours. Following irradiation, the tracers were converted to chloride salts by dissolution in concentrated HCl (Macron, ACS grade) and dissolved in appropriate aqueous phases for extraction. A combined $^{147}\text{Pm}/^{241}\text{Am}$ radiotracer solution (Eckert & Ziegler) was also used in this investigation. The aqueous phase used for extraction into HDEHP solutions was 0.5M (H^+/NH_4^+) citrate + 25mM DTPA at $\text{pH} = 3.15 \pm 0.05$, while for extraction in HEH[EHP] solutions, 0.5M (H^+/NH_4^+) citrate + 7mM DTPA at $\text{pH} = 3.15 \pm 0.05$ were used. Organic phase preequilibration and metal extraction was performed by contacting the extracting organic phase with the aqueous phases via vigorous shaking for 10 minutes using a vortex mixer. Extraction was performed in 4.5 mL polyvials followed by centrifugation at 3000rpm for 5 minutes or until phase disengagement. Phases were separated using a fine tipped transfer pipet. Prior to metal extraction, the organic phases were preequilibrated once through vortexing with a 3:1 aq:org ratio, followed by extraction of individual metals with a 1:1 aq:org ratio. Distribution ratios were determined through radiometry of aliquots of each liquid phase. Pr, Nd, Eu, and Tb were measured using gamma spectroscopy on a NaI(Tl) scintillation counter (Packard COBRA II), while Am and Pm were measured using LSC with α/β discrimination (PerkinElmer Tri-carb).

6.3.2 Adduct Formation Constant Slope Analysis

As seen in previous investigations, the extraction ability of HDEHP in particular is affected by the presence of other extractant molecules in solution.^{1,8} The ability of a metal complexant to coordinate with a metal in an organic phase in conjunction with another organic phase ligand can be determined by the ability for metals to partition while varying one ligand and holding the other constant. This relationship is shown in Equation 6.1.⁹

$$D = \frac{[M]_{org}}{[M]_{aq}} = \frac{[MA] + [MAE] + [MAE^2] + \dots}{[M]} = D_0 + D_0K_1[\bar{E}] + D_0K_2[\bar{E}]^2 + \dots (6.1)$$

In this equation, “A” is the ligand held constant, while “E” is the varied ligand. D_0 is the initial distribution of metals with the constant ligand, while K_n is the equilibrium constant of the individual stoichiometric combinations possible in solution. The relationship between the varied extractant and the D-values is shown in Equation 6.2.

$$\frac{D}{D_0} - 1 = K_1[\bar{E}] + K_2[\bar{E}]^2 + \dots \quad (6.2)$$

Distribution ratios were determined with constant, 0.5M cation exchange extractant and varying DGA concentrations. Plots of $\log\left(\frac{D}{D_0} - 1\right)$ vs. $\log([DGA])$ for each ligand combination are shown in Figure 6.6A for TODGA and 6.6B for T2EHDGA. In these systems, most metal distribution increases with respect to DGA concentration with a slope of 1, indicating that one DGA molecule contributes to intermolecular adducts in the organic phase. Terbium shows a slope less than 1 however, potentially indicating mixed species or

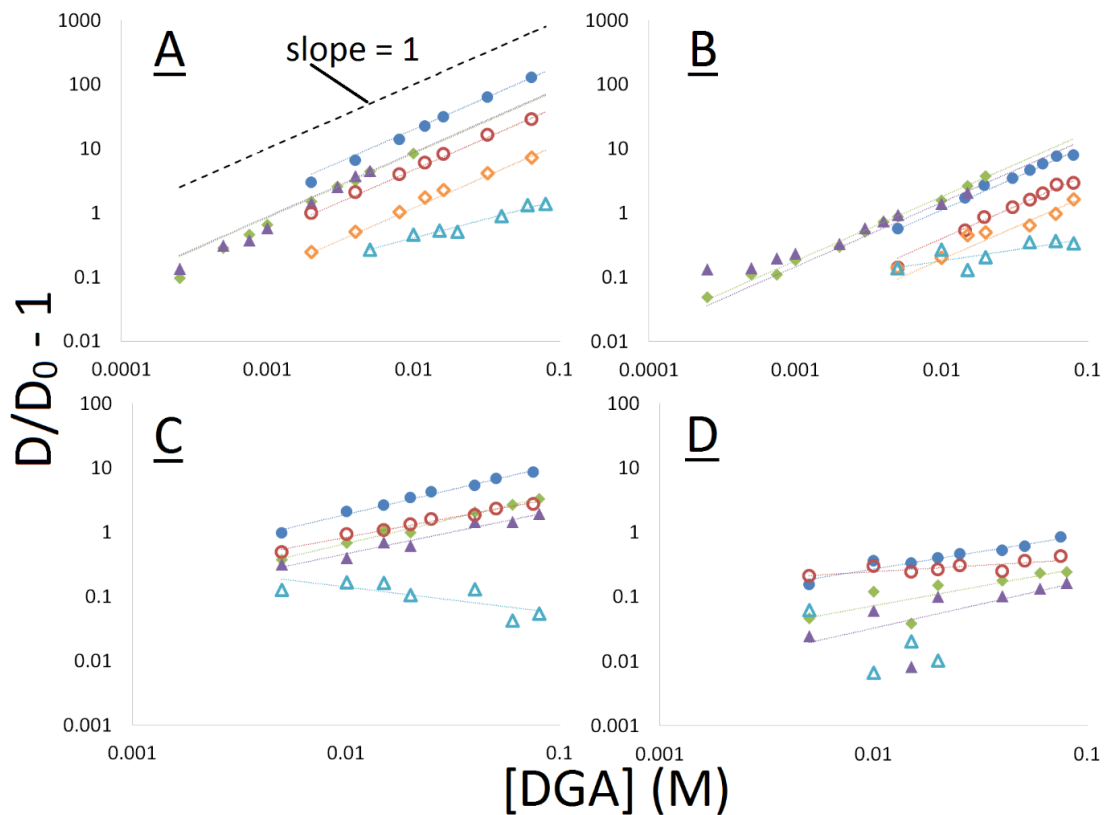


Figure 6.6 – Distribution of americium (closed circles), praseodymium (closed diamonds), neodymium (closed triangles), promethium (open circles), europium (open diamonds), and terbium (open triangles) into organic phases of 0.5M HDEHP with varying TODGA (A) and T2EHDGA (B) or 0.5M HEH[EHP] with varying TODGA (C) or T2EHDGA (D)

other competition in the organic phase. A trans-lanthanide trend is evidenced, as lighter lanthanides seem to be complexed by intermolecular adducts more favorably than heavier lanthanides, with americium forming adducts as effectively as the lighter lanthanides. Finally, in the HDEHP – TODGA system, adduct formation is generally stronger than in the HDEHP – T2EHDGA system by about an order of magnitude. The equilibrium constants of adduct formation for metals besides terbium are shown in Table 6.1.

Table 6.1 – Logarithmic Equilibrium

Constants of Adduct Formation in

HDEHP – DGA systems

	HDEHP - TODGA	HDEHP - T2EHDGA
Am	3.30	2.05
Pr	2.92	2.25
Nd	2.94	2.16
Pm	2.67	1.60
Eu	2.07	1.28

Metal extraction into the 0.5M HEH[EHP] systems with varying DGA are shown in Figure 6.6C for TODGA and 6.6D for T2EHDGA. Neither system produces trend data with a slope greater than one suggesting either multiple species in the organic phase, or possible competition between free adducts in the organic phase with the metal-bound species, lowering the HEH[EHP] concentration available for extraction. Further investigation will be necessary to determine the cause of this non-linearity, however it is unlikely that multiple DGA molecules are involved in the individual metal-ligand species. In these systems, americium still forms adducts seemingly most effectively, however the lanthanide which forms interligand metal species most effectively shifts to promethium. In these HEH[EHP] systems, terbium appears to show a negative slope of extraction when the DGA concentration is increased, possibly as a result of the inability of intermolecular adducts to form a metal complex with formation in the bulk organic reducing the effective HEH[EHP] concentration. Furthermore, in the HEH[EHP] – T2EHDGA system, the distribution of terbium was lower than that of the pure HEH[EHP] system as the T2EHDGA concentration increases. Overall, however, the ability for intermolecular adducts to form metal complexes in these systems is low, particularly in the HEH[EHP] – T2EHDGA system, where evidence of their formation is nearly nonexistent.

6.4 Variable Nitric Acid Extraction Spectra

Neodymium was extracted from aqueous phases of varying nitric acid strength to determine how organic phase complexation changes as a function of the acidity of the aqueous phase. The HDEHP in this study was obtained from Alfa Aesar at 97% purity and was purified to >99% purity using the copper precipitation technique as confirmed by ^{31}P NMR.² The HEH[EHP] in this study was obtained from Yick-Vic Chemicals & Pharmaceuticals at 95% purity and was purified to 99% purity using the third phase formation purification technique as confirmed by ^{31}P NMR spectroscopy.¹⁰ The diglycolamides TODGA and T2EHDGA were obtained from Eichrom Technologies at >99% purity and used as delivered. The n-dodecane was purchased from Acros Organics at 99% purity and used as delivered.

Nitric acid solutions were prepared from concentrated nitric acid (Sigma Aldrich, ACS grade) diluted with deionized water (18.1M Ω -cm, Millipore). Acid concentrations of the solution were checked via acid-base titration. Neodymium solutions were prepared using $\text{Nd}(\text{NO}_3)_3$ (Sigma Alrich, 99.9%) with the concentration checked using EDTA titrations with xylenol orange as an indicator. Organic phase preequilibration and metal extraction was performed by contacting the extracting organic phase with the aqueous phases via vigorous shaking for 10 minutes using a vortex mixer. Extraction was performed in 4.5 mL polyvials followed by centrifugation at 3000rpm for 5 minutes or until phase disengagement. Phases were separated using a fine tipped transfer pipet. Distribution ratios of the neodymium was determined using a colorimetric technique with Arsenazo III at pH 9 buffered by triethanolamine and compared to a calibration curve.⁴ Spectra were collected on a Cary 500e UV-Vis spectrometer kept at 20 °C with a jacketed cell.

UV-Vis spectra of neodymium extracted into organic phases containing 1M cation exchange extractant + 75mM DGA from varying HNO_3 concentrations are shown in Figure 6.7. These spectra are further compared to the spectra metal extracted into just 1M cation exchange ligand for comparison. For HDEHP combinations with both DGAs, there is almost no speciation change between extraction from 0.001M HNO_3 to 1M HNO_3 . These spectra are further incomparable to the spectra of extraction into just 1M HDEHP, which indicates that extraction into a typical ALSEP ligand ratio from low acidity would produce a metal complexation environment quite different from that of pure HDEHP, which is the organic ligand present in the TALSPEAK Process. It does appear, however, that there is a slightly more noticeable spectrum shift in the HDEHP – T2EHDGA combination over the HDEHP

– TODGA combination, as there appears to be a more significant peak shoulder present at 570nm. This peak is prominent in cation exchange extractant spectra and are likely indicative of a 6 coordinate metal.⁶ In the HDEHP – TODGA combination however, this shoulder is very small, indicating a larger coordination number for the complexed metal across the aqueous range studied. Furthermore, the spectrum across the aqueous range does not resemble that of Nd extracted into a pure DGA organic phase, shown in Figure 6.8. As the spectrum remains consistent across a range of aqueous phases, intermolecular adducts formed by these ligand combinations are likely powerfully complexing cation exchangers. This is similar to what was observed with HDEHP – CMPO combinations in the previously investigated TRUSPEAK Process.¹¹

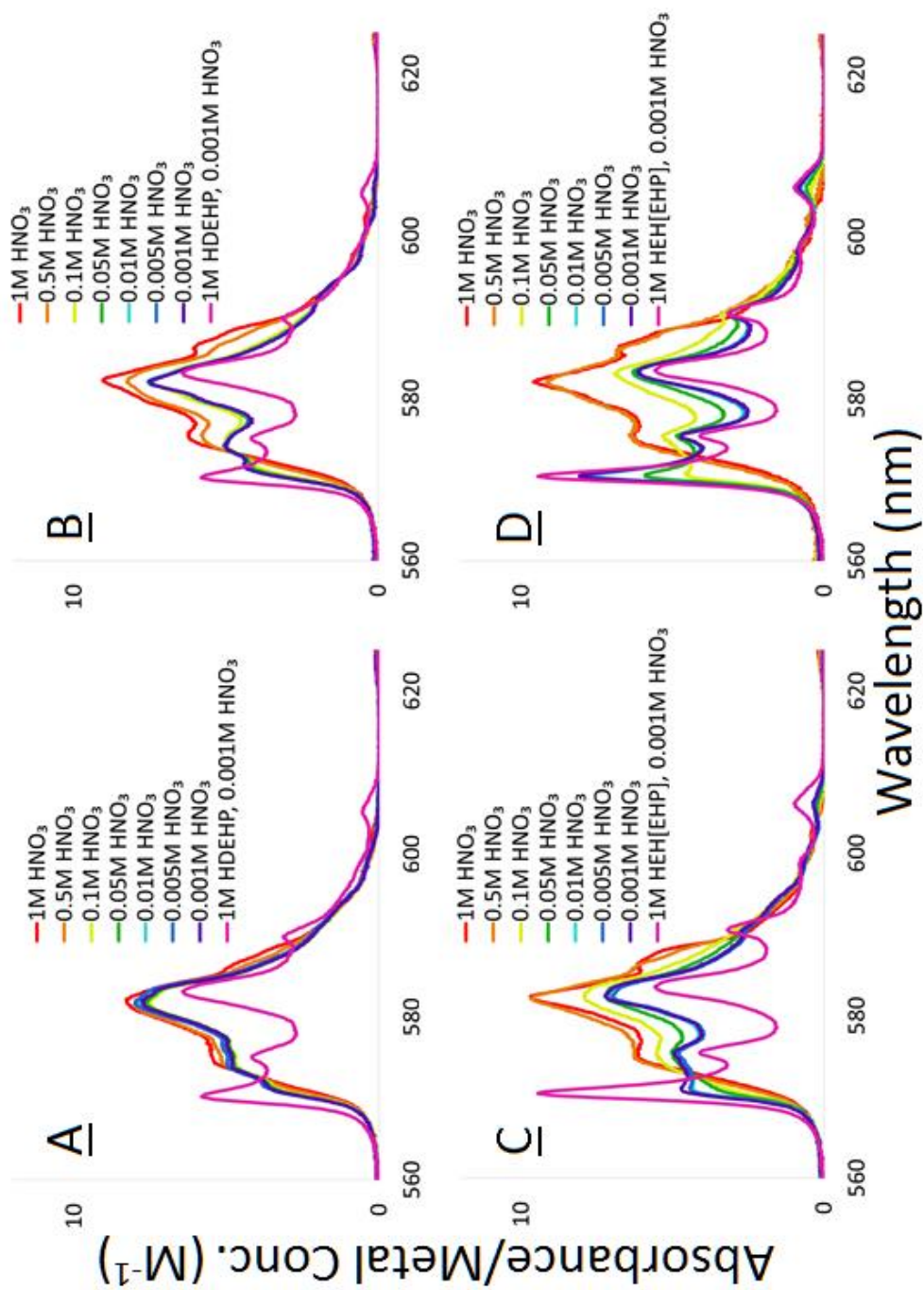


Figure 6.7 – UV-Vis Spectra of Organic Phase Neodymium Extracted from Varying Concentrations of HNO_3 , Extracted into (A) 1M HDEHP + 75mM TODGA, (B) 1M HDEHP + 75mM T2EHDGA, (C) 1M HEH[EHP] + 75mM TODGA, (D) 1M HEH[EHP] + 75mM T2EHDGA

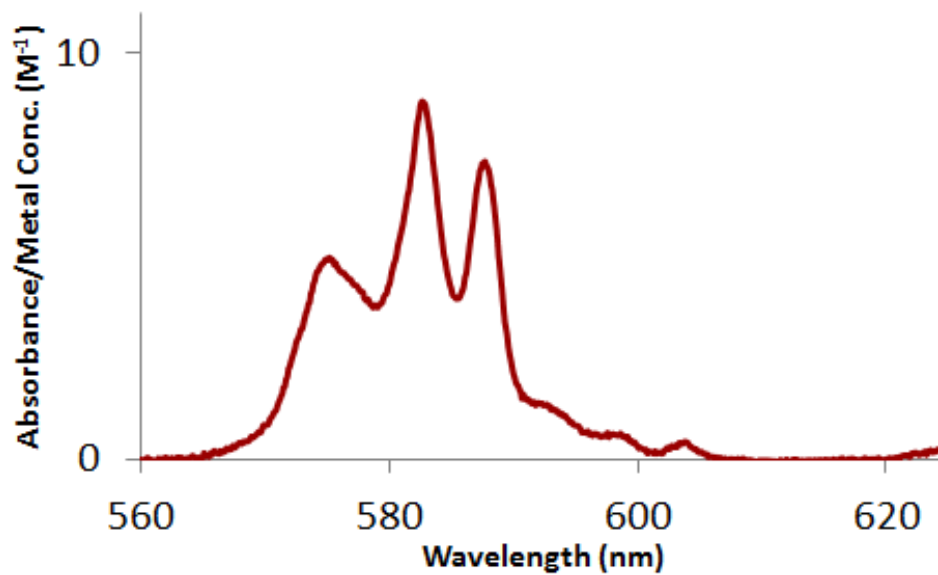


Figure 6.8 – UV-Vis Spectrum of Organic Phase Nd Extracted into 100mM TODGA from 3M HNO_3

For the HEH[EHP] combinations, significantly greater spectrum shifting is noticed across the aqueous range. The HEH[EHP] – TODGA combination shows slightly more spectrum shifting than the HDEHP – TODGA organic phase, with a more prominent 570nm peak seen with lower acidity aqueous phases. The spectrum produced by extraction from the lowest acidity organic phase (0.001M) still produces a spectrum that does not resemble extraction into pure HEH[EHP] however, indicating that intermolecular adducts are likely still forming in these systems. When extracting Nd into HEH[EHP] – T2EHDGA organic phases however, the spectra shift significantly across the aqueous range. The lowest acidity aqueous phase (0.001M HNO_3) produces a spectrum very closely matching the spectrum of pure cation exchange extractant, meaning that the complexation of the metal is nearly identical when extracted into 1M HEH[EHP] and 1M HEH[EHP] + 75mM T2EHDGA. As there are minimal nitrate counterions which would be necessary for Nd-T2EHDGA complexes, this indicates that there are minimal intermolecular adducts complexing the metal to produce spectrum changes. Furthermore, when the acidity increases, the spectrum begin to resemble that of the spectrum produced when metal is extracted into HDEHP – DGA organic phases. As intermolecular adducts have been determined to be minimally present in the HEH[EHP] – T2EHDGA combined organic phases, and the complexes do not resemble that of pure

DGA complexation, it is likely that when extraction is performed from aqueous phases of significant nitrate concentration, there are likely mixed complexes forming with the metal at aqueous ranges between the typically prescribed aqueous ranges for extraction and stripping in the ALSEP Process.

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VII. Research Conclusions

This investigation addresses the nature of chemical interactions in the organic phases of solvent extraction systems currently under development. Determination of the nature of chemical interactions in these systems is necessary for understanding observed process behavior, performing systems mass balances, calculating the chemical yields of desired species, and predicting the results of process transients. These efforts lead to process optimization and advise future process development

7.1 Metal Complexation with Cation Exchange Ligands

Previous investigations into the nature of f-element complexation in HDEHP organic phases have produced several explanations for observed spectroscopic data. The UV-Vis spectrum of neodymium in HDEHP was reported to shift with an increase in metal loading percentage with an absorbance peak at 570 nm decreasing and a peak at 583 nm increasing as the concentration of HDEHP increased and organic phase metal concentration remained constant. This spectrum red shifting behavior has previously been attributed to an increase in the coordination number of the metal. A separate, more recent study reported that the complexation of neodymium in HDEHP organic phases was consistent at all metal concentrations measured and the observed UV-Vis spectrum shifts were the result of impure extractant molecules. This investigation confirmed that complexation is constant at all metal loadings and that the UV-Vis spectrum of neodymium changes with relative to the HDEHP concentration in the organic phase. Karl Fischer titrations determined that the water extracted to the organic phase was independent of metal concentration at all concentrations studied (0 – 30 mM), but increased with an increase in HDEHP concentration. Furthermore, the water concentration in the organic phase was not directly proportional to the HDEHP concentration, with higher HDEHP concentrations leading to higher relative water concentrations. When the post extraction organic phases were desiccated with molecular sieves, a drop in organic water concentration led to a corresponding shift in the UV-Vis spectrum, suggesting a decrease in the metal coordination number. This strongly suggests the presence of water in the inner coordination sphere of the metal complex. Consequently, the greater relative concentration of water present in organic phases of higher HDEHP concentration leads to the observed neodymium spectrum changes.

Additional f-elements were investigated to observe any potential trans-lanthanide behavior due to changes in their effective cation charge or differences with actinides. Americium and praseodymium both appeared to show a decrease in metal complex symmetry with an increase in HDEHP concentration, however samarium, holmium, and erbium showed the same UV-Vis spectra regardless of HDEHP concentration. Water concentration in the post-extraction organic phases for all metals aside from americium (not measured) was found to be consistent with the water concentration determined in the neodymium. This suggests that, as lanthanides, and potentially actinides, contract, they are less able to accommodate inner coordination sphere water. This could have an effect on extraction and metal partitioning as well as process monitoring.

A similar study was performed in HEH[EHP] organic phases for comparison. The UV-Vis spectrum of Nd was not affected by the extractant concentration in the two concentrations investigated (2 M and 0.5 M). The spectrum had a large peak at 570 nm with a small 583 nm peak, resembling that of the lowest concentration or fully desiccated HDEHP samples. While HEH[EHP] did not extract water as strongly as HDEHP, a similar flat profile was seen for all metal concentrations. Americium, samarium, holmium, and erbium similarly show consistent spectra based on HEH[EHP] concentration, however praseodymium produced a different spectra at different ligand concentrations. This indicates that water cannot penetrate the inner coordination sphere of the metal except at the lightest, highest ionic radii f-elements. This could be an effect of the reduced ability of HEH[EHP] to extract water, the stronger bond between the -EH[EHP] anion and the metal, or some combination of factors.

7.2 Organic Extractant Interaction in the Absence of Metal

Combinations of all potential ALSEP ligands were probed for their ability to form interligand adducts in metal-free organic phases. The primary means of adduct formation was through the acid proton of the cation exchange ligand hydrogen bonding to a functional group on the DGA. The DGA signals in the IR spectrum do not show significant shifting, potentially indicating electronic delocalization across the DGA functional group, or donation of electron density from the nitrogen of the amide group.

For all combinations of either HDEHP or HEH[EHP] with either TODGA or T2EHDGA, none form interligand adducts as prevalently as HDEHP and CMPO. This

represents an immediate improvement of the ALSEP Process chemical formulation over that of the TRUSPEAK Process, as interligand adduct formed between HDEHP and CMPO were found to be the primary reason for undesired process characteristics of the TRUSPEAK Process. Of the combinations investigated, HDEHP - TODGA forms adducts most prevalently, followed by HEH[EHP] - TODGA, HDEHP - T2EHDGA, and HEH[EHP] - T2EHDGA. In general, HDEHP was able to form interligand adducts more strongly than HEH[EHP], while TODGA was able to form adducts more strongly than T2EHDGA.

7.3 Organic Extractant Interaction in the Presence of Metals

Several trends were seen when investigating the ability for ALSEP ligands to form interligand adduct complexes with metals extracted to organic phases. Slope analysis revealed that extraction from nitrate free, higher pH aqueous phases results in adducts with at most one DGA molecule coordinated to the metal. Several systems appear to involve a fractional stoichiometric contribution of a DGA which could be indicative of mixed species, or potentially competition between non-metal adduct formation in the organic phase and complexation with the metal.

A trans-lanthanide trend of the ability of adducts to form ternary complexes with metals is also seen for all ligand combination where the lighter, higher ionic radii form complexes with interligand adducts more easily than the heavier, smaller lanthanides. Americium is seen in all systems to form complexes with adducts as strongly or more strongly than with all lanthanides measured. Finally, it was observed that, as with the non-metal loaded organic phases, HDEHP - TODGA shows the greatest ability to form interligand adducts with metals while HEH[EHP] - T2EHDGA shows the least ability to form adduct complexes with metals. HDEHP - T2EHDGA and HEH[EHP] - TODGA show a relatively similar ability. A final point of interest is that for terbium, the heaviest lanthanide measured, D-value suppression is seen with increasing DGA in both HEH[EHP] systems. This further suggests that the non-linearity of the slope analysis could be indicative of the reduced ability of adducts to complex with heavier f-elements could lead to competition between non-metal adducts reducing the concentration of free cation exchange ligand available for extraction.

Job's method plot further shows that the stoichiometry of metal-adduct complexes are six cation exchange ligands to one solvating ligand for HDEHP - T2EHDGA with americium and europium, as well as for HEH[EHP] - TODGA with americium. HEH[EHP] - TODGA

with europium and the HEH[EHP] - T2EHDGA combination with both metals do not produce peak behavior, indicating that the formation of adduct complexes with these metals is not strong enough to be measured stoichiometrically with this method. For the HDEHP - TODGA combinations for both metals however, the observed stoichiometry of complexation with the metal is four HDEHP molecules to one TODGA molecule. Coupled with the UV-Vis investigations, this suggests multiple potential complexes formed in the organic phase. As the slope analysis strongly suggest only one DGA present in the metal complex, these species are likely either dimer breakup or polymerization of metal complexes as suggested in other reported investigations.

UV-Vis titrations reveal further information about the metal complexes formed in ALSEP organic phases. The extraction with cation exchange ligands from a nitrate free, high pH aqueous phase followed by the titration addition of DGAs revealed that ternary complexes are formed with metals without the presence of aqueous phase anions. The adduct formation reveals a UV-Vis spectrum change in neodymium and americium similar to that of an increase in organic phase water concentration despite drying the HDEHP organic phases following extraction, suggesting that interligand adducts increase the coordination number of the metal. For the HDEHP - TODGA combination, it appears that multiple complexes may be forming with neodymium and americium in the organic phase, supporting the conclusions about the Job's method plot. When the titrations data was modeled by non-linear least squares regression fitting, the order of ability of interligand complexformation with metals was further confirmed to be strongest with HDEHP - TODGA, followed by HDEHP - T2EHDGA, HEH[EHP] - TODGA, and finally HEH[EHP] - T2EHDGA.

7.4 Nitrate Effect on Organic Phase Metal Speciation

The presence of nitrate in organic phases has a great influence on the metal speciation in ligand combinations used in the ALSEP Process. In solutions of HEH[EHP] and either DGA, when either neodymium and holmium were extracted from a nitrate-free aqueous phase, the metal was seen to complex only with HEH[EHP] via IR spectroscopy. When nitrate was added to the metal-loaded organic phase, the complexation was seen to shift from binding with HEH[EHP] to with the DGA. The nature of the ligand bonds was similar to that seen in metal extraction from a high nitric acid concentration aqueous phases. This result justified that

the titration addition of nitrate as a means of determining the metal complexation which would exist when extracting from variable nitric acid concentrations.

Through UV-Vis spectroscopic titration addition of DGA-nitrate to solutions of either neodymium or holmium extracted into HEH[EHP], TODGA showed a greater ability to complex metals than T2EHDGA. This seems logical as TODGA has a simpler molecular structure and is a more powerful extractant than T2EHDGA indicating that bond formation is more favorable. Furthermore, neodymium forms complexes with DGAs more favorably than holmium, indicating that heavier lanthanides may possess a more complicated bonding environment than lighter lanthanides.

7.5 Overall Conclusions

In general, for the potential ligand combinations proposed for the ALSEP Process, HDEHP - TODGA shows the greatest ability to form interligand adducts in pre-extraction organic phases as well as to complex metals following extraction. Conversely, HEH[EHP] - T2EHDGA shows the lowest ability to form interligand adducts in metal-free organic phases, and shows little to no ability to form interligand adduct complexes with extracted metals. Through this measure alone, HEH[EHP] - T2EHDGA is the suggested ligand combination of choice for the ALSEP Process, however several other factors must be taken into account, such as process kinetics and distribution and partitioning optimization.