Award No. DE-NE0000720
Project No. 13-5124

Organic Speciation and Interactions in ALSEP - One Step Partitioning Process of Minor Actinides, Lanthanides, and Fission Products

Fuel Cycle

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NEUP Nuclear Energy University Programs
U.S. Department of Energy

FINAL REPORT

Title of Project:	**Organic Speciation and Interactions in ALSEP – One Step Partitioning Process of Minor Actinides, Lanthanides and Fission Products**
Workscope:	FC-1.2: Advanced Separations Methods
Award number:	DE-NE0000720
Contract number:	13-5124
Covering Period:	January 1, 2014 to December 31, 2017
Date of Report:	March 31, 2018
Recipient:	Oregon State University
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I. ABSTRACT

Research conducted in this project focused on speciation characterization of the ALSEP extraction system (similar to the TALSPEAK-like application) which addresses recovery of minor actinides and lanthanides from PUREX raffinate. The ALSEP (Actinide-Lanthanide Separation) system proposes a trivalent minor actinide/lanthanide group extraction followed by a selective actinide strip to effectively partition minor actinides, lanthanides, and other fission products. The group extraction is achieved by a mixed organic solvent, combining acidic and neutral extracting ligands. The objective of this work is investigation the interactions of the acidic and neutral ligands with each other in the extraction organic solvent and with desired metals.

Four combinations of a cation-exchange ligand (either HDEHP or HEH[EHP]) and a neutral solvating ligand (either TODGA or T2EHDGA) in n-dodecane were studied. Interligand dimers in these combinations were investigated with NMR and FTIR, the strongest interaction was observed for HDEHP+TODGA and weakest for T2EHDGA+HEH[EHP]. Complexes of the trivalent Am and lanthanides Nd, Eu, Ho, Pr in these binary ligand mixtures were probed with spectroscopic (UV–vis, time-resolved fluorescence, XAFS and SAXS-spectroscopies) and extraction (Job's plot, slope analysis) methods; co-extracted water and nitric acid were analyzed by titration methods. Comparison of the collected spectra showed significant shifting for both DGA ligands with HDEHP, while both combinations of HEH[EHP]+DGA displayed much smaller spectral changes. Data were modeled with HypSpec program, and stability constants for extracted complexes were calculated. Aggregation in these systems were studied by SAXS (small-angle X-ray scattering) spectroscopy and interfacial tension, size of aggregates were measured.

Two PhD students graduated (2017, 2018) and one student continues her PhD study.

Nomenclature:

HEH[EHP]): 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester
HDEHP: di-(2-ethylhexyl)phosphoric acid
TODGA: N,N,N',N'-tetraoctyl diglycolamide
T2EHDGA: N,N,N',N'-tetra-2-ethylhexyl diglycolamide

U.S. DEPARTMENT OF ENERGY

Nuclear Energy

Organic Speciation and Interactions in ALSEP – One Step Partitioning Process of Minor Actinides, Lanthanides and Fission Products

OVERVIEW

Purpose: to improve the state of knowledge on chemistry of mixed ligand ternary complexes with metal of interest (actinides and lanthanides fission products) formed in the combined organic solvent currently under development for advanced nuclear fuel reprocessing, and ultimately to identify the optimal composition of the ALSEP extraction organic phase.

Objectives:

- Collection and analysis of information on the molecular-scale interactions between molecules of extractants and desired metals occurring in the combined extraction organic phase proposed for the ALSEP separation process
- Design the optimal composition of the ALSEP extraction organic phase
- Quantification of equilibrium formation constant for adducts of metals with organic solvent
- Development a database for a speciation model of the organic phase that would improve predictability of behavior during the process and allow for extraction process scaling.

IMPACT

Logical Path:

Investigation of thermodynamics of molecular interactions and formation of adducts and ternary complexes of metals, combining acidic (HDEHP, HEHAP) and neutral ligands (DGA) in the mixed extraction system:

Solvent extraction	Speciation analysis of organic solvent with varying concentrations of studied ligands and metals			Evaluation of data
	UV-Vis-NIR, titration	FTIR, NMR	XAFS, SAXS	

Outcomes:

- Database of speciation characteristics for the ternary complexes and adducts formed in the combined ALSEPP organic solvent
- Design of the optimal composition of the ALSEP process, allowing for scaling and development of efficient methods for advanced nuclear fuel reprocessing

DETAILS

Principal Investigator: Alena Paulenova

Institution: Oregon State University

Collaborators: Institution Names (use abbreviations)

Duration: 01/13/2014-01/12/2017 **Total Funding Level:** $481,700

TPOC: Artem V. Gelis (Argonne National Laboratory

Federal Manager: Jim Bresee

Workscope: FC-1.2

PICSNE Workpackage #: NU-13-OR-OSU -0201-02

RESULTS

Accomplishments:

- Four combinations of a cation-exchange ligand (either HDEHP or HEH[EHP]) and a neutral solvating ligand (either TODGA or T2EHDGA) in n-dodecane studied:
- Interligand dimers in these combinations were investigated with NMR and FTIR, the strongest interaction observed for HDEHP+TODGA and weakest for T2EHDGA+HEH[EHP].
- Complexes of the trivalent Am and lanthanides Nd, Eu, Ho, Pr in these binary ligand mixtures were probed with spectroscopic (UV–vis, time-resolved fluorescence, XAFS and SAXS-spectroscopies) and extraction (Job's plot, slope analysis) methods; co-extracted water and nitric acid were analyzed by titration methods.
- Comparison of the collected spectra showed significant shifting for both HDEHP-DGA systems, while both combinations of HEH[EHP]+DGA displayed much smaller spectral changes. Data were modeled with Hypspec program, and stability constants for extracted complexes were calculated.
- Aggregation in these systems were studied by SAXS (small-angle X-ray scattering) and interfacial tension, size of aggregates were measured.
- Two PhD students graduated (2017, 2018) and one student continues her PhD study.

II. PROJECT ORGANIZATIONAL DETAILS:

The work on the project was managed via weekly research meetings held with students involved in this project. In addition, we held frequent ad hoc one-on-one meetings, practically on a daily basis. Students were encouraged to act both independently and collaboratively - seeking advice as needed from the PI, National Lab partners, and colleagues. Quarterly and annual reports with achieved accomplishments and financial status were submitted by the assigned deadlines. Students presented their results on the international and national conferences, with travel expenses mostly covered by our university.

III. LIST OF PUBLICATIONS and RELEASED MATERIALS:

- *Extraction of Water and Speciation of Trivalent Lanthanides and Americium in Organophosphorus Extractants,* B.J. Gullekson, A.T. Breshears, M. Alex Brown, J. B. Essner, G. A. Baker, J. R. Walensky, A. Paulenova, and A. V. Gelis, Inorg. Chem. (2016,) 55 (24) 12675–12685.
- *Speciation of Select f-Elements with Lipophilic Phosphorus Acids and Diglycol Amides in the ALSEP Backward-Extraction Regime,* Brian J. Gullekson, M. Alex Brown, Alena Paulenova, and Artem V. Gelis, *Ind. Eng. Chem. Res.* (2017) 56 (42), 12174–12183.
- *Effect of Nitric Acid on Speciation of Lanthanides in the ALSEP Solvent, Brian J. Gullekson, Vanessa E. Holfeltz, Alena Paulenova, Artem V. Gelis* (Hydrometallurgy, submitted).
- *Aggregation in the ALSEP-relevant Organic Solvents,* A.Paulenova, Y, Karsleyan-Isaichykava, B.J. Gullekson, A.V. Gelis, Actinide and Fission Product Partitioning and Transmutation; OECD, 15th Info-Ex Mtng; Manchester, UK, 30 Sept.‑3 Oct. 2018.
- *Speciation of f-Elements Complexes in the HEH[EHP] Mixtures with Selected Diglycoamides in n-Dodecane*, Paulenova, A., Gullekson, B., Gelis, A., Brown, A., Isaichykava, Y., GLOBAL 2017, Intl. Nuc. Fuel Cycle Conf., Sept. 24-29, 2017, Seoul, South Korea.
- *Organic Phase Speciation in the Mixed Solvents of HEH[EHP] with Selected Diglycoamides in n-Dodecane*, Paulenova, A., Gullekson, B.,Isaichykava, Y., Gelis, A., Brown, A., APSORC 2017, 6th Asia-Pacific Symp. Radiochemistry, Jeju, South Korea, Sept. 17- 22, 2017.
- *Interlined Adducts in the Combined Extraction Solvents*, Y. Isaichykava, C. Knaus, B. Gullekson, A. Paulenova, NORM, 72nd ACS Annual NW Mtng. 2017, June 25-28, 2017, Corvallis, OR, p.227.
- *Aggregation Properties of Diglycoamide and Organophosporus Ligands in Solvent Extraction*, Y. Isaichykava, C. Knaus, A. Paulenova, A. Gelis, The 41st Actinide Separation Conference, Argonne, APS Conf. Center, Lemont, IL, May 23-25, 2017.
- *Speciation of Lanthanides and Americium with Organophosphorus Acids and Effect of Co-extracted Water,* A. Paulenova, B. Gullekson, M. Nyman, P. Molina, A. Brown, A. Gelis, Actinide and Fission Product Partitioning and Transmutation; OECD, 14th Info-Ex Mtng; San Diego, CA, 17-20 Oct. 2016.

- *HEH[EHP] Behavior in the ALSEP Process*, V. Holfeltz, T. Levistkaia, G. Lumetta, A. Paulenova; Atalante 2016, Nuclear Chem. for Sustainable Fuel Cycles, Montpellier, June 5-10, 2016, ATAL-027.
- *Study of Organic Phase Lanthanide Complexes in ALSEP Process*, Paulenova, A., B.J. Gullekson, A.V. Gelis; Atalante 2016, Nuclear Chem. for Sustainable Fuel Cycles, Montpellier, June 5-10, 2016, ATAL-028.
- *Chemistry of a Combined Extraction System for Separation of Trivalent Actinides and Lanthanides*; Paulenova, A., B.J. Gullekson, A.V. Gelis; PacifiChem 2015, Honolulu, Dec 1520 (2015) 303
- *Trans-Lanthanide Comparison of Metal Organic Complexes in Actinide Lanthanide Partitioning System*, B.J. Gullekson, A. Paulenova, A. V. Gelis, The Nuclear Fuel Cycle for a Low-Carbon, Global 2015, Paris, Sept 21-24, (2015); Paper 4f1-5
- *Effect of Acidic Extractant and Acid Concentration on Extraction Behavior in the ALSEP System*; V. Holfeltz, A. Paulenova; 39th Annual Actinide Separations Conf., Salt Lake City, UT, May 18-21, 2015.
- *Spectroscopic study of the ALSEP Extraction System*; Brian J. Gullekson, A. Paulenova; 39th Annual Actinide Separations Conf., Salt Lake City, UT, May 18-21, 2015.
- *Investigation of Ternary Complexes in Combined Organic Solvent for ALSEP*, A. Paulenova, B.J. Gullekson, A.V. Gelis, First SACSESS Intl. Workshop, Warsaw, Poland, Apr 22-24, 2015.
- *Fundamental Solvent Characteristics of ALSEP for Nuclear Fuel Reprocessing*. Brown, M.A., Gullekson, B.J., Kropf, J.A., Paulenova, A., Gelis, A.V., MARC-X., 2015, April 12-17, Log: 463.
- *The f-Element Complexation in Mixed Extractant UNF Reprocessing*; B.J. Gullekson, V.E. Holfeltz, A.Paulenova, A.V. Gelis, The 2015 Summer ANS Mtng, San Antonio, June 7-11, 2015.
- *Investigation of the Influence of Extracted Aqueous Phase Species on Metal Complexation in the ALSEP Process*, B.J. Gullekson, A. V. Gelis, A. Paulenova, 18th Symp. Separation Sci. Technology, Energy Applications, Gatlinburg, TN, Oct. 27-30, 2014
- *Complexes formed in ALSEP Organic Phase,* Actinide and Fission Product Partitioning and Transmutation; OECD, 13th *Info-Ex Mtng*; Seoul, Korea, 23-26 Sept, 2014.
- *Speciation of lanthanides in proposed ALSEP organic phases*: B. J. Gullekson, A. Paulenova, A. V. Gelis. 248th ACS Natl. Mtng, Aug. 10-14, 2014, San Francisco, CA, p.85
- DOE Materials Recovery and Waste Form Development Meeting, Gaithersburg, May 2015, Richland, April 2016 (presented by A. Paulenova).
- *Application of diglycoamides in ALSEP*, GENIORS Int Meeting, Prague, Nov. 21-22, 2017, presented by T. Todd.

IV. TECHNICAL SUMMARY OF THE WORK ACCOMPLISHED:

Several multistage solvent extraction methods that address the processing of the aqueous raffinate streams resultant from the PUREX process were developed over the decades; however, separation of trivalent minor actinides and lanthanides represents a significant technical challenge in used nuclear fuel reprocessing. In recent years, several mixed extractant solvent extraction processes have been developed for separation of trivalent minor actinides (AN) and lanthanides (LN) from the remaining fission products.[1]

Typically, a group extraction of trivalent f-elements is performed by an extraction mixture of two ligands combined in a single organic phase[2]: an acidic, cation-exchange ligand, extracting at lower acidity of aqueous phase and a neutral, solvating ligand, which requires a presence of extractable anions for balancing the metal cation charge. Both the trivalent actinides and lanthanides are co-extracted from a highly acidic aqueous phase via complexation with the solvating ligand, followed by a selective strip of one f-element group using a buffered aqueous phase while retaining the other group complexed with the cation-exchange ligand in the organic phase.[3]

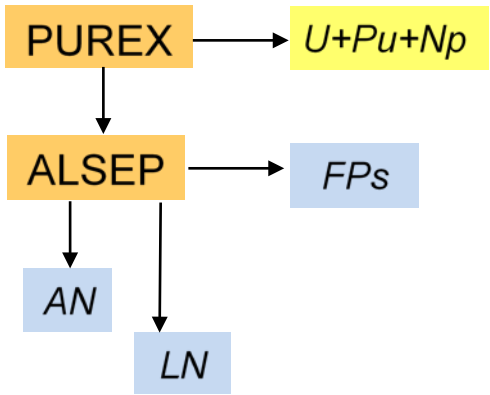

Figure 1. Conceptual ALSEP scheme

The Actinide-Lanthanide Separation Process[4] (ALSEP) is an advanced, single solvent extraction process currently under development, similar to previously attempted TRUSPEAK[5] where TRUEX and TALSPEAK processes were combined. This strategy takes advantage of different chemical operating conditions needed for a neutral solvating ligand (strongly acidic, typically HNO_3) and a chelating acidic ligand (buffered, low acidic aqueous phase). With a solvent mixture of a neutral and acidic extractant, a group extraction of AN(III) and LN(III) is then achieved, followed by an actinide strip utilizing a buffered, TALSPEAK[2] type aqueous phase.

Several ligands were tested and the mixed organic solvent based on a combination of the acidic HEH[EHP] (2-ethylhexyl-phosphonic acid mono-2-ethylhexyl ester) and neutral (either TODGA, N,N,N',N'-tetraoctyl-diglycolamide, or T2EHDGA, N,N,N',N'- tetra(2 ethylhexyl)diglycolamide) ligands has shown a much better extraction behavior, as well as more efficient Ln/An(III) separations than the previous similar efforts toward mixed extractant system development.[6]

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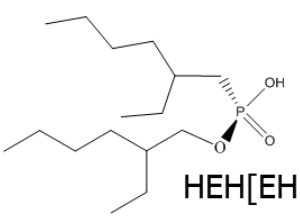
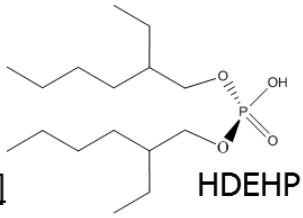
1. KL Nash, C. Madic, JN Mathur, J. Lacquemont, "Actinide Separation Science and Technology," in Chemistry of the Actinide and Transactinide Elements, L.R. Morss, N.M. Edelstein, J. Fuger, Eds., Springer: Dordrecht, The Netherlands, Vol. 4, pp 2622-2798, (2006).
2. M. Nilsson, K.L. Nash, Solvent Extraction Ion Exchange Vol. 25 (2007) 665-701;
3. Braley, J.C.; Grimes, T.S.; Nash, K.L.; Ind. Eng. Chem. Res., 51 (2012), 629–638.
4. Gelis, A. V. Actinide and Lanthanide Separation Process (ALSEP). US Patent # 8354085.2013
5. Lumetta, GJ.; Gelis, AV; Braley, JC, et al., Solvent Extr. Ion Exch. **2013**, *31*, 3, p.223
6. Gelis AV, and GJ Lumetta, Industrial Eng. Chem. Research 53 (2014)1624-1631

Cation-Exchange Ligands:

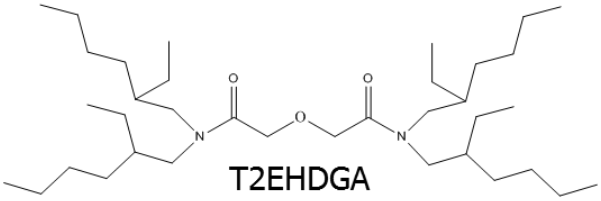


HEH[EHP]

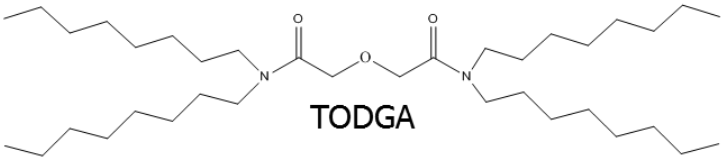


HDEHP

Solvating Ligands:



T2EHDGA



TODGA

Researchers at Oregon State University collaborate with Argonne National Laboratory on characterization of the ALSEP extraction systems, in order to better understand and to possibly predict the extraction and stripping behavior of Ln/An(III) in these mixtures. Objectives of this project were:

1. The primary objective of this investigation was documentation of the molecular interactions of ligands occurring in the organic solvent proposed for the ALSEP extraction separation process. Characteristics of the **inter-ligand adducts and their effects on coextraction of the considered metals** from PUREX raffinate as well as on their following partitioning by selective stripping were studied by FTIR and NMR spectroscopies and titration of nitric acid and water in organic phase. Using various spectroscopic methods, we attempted to quantify the ability of extractants to bind f-elements into extractable complexes, including formation of their own inter-molecular adducts and larger aggregates of metal complexes. From the studied combinations, the mixture of HEH[EHP]-T2EHDGA appeared to have much lower tendency to form intermolecular adducts in the organic phase than the combination of HEH[EHP]-TODGA. Stability constants of the interligand adducts were quantified and reported below this objective summary.
2. The second objective was characterization of the **effect of nitric acid on the lanthanide and americium speciation in ALSEP solvent**. In order to fully understand the multifaceted interaction and metal speciation in the ALSEP organic phases, infrared and UV-Vis spectroscopic studies were conducted with select lanthanides in the organic solvents combining an acidic ligand HEH[EHP] and either TODGA or T2EHDGA. The difference in complexation of lanthanide cations with TODGA and T2EHDGA in the presence of HEH[EHP] was investigated as a function of varying nitric acid concentration in organic solvent. It was observed that lanthanides extracted from low nitric acid concentration as chelates with three dimers of HEH[EHP] change their coordination to solvate coordination with diglycolamides as the nitric concentration increases. In the presence of HEH[EHP], the ability of both TODGA and T2EHDGA to form solvates with metal nitrates is stronger with neodymium than with holmium, and T2EHDGA also forms weaker solvate complexes with metal-nitrates than its straight chain isomer TODGA.
3. **Stoichiometry of the metal ternary complex species** formed in the organic phase under both the extraction and stripping conditions were determined by the Job's plot and the slope analysis of distribution ratios methods. Job's plot analysis with Am and Eu radiotracers revealed that their ternary complexes contain 6 molecules of organophosphorus acid and one molecule of DGA. The UV-Vis spectra collected for Nd and Am in the organic phase lend further insight into the nature of metal complexation in the mixed ligand systems: with an increasing concentration of DGA, an increase in the metal coordination number and decrease in the complex symmetry was observed. Appreciable ternary complex formation was seen among HDEHP with DGA components and to a lesser extent with HEH[EHP]. Ternary complex formation constants were determined by absorption spectroscopy and the slope analysis. The effect of the adduct formation on the extraction performance and the Ln/An selectivity was evidenced. The ternary complexes have the tendency to extract larger trivalent cations as Am and Nd over Eu, thus diminishing the overall Ln/Am selectivity of the process. Also, previously unreported

extraction constants were derived for HEH[EHP] with Am and Pm as well as coordination information for Nd-HEH[EHP] and Nd-T2EHDGA complexes.

4. **Effect of co-extracted water** on speciation of trivalent lanthanides complexes was Complexes was probed with UV–vis, X-ray absorption fine structure, and time-resolved fluorescence spectroscopy while the water concentration was determined by Karl Fischer titrations. In particular, our work focuses on the Nd-hypersensitive UV–vis absorbance region to identify the cause of changing absorbance values at 570 and 583 nm in relation to the pseudooctahedral Nd environment when coordinated with three HDEHP dimers. In contrast to recently reported interpretations, we established that while impurities have an effect on this electronic transition band, a high water content can cause distortion of the pseudooctahedral symmetry of the six-coordinate Nd, resembling the reported spectra of the seven-coordinate Nd compounds. Extended X-ray absorption fine structure analysis of the Nd in high-concentration HDEHP solutions also points to an increase in the coordination number from 6 to 7. The spectral behavior of other lanthanides (Pr, Ho, Sm, and Er) and AmIII as a function of the HDEHP concentration suggests that water coordination with the metal likely depends on the metal's effective charge. Fluorescence data using lifetime studies and excitation and emission spectra support the inclusion of water in the Eu coordination sphere. Further, the role of the effective charge was confirmed by a comparison of the Gibbs free energies of six- and seven-coordinate La-HDEHP–H_2O and Lu-HDEHP–H_2O complexes using density functional theory. In contrast, HEH[EHP], the phosphonic acid analogue of HDEHP, exhibits a smaller capacity for water, and the electronic absorption spectra of Nd or Am appear to be unchanged, although the Pr spectra show a noticeable change in intensity as a function of the water content. Electronic absorption extinction coefficients of AmIII, NdIII, PrIII, SmIII, ErIII, and HoIII as a function of the HDEHP concentration are reported for the first time.

5. Experimental investigation of the molecular and **supramolecular speciation in ALSEP organic phase** by titration of water, proton and nitrate in organic phase was performed by application of UV-Vis, FTIR, XAFS, SAXS spectroscopies and most of results were published. Two more manuscripts about aggregation behavior are in progress.

V. STATEMENTS OF EACH OBJECTIVE AND DESCRIPTION OF THE EFFORT PERFORMED AND THE ACCOMPLISHMENTS ACHIEVED:

Objective 1. Association of ligands and formation of mixed adducts FTIR

FTIR 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 1.1. The peak assignments for the cation exchange ligands and the two DGAs are shown in Table 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 1.1 – IR Peak Assignments for ALSEP Ligands

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

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. This is defined by the equilibria in Equations 1.1A and 1.1B and the equilibrium constants in Equations 1.2A and 1.2B.

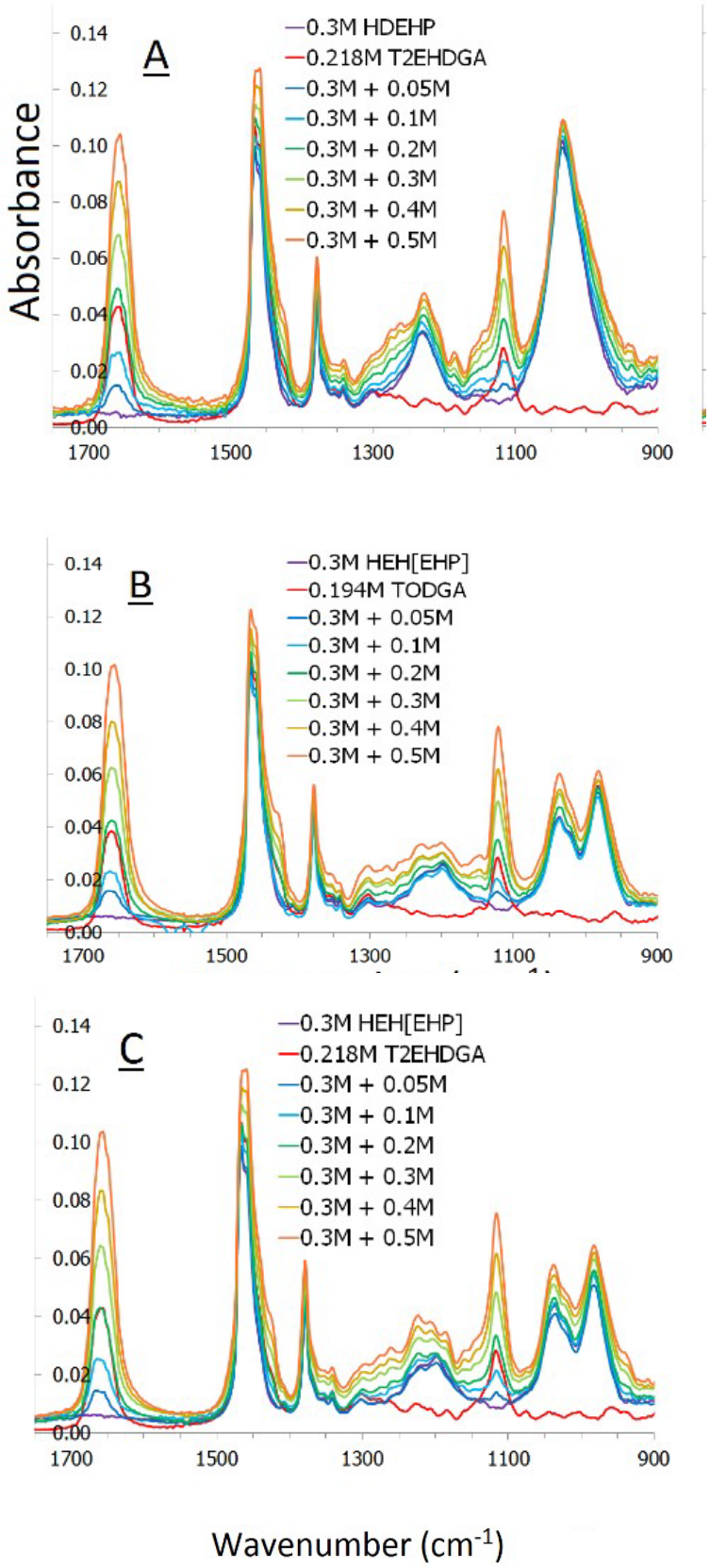


Figure 1.1 – IR Spectra of a Constant Concentration of a Cation Exchange Extractant and Variable DGA for the Mi
and T2EHDGA, (B) HEH[EHP] and TODGA, and (C) HEH[EHP] and T2EHDGA

$$2\overline{HA} \rightleftharpoons (\overline{HA})_2 \qquad (1.1\ A)$$

$$\overline{HA} + \overline{DGA} \rightleftharpoons \overline{HA - D} \qquad (1.1\ B$$

$$K_{dim} = \frac{[(\overline{HA})_2]}{[\overline{HA}]^2} \qquad (1.2\ A)$$

$$K_{add} = \frac{[\overline{HA - DGA}]}{[\overline{HA}][\overline{DGA}]} \qquad (1.2\ B)$$

The obtained spectrophotometric data were fitted to this model using the HypSpec software program. 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[1]. The adduct formation constant for each combination of cation exchange and solvating ligands are shown in Table 1.2. 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.[2]

Table 1.2 Log(K) Values of Adduct Formed by the Neutral and Cation -Exchange Ligands

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

1. Miyake, Y.; Matsuyama, H.; Nishida, M.; Nakai, M.; Nagase, N.; Teramoto, M., Hydrometallurgy, 23, 19-35, 1990
2. Tkac, P.; Vandegrift, G. F.; Lumetta, G. J.; Gelis, A. V., Industrial and Engineering Chemistry Research, 51(31), 10433-10444, 2012

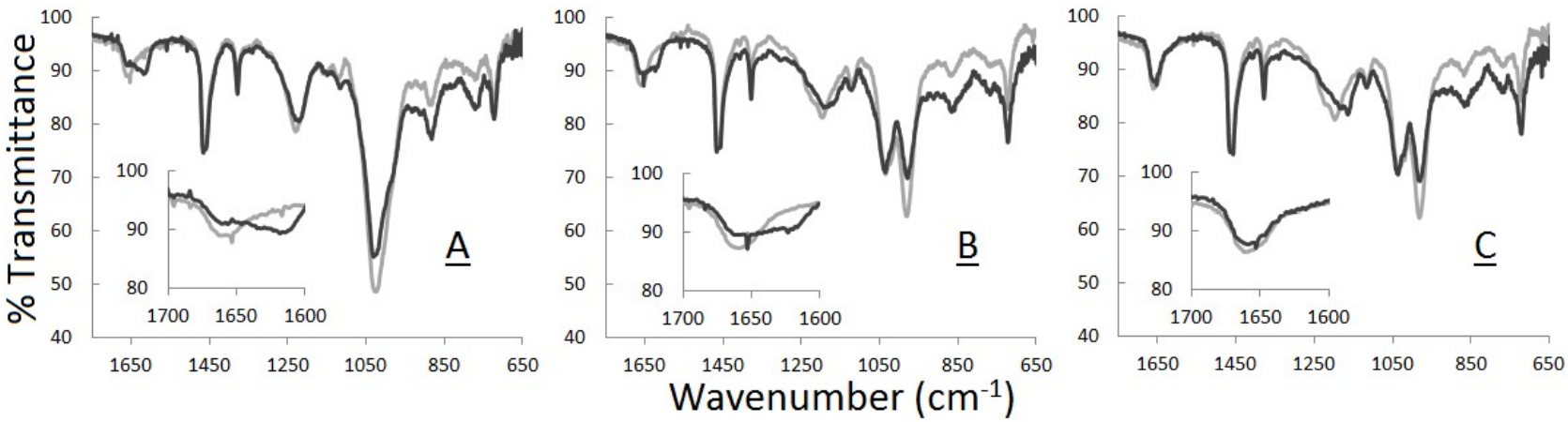


Figure 1.2 – IR Spectra of the ALSEP Organic Solutions Prior to Extraction of Metal (light lines) and Following Metal Loading from a pH 2.8 HCl aqueous phase (dark lines). Combination are (A) 1 M HDEHP + 200 mM T2EHDGA, (B) 1 M HEH[EHP] + 200 mM TODGA, (C) 1 M HEH[EHP] + 200 mM T2EHDGA.

Presence of metals:

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 1.2. 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 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.

Objective 2. Effects of Co-Extractred Nitric Acid On Metal Speciation

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Effect of Nitric Acid on Speciation of Lanthanides in the ALSEP Solvent

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ABSTRACT

In order to fully understand the multifaceted interaction and metal speciation in the ALSEP organic phases, infrared and UV-Vis spectroscopic studies were conducted with select lanthanides in the organic solvents combining an acidic ligand HEH[EHP] and either TODGA or T2EHDGA. The difference in complexation of lanthanide cations with TODGA and T2EHDGA in the presence of HEH[EHP] was investigated as a function of varying nitric acid concentration in organic solvent. It was observed that lanthanides extracted from low nitric acid concentration as chelates with three dimers of HEH[EHP] change their coordination to solvate coordination with diglycolamides as the nitric concentration increases. In the presence of HEH[EHP], the ability of both TODGA and T2EHDGA to form solvates with metal nitrates is stronger with neodymium than with holmium, and T2EHDGA also forms weaker solvate complexes with metal-nitrates than its straight chain isomer TODGA.

Keywords: HEH[EHP], TODGA, T2EHDGA, neodymium, holmium, ALSEP

INTRODUCTION

Separations of trivalent minor actinides and lanthanides represent a significant technical challenge in the 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 their irradiation in 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. The lanthanide 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 co-extracted from a highly acidic aqueous phase via complexation with the solvating ligand, followed by a selective strip of one f-element group using a buffered aqueous phase and a holdback of the other group 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, 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-ethylhexylphosphonic acid mono-2-ethyl-hexyl ester (HEH[EHP], Figure 1) in conjunction with either tetraoctyl- diglycolamide (TODGA, Figure 1) or tetra-2-ethylhexyldiglycolamide (T2EHDGA, Figure 1) in n-dodecane diluent allows for co-extraction of trivalent actinides and lanthanides from high nitric acid concentration aqueous phases and possess the ability to selectively retain lanthanides in the organic phase when contacted with a buffered aqueous stripping solution of a polyaminocarboxylate ligand.[12] Furthermore, the stripping stage displays the favourable pH stability that has been demonstrated in extraction processes with HEH[EHP].[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 metal charge balancing nitrate anion is introduced. This could assist in the determination of process boundary conditions for industrial scale operations.

The water extracted into organic phase titrated with the Karl Fischer reagent using the Mettler Toledo DL58 autotitrator. The observed data on behaviour of water with organophosphorus acidic extractant were so comprehensive that they are separately discussed in our recent report (Inorganic Chemistry, 2016, 55 (24), pp 12675–12685).

EXPERIMENTAL

Reagents

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) and ^{31}P NMR.[15] The diglycolamides TODGA and T2EHDGA were obtained from Marshallton Research Laboratories 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. Solutions of HEH[EHP] and HEH[EHP]-DGA were prepared in n-dodecane diluent. Solutions of TODGA and T2EHDGA for use in spectroscopy experiments were prepared in TCE diluent.

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. Final pH value of the solution was 2.80 as checked with an Orion 8165 BNWP pH electrode. Aqueous phase metal solutions for TODGA and T2EHDGA extraction were prepared using $Nd(NO_3)_3$ (Alfa Aesar, 99.9%) and $Ho(NO_3)_3$ (Alfa Aesar, 99.9%) dissolved into 3M nitric acid (Mallinckrodt, ACS grade). All aqueous phases were prepared using 18.1 MΩ-cm deionized water generated using a Millipore system.

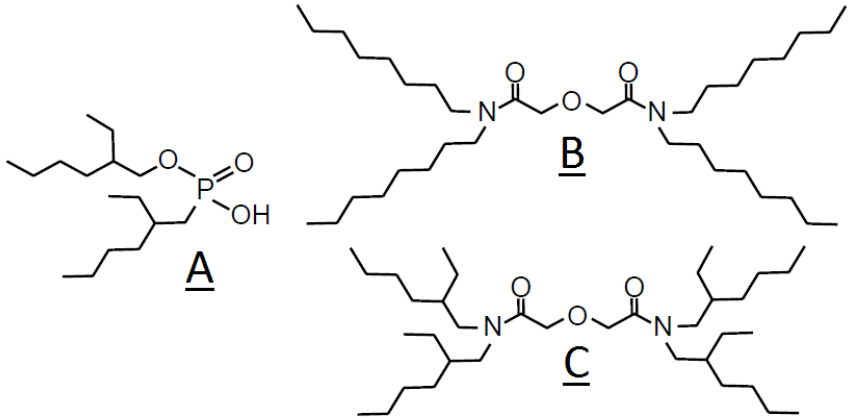

Figure 1. Cation Exchange Ligand HEH[EHP] (A) and Solvating Ligands TODGA (B) and T2EHDGA (C)

Distribution Study

Distribution ratios (D) of europium were measured with the radiotracer Eu-152/154 prepared by the thermal n-activation of natural Eu-151/153 in the OSU TRIGA Reactor. Solutions of variable concentration HEH[EHP] with either TODGA or T2EHDGA in n-dodecane were twice pre-equilibrated in 1:2 volume ratio with aqueous nitric acid solutions of desired concentration (0.1 – 5M) prior to extraction. Extraction samples were prepared by combining 1 mL of each of the pre-equilibrated organic phase and fresh nitric acid solution in small 4.5 mL screw cap polyvials, spiked with the radiotracer and agitated for ten minutes on a vortex mixer, followed by centrifugation until the phase disengagement. Phases were separated using a fine tipped transfer pipette. The equilibrium activity concentrations of Eu were determined by counting the aliquots of the organic and aqueous phases using a Cobra-II autogamma counter with 3" NaI(Tl) detector (Packard). Values of Eu distribution ratio were calculated as the activity concentrations ratios $D= A_{org}/A_{aq}$.

Distribution of neodymium and holmium for spectrometric studies were prepared in the same manner. Concentration of extracted lanthanides was determined as the difference in their concentrations in the pre- and post-extraction aqueous phase, measured colorimetrically with Arsenazo III.[21] Concentrations of nitric acid extracted to the organic phase was determined by titration of the pre- and post-extraction aqueous phase with NaOH, freshly standardized with potassium biphtalate.

Infrared Spectroscopy

For the infrared (IR) spectroscopic investigation, two sets of solvent extraction organic phases were prepared by multiple extractions to achieve adequate metal loading for observation of ligand-metal bond interactions: a) 1M HEH[EHP] in n-dodecane solutions were metal loaded by performing five-fold extraction with either 8.23 mM Nd or a 12.9 mM Ho dissolved in 0.001M HCl and b) 0.2 M solutions of either TODGA or T2EHDGA in trichloroethylene (TCE) were metal loaded by performing four-fold solvent extraction with either a 13.8 mM Nd or a 15.5 mM Ho dissolved in 3 M HNO_3 solution. The metal-free, HNO_3 loaded organic phase was prepared by contacting the organic phase once with a 3M HNO_3 aqueous 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.

UV-Vis Spectrophotometric Titration

Metals were first extracted to the 1M HEH[EHP]/n-dodecane organic phase by solvent extraction performed with either 10.6 mM Nd or 12.9 mM Ho dissolved in 0.001M HCl. The UV-Vis spectra of the organic phase were collected with n-dodecane as a background spectrum in a 1 cm quartz cuvette with a Cary 6000i UV-Vis-NIR spectrometer with a temperature jacket held at 20°C. The UV-Vis spectrum were collected after each 0.1 mL added increment of the titrant solution. Titrant solutions were prepared as 200mM TODGA or T2EHDGA in 1M HEH[EHP]/n-dodecane and preequilibrated with 3M nitric acid. Spectroscopic data were modelled using the non-linear least squares regression fitting spectral analysis software Hypspec.[16]

RESULTS

Metal Distribution Data

The effect of varying the organic phase extractant composition on the distribution of trivalent lanthanides can suggest the nature of metal extraction in ALSEP systems. The values of distribution ratio (D) of europium are presented in Figure 2 as a function of varying concentrations of aqueous phase nitric acid concentration (0 - 5 M). As the nitric acid concentration increases, the D-values exhibit a spoon-shape dependence, as expected for both combinations of the cation-exchanging ligand HEH[EHP] with either TODGA or T2EHDGA solvating ligands. Distribution ratios with TODGA are higher than with its branched isomer T2EHDGA. The minima in the observed D-values suggest different extraction mechanisms and therefore different metal speciation when extracting from low and high aqueous phase nitric acid concentration.

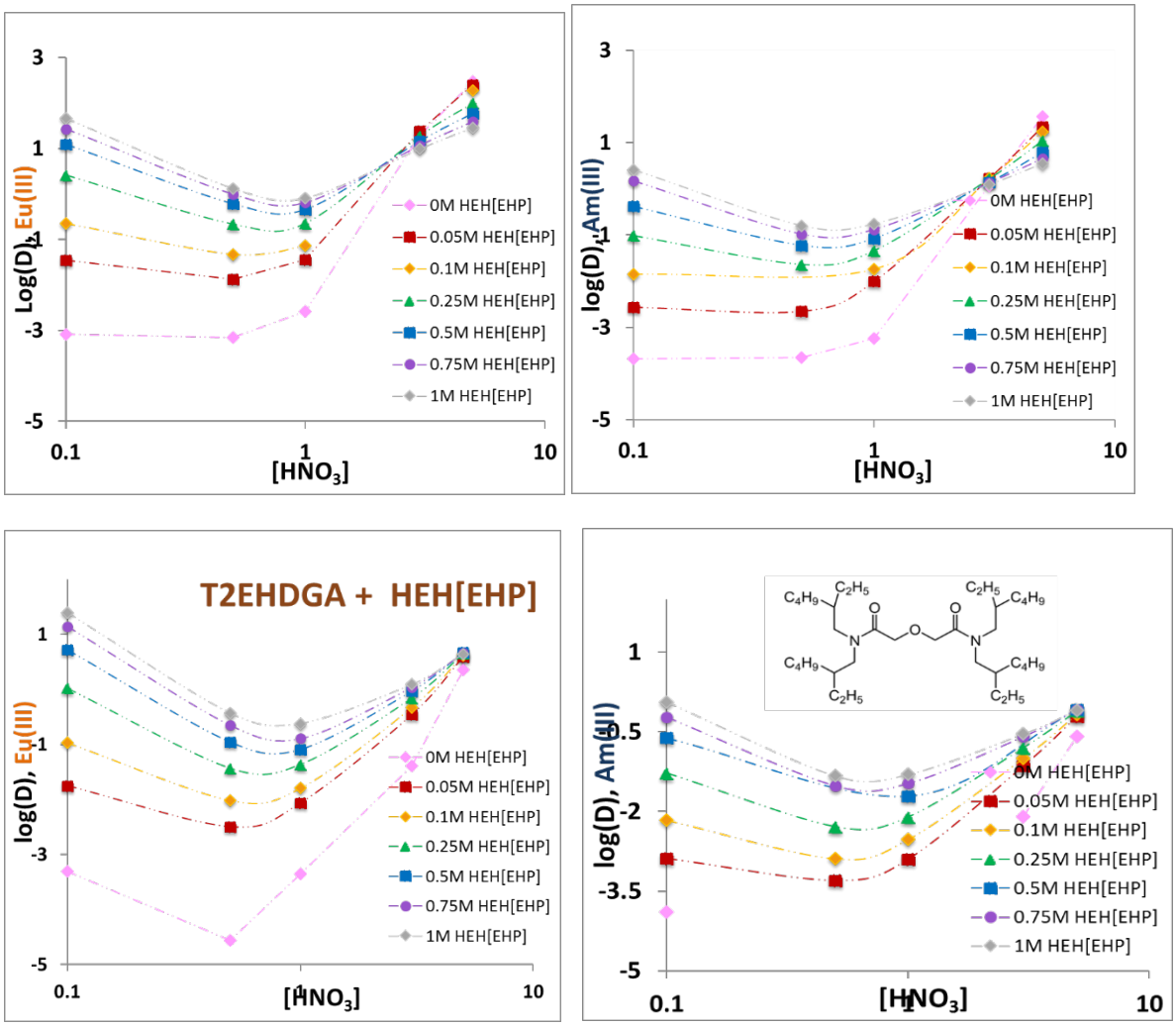

Figure 2 A-D. The observed distribution ratios

Extraction mechanisms are usually studied by varying the concentration of one of the ligands, while concentrations of all others components are held constant. Plotting the distribution ratio against the concentration of the varied ligand allows to graphically solve the average number of ligand molecules in the extracted complex as being equivalent to the value of the slope in a log-log plot. Such plots for varying concentrations of HEH[EHP] and constant TODGA or T2EHDGA concentrations are displayed in Figure 3.

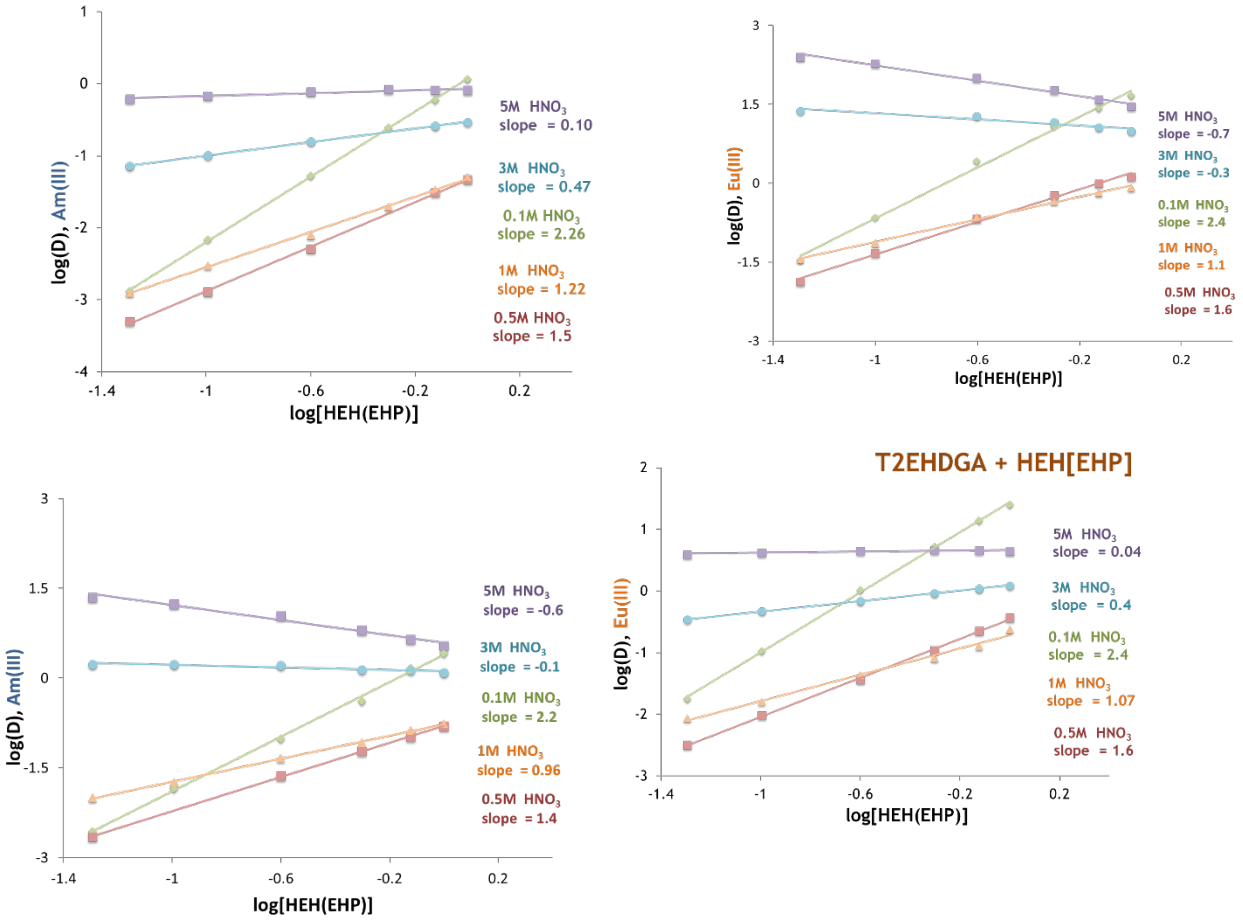

Figure 3 A-D. Collected extraction slopes.

As the concentration of nitric acid in the aqueous phase increases, the value of the slope decreases from 2.4 to zero, confirming that the chelate type coordination of extracted metals with dimers of acidic extractant HEH[EHP] only occurs at low nitric acid concentration. As the aqueous concentration of nitric acid increases to 3M and above, the slopes for T2EHDGA in Figure 3B become horizontal, indicating that HEH[EHP] no longer presents in the extracted metal complexes, and instead, metal cations form a solvate complex with the DGA where the metal cation charge must be compensated with nitrate anion supplied by the coextracted nitric acid. For high nitric acid concentrations in the HEH[EHP] +TODGA system (Figure 3A), even a slightly negative slope was observed which could suggest a slight antagonistic effect of HEH[EHP] as its concentration increases.

Such extraction behaviour with increasing concentrations of acidic extractant and aqueous nitric acid concentration different mechanism and different extracted species in the regions of the low and high nitric acid concentrations. The intermediate slopes suggest the presence of ternary chelate-solvate coordinated complexes in the studied organic extraction phases. Anticipating no free nitric acid in the n-dodecane organic phase, all nitric acid can be assumed existing only in adducts with a diglycoamide $DGA{\cdot}HNO_3$ [18], and the ternary complexes of lanthanides expected in organic phase could be ascribed with a general formula of $M(HA_2)_n{\cdot}(DGA{\cdot}NO_3)_{3-n}$, where M stands for a trivalent metal cation, which charge is compensated by either monodeprotonated dimer HA_2 of HEH[EHP] or nitrate anion or both of them. Solution of this stoichiometry prompted our further examination of the effect of extracted nitric acid on chemical speciation in organic phase.

Infrared Spectroscopy

Infrared (IR) spectra of the organic phase combinations of HEH[EHP] and either TODGA or T2EHDGA in n-dodecane can reveal the qualitative nature of metal-ligand bonds in these mixed extractant systems. Only IR spectra for holmium extraction into the HEH[EHP]+TODGA system are displayed in the text, but they are representative for both studied metals into both extraction systems of HEH[EHP]+TODGA and HEH[EHP]+T2EHDGA as shown in the supplemental information.

Figure 4 compares four spectral lines of two extractants collected prior to extraction (dash lines) and after extraction of Ho (solid lines). The red lines represent 0.2 M TODGA in TCE and the green lines show the mixtures of 0.2 M TODGA with 1 M HEH[EHP] in n-dodecane. The IR spectra in the region of the carbonyl group, one of the metal binding functional groups of the TODGA molecule collected prior to extraction with these two organic solvents are practically identical, with the band appearing at 1660 cm^{-1}. However, following extraction of metal, the absorbance band in the spectrum of 0.2M **TO**DGA/TCE shifts to 1610 cm^{-1}(red solid line). The same shift was observed when to the solution of holmium extracted with 0.2 M **TO**DGA+1M HEH[EHP] in n-dodecane an equivalent volume of 0.2 M **TO**DGA+1 M HEH[EHP] pre-equilibrated with 3 M nitric acid has been added (green solid line). This result suggests that the dipole moment of the carbonyl group in the molecule of **TO**DGA is affected similarly both by the extracted metal and by inclusion into a metal loaded organic phase in the presence of nitric acid.

The transmittance spectra corresponding to the phosphoryl group of HEH[EHP] (1300 – 1100 cm^{-1}) and the P-O-C and P-C bonds of the HEH[EHP] functional group (1100 – 900 cm^{-1}) are shown in Figure 5. Also shown is the ether band of TODGA at 1140 cm^{-1}. In similar manner to Figure 4 above, two dashed spectral lines displayed in Figure [5] show the extractants prior to metal extraction: 1 M HEH[EHP] and 1 M HEH[EHP] with 0.2 M TODGA. The solid lines show the spectra collected following the metal extraction: 1M HEH[EHP] after extraction of Ho (blue solid line), and the same after the addition of an equivalent volume of 1 M HEH[EHP] + 0.2 M TODGA pre-equilibrated with 3 M nitric acid (green solid line). 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}) is greater than the P-O-C bond (1040 cm^{-1}). Following extraction of holmium, the P-C and P-O-C bonds absorb with equal intensity, while the primary phosphoryl absorbance band shifts to 1160 cm^{-1}, confirming binding with extracted metal cation. ~~Following~~ After addition of the organic phase containing 1 M HEH[EHP] + 0.2 M TODGA pre-equilibrated with 3M nitric acid , the spectrum reverts to that of the pre-extraction HEH[EHP]

spectrum in this region. Furthermore, the TODGA ether band is observed to broaden from the sharp peak present prior to extraction to the wide band present following addition of the nitric acid containing solution to the metal loaded HEH[EHP] solution, which was not seen when TODGA solution was not preequilibrated with nitric acid.

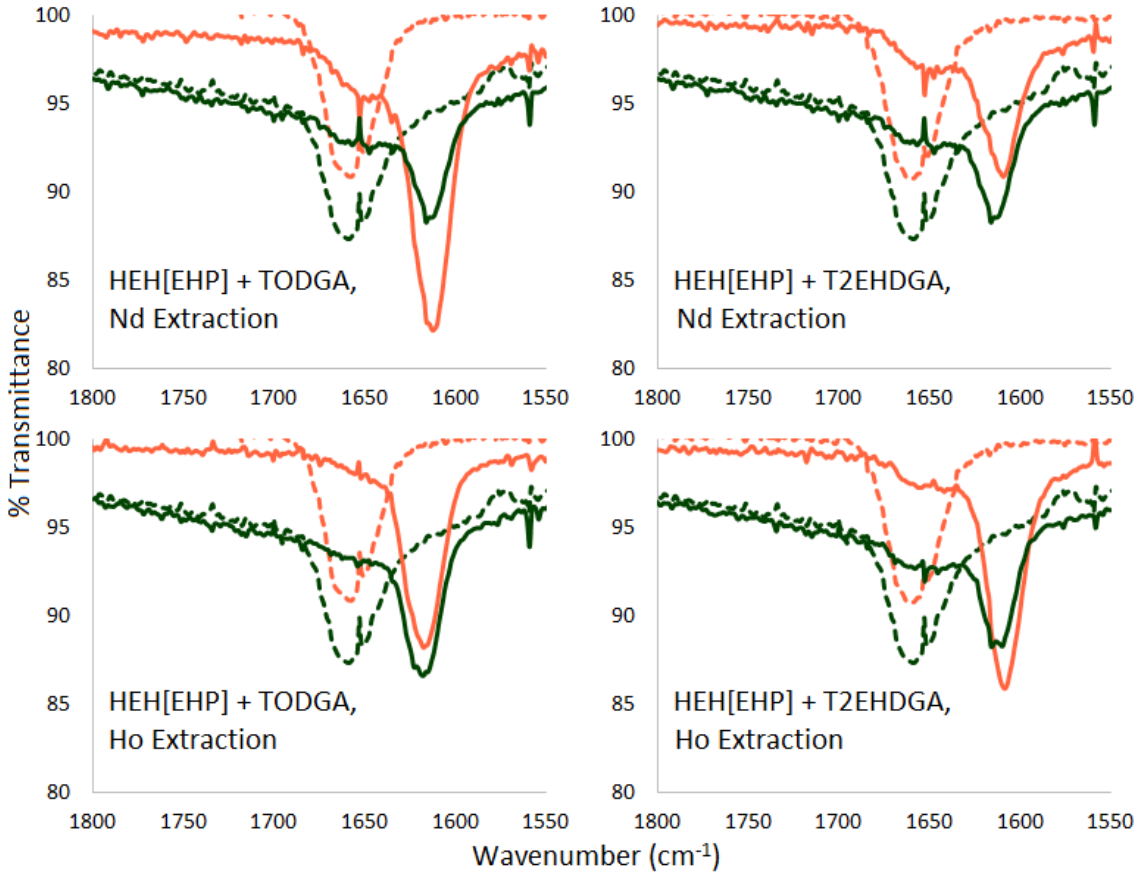

Figure 4. IR Spectra of the carbonyl absorbance of TODGA in solutions of 0.2M TODGA before extraction (red dashes), 1M HEH[EHP] + 0.2M TODGA before extraction (green dashes), 0.2M TODGA after Ho extraction (red solid line), and 1M HEH[EHP] after Ho extraction after the addition of 0.2M TODGA (green solid line) preequilibrated with 3M HNO_3.

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 switch from the cation-exchange complexation toward that of solvate complexation of metal cations with DGA and nitrate. It also suggests that the proton released from the molecule of nitric acid is captured by the deprotonated dimer of acidic extractant to form a neutral species in organic phase [10].

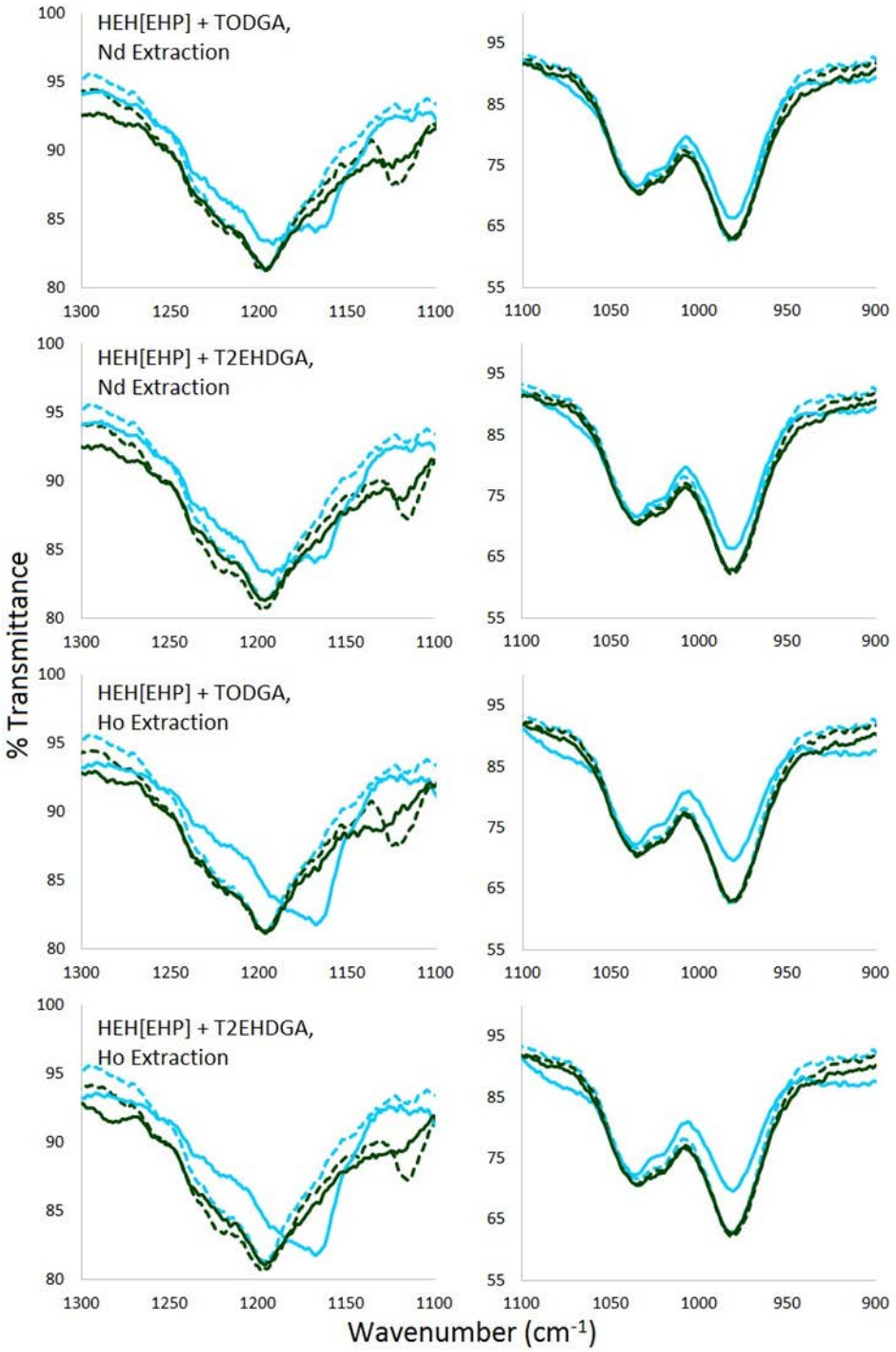

Figure 5. Infrared spectra of the phosphoryl group and the P-O-C and P-C group of HEH[EHP] in solutions of 1M HEH[EHP] before extraction (turquoise dashes), 1M HEH[EHP] + 0.2M DGA before extraction (dark green dashes), 1M HEH[EHP] following Ho extraction (turquoise-solid line), and 1M HEH[EHP] Ho extraction after addition of pre-equilibrated DGA (dark green solid line)

Assuming no free nitric acid in the organic phase but all bound in the DGA·HNO3 adducts, for both directions of combining the chelating and solvating extractants, two general equations (Equations 1 and 2) can be written for equilibria of studied lanthanides with mixed extractants:

$$M(HA_2)_3 + n(DGA \cdot HNO_3) \rightleftarrows M(HA_2)_{3-n}(DGA)_n(NO_3)_n + nH_2A_2 \quad (1)$$

$$M(DGA)_3(NO_3)_3 + nH_2A_2 \rightleftarrows M(HA_2)_n\,(DGA)_{3-n}(NO_3)_{3-n} + n(DGA \cdot HNO_3) \quad (2)$$

For cation charge compensation of the studied trivalent metals, the sum of coordinated nitrates and monodeprotonated dimers of acidic extractant must be equal three, however, the number of coordinated diglycoamide molecules is to be confirmed by additional methods.

Spectrophotometric Titration

UV-Vis spectroscopy was used applied to probe the neodymium and holmium complexes formed in the extraction organic phases as a function of the nitric acid and DGA concentrations. 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 observations have shown that the spectra of Nd and Ho were first extracted into the 1M HEH[EHP]/n-dodecane organic phase from 0.001M HCl, so the metal cation is assumed fully coordinated with three monodeprotonated dimers of the cation exchange ligand HEH[EHP] as the extraction of hydrochloric acid and chloride ion is negligible. The organic phase was transferred to cuvette and titrated with 0.2M TODGA or T2EHDGA, preequilibrated with 3M nitric acid. The same 1M concentration of HEH[EHP] was held in both the titrated and titrant solutions to avoid its dilution and consequent effects on studied speciation. The UV-Vis spectra were collected after each added 0.1 mL increment of the titrant solution. 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.

Our recent investigations (14] have shown that the spectra of either neodymium or holmium extracted into 1M HEH[EHP] and diluted with 1M HEH[EHP] and either TODGA or T2EHDGA remain constant, except for neodymium when introduced to TODGA. The slight shift in the spectrum observed for Nd with HEH[EHP] at high TODGA concentrations indicated coordination of metal cation with interligand adducts present in n-dodecane solution. [14]

Figure 6 compares the spectra of neodymium and holmium titrated with solutions of solvating ligands pre-equlibrated with 3M nitric acid. The spectra of both metals 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 nitric acid into TODGA or T2EHDGA solutions in TCE diluent, suggesting that coordination of the metal cation at this point is solely due to solvation with the diglycoamide and charge balancing nitrate anion.

As was observed in the HDEHP + TODGA mixed solvent extraction, the mode of complexation shifts with respect to the nitric acid concentration in the aqueous extraction phase. At a low concentration of HNO_3 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 the extraction from the high concentration of HNO_3 in the aqueous phase, the coordination is primarily dominated by the DGA, although the presence of the cation exchange ligand might still provide a solvating and 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 concentration of DGA and nitrate in organic phase increases. , however there are no clean isosbestic points in the spectra observed.

Based on the recently reported 1:1 adducts of HNO_3 with TODGA [18] also the T2EDGA:HNO_3 adduct species are presumed to be the dominating species in the organic solvents studied in this work. As no free nitric acid is anticipated in the organic phase, it is assumed that the DGA·HNO3 adduct is the interacting complexing species that exchanges for a dimer of the acidic extractant HEH[EHP. One of possible mechanisms for their interaction is that upon coordination of nitrate adduct to metal center, the proton released from HNO_3 is captured by the deprotonated dimer to form a neutral species in organic phase (10). Such reprotonation of acidic extractant is also favoured by the results of our infrared spectroscopic experiment discussed above. Increased concentration of nitric acid in organic phase either by adding of the nitric acid pre-equilibrated organic phase or by metal extraction from aqueous phase of higher nitric acid concentration was driving the solvate complexation of metal cation with DGA and supplied protons for neutralization of the acidic extractant.

Four species and three equilibria as shown in Equations 3 – 5 are considered in our chemical model for replacement of the HEH[EHP] dimer. In these equations, M represents a metal cation either Nd^{3+} or Ho^{3+}, and HA_2 and H_2A_2 are the deprotonated and protonated dimer of HEH[EHP], respectively:

$$M(HA_2)_3 + \overline{DGA \cdot HNO_3} \rightleftharpoons \overline{M(HA_2)_2NO_3 \cdot DGA} + H_2A_2 \quad (3)$$

$$M(HA_2)_2NO_3 \cdot DGA + \overline{DGA \cdot HNO_3} \rightleftharpoons \overline{M(HA_2)(NO_3)_2 \cdot (DGA)_2} + H_2A_2 \quad (4)$$

$$M(HA_2)(NO_3)_2 \cdot (DGA)_2 + \overline{DGA \cdot HNO_3} \rightleftharpoons \overline{M(NO_3)_3 \cdot (DGA)_3} + H_2A_2 \quad (5)$$

These chemical equilibria are governed by the equilibrium conditional stability constants as shown in Equations 6 – 8.

$$\beta_{121} = \frac{[M(HA_2)_2NO_3][H_2A_2]}{[M(HA_2)_3][DGA \cdot HNO_3]} \quad (6)$$

$$\beta_{112} = \frac{[M(HA_2)(NO_3)_2 \cdot (DGA)_2][H_2A_2]^2}{[M(HA_2)_3][DGA \cdot HNO_3]^2} \quad (7)$$

$$\beta_{103} = \frac{[M(NO_3)_3(DGA)_3][H_2A_2]^3}{[M(HA_2)_3][DGA \cdot HNO_3]^3} \quad (8)$$

The obtained spectrophotometric data were fitted to this model using the HypSpec software [16] program.

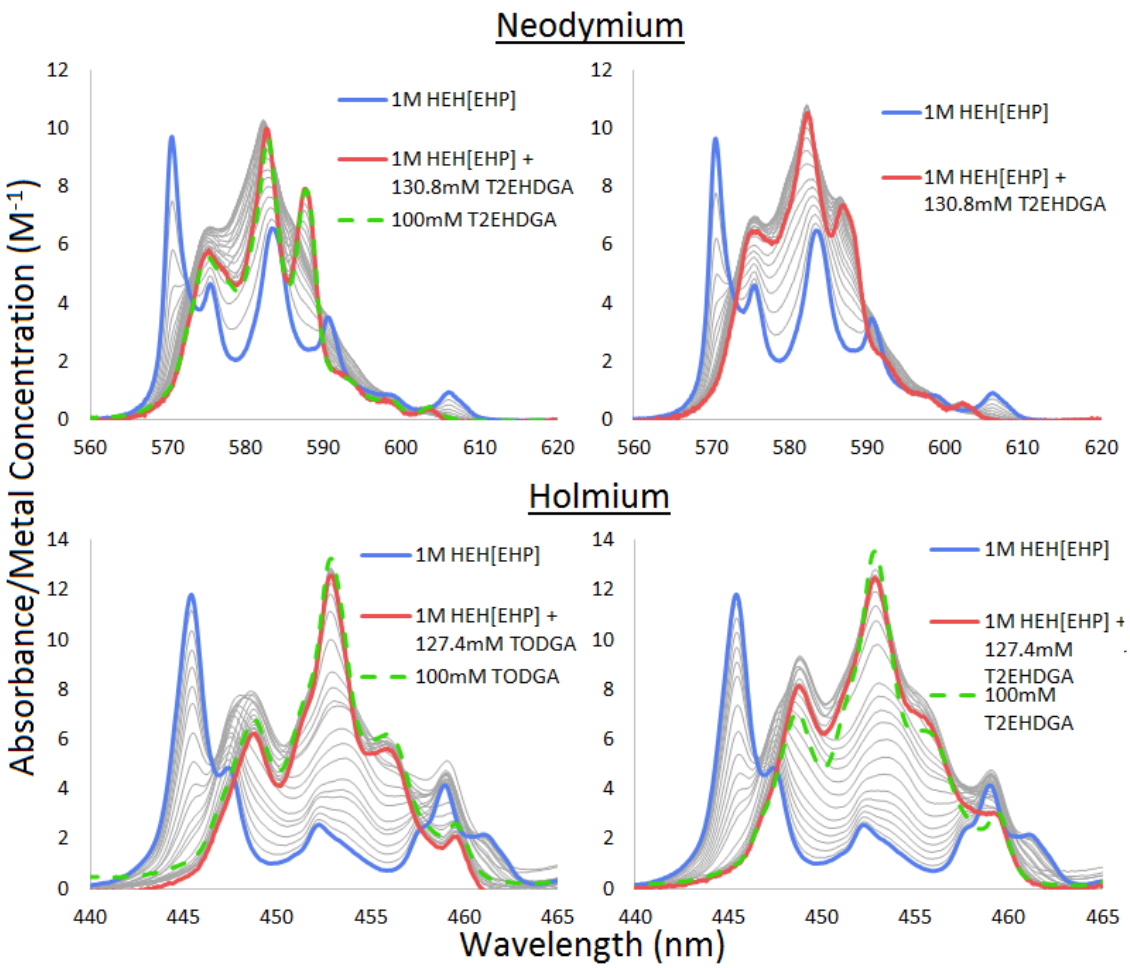

Figure 6. UV-Vis spectra of holmium and neodymium extracted from 0.001M HCl into organic phase of 1M HEH[EHP] (blue lines) and titrated with a solution of 0.2M TODGA or T2EHDGA in n-dodecane pre-equilibrated with 3M nitric acid (grey lines). The red spectral lines represent the titrated sample of extracted Nd containing 130.8mM TODGA or T2EDGA (above) and Ho with 127.4 mM of TODGA or T2EDGA (below). The green lines are spectra of metals with TODGA or T2EDGA alone in TCE diluent.

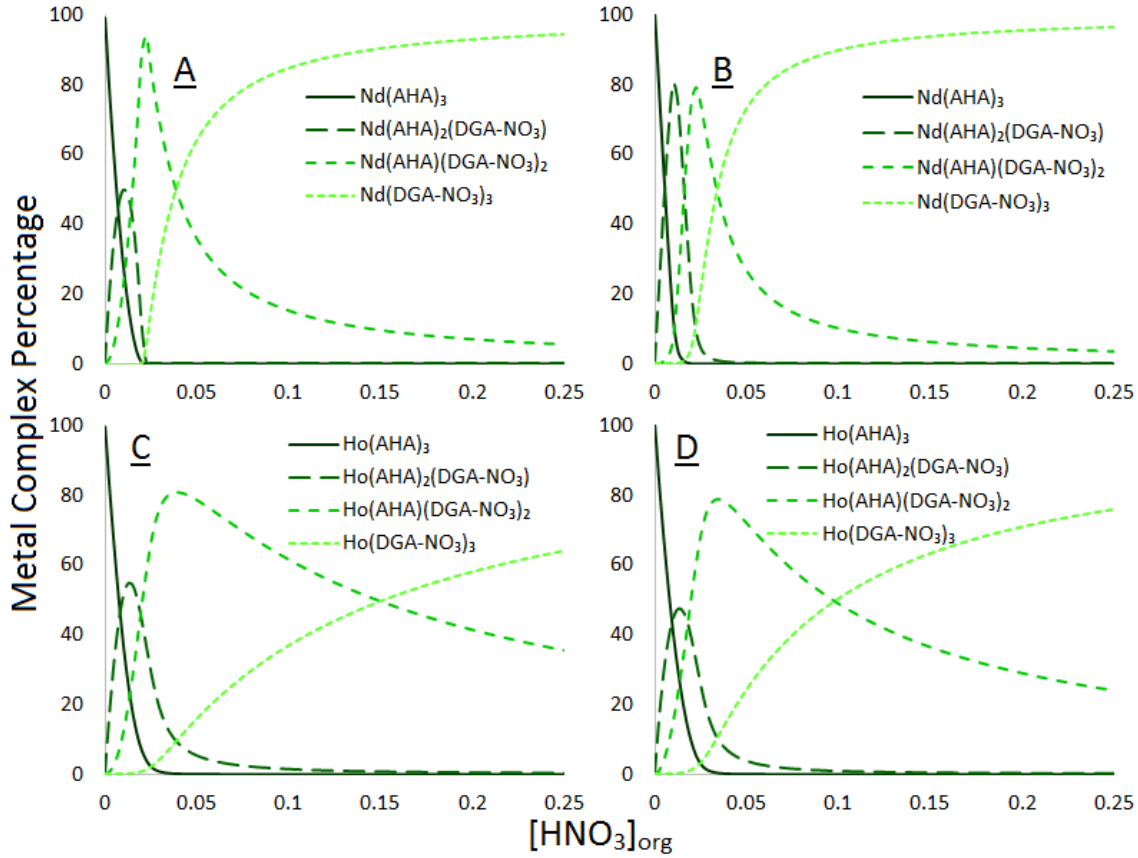

Figure 7. Speciation diagrams of metal complexation with varying organic phase nitrate concentration for neodymium in 1M HEH[EHP]+0.2M TODGA (A), 1M HEH[EHP]+0.2M T2EHDGA (B), holmium in 1M HEH[EHP]+0.2M TODGA (C) and 1M HEH[EHP]+0.2M T2EHDGA (D).

Speciation modelling

The values of the conditional stability constants (Eq. 6-8) were calculated by setting a constant arbitrary value for the conditional stability constant β_{130} of the M(EH[EHP]·HEH[EHP])$_3$ species. The other conditional stability constants were normalized to this constant to display the relative ability of these complexes to form in the presence of nitrate in the organic phase. The obtained values of constants and their 2-sigma uncertainties, calculated from multiple titrations are shown in Table 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 confirm that TODGA is a more powerful metal extractant than T2EHDGA as its relative ability to form metal nitrate solvates is greater than with T2EHDGA. Furthermore, neodymium shows a greater ability to form DGA complexes than holmium. This likely indicates that the electrostatic interactions of the HEH[EHP] dominates in the interactions with the heavier, smaller lanthanide cations where the DGA interactions are likely sufferring from increased steric hindrance.

Table 1. Relative values of the conditional stability constants $\log_{10}(\beta)$ for extracted complexes of holmium and neodymium in solutions of HEH[EHP] and either TODGA or T2EHDGA in n-dodecane:

Extracted Complex	$\log_{10}$	Neodymium		Holmium	
		TODGA	T2EHDGA	TODGA	T2EHDGA
$M(HA_2)_3$	β_{130}	1	1	1	1
$M(HA_2)_2NO_3\cdot$ DGA	β_{121}	3.28±0.07	2.37±0.05	1.98±0.07	1.620±0.01
$M(HA_2)(NO_3)_2\cdot$ $(DGA)_2$	B_{112}	5.36±0.12	3.33±0.07	2.81±0.09	2.12±0.01
$M\cdot$ $(NO_3)_3$ $(DGA_3$	β_{103}	6.16±0.13	3.90±0.08	3.52±0.11	3.06±0.01

The distribution of holmium and neodymium species as a function of coextracted nitric acid was modelled with the calculated conditional constants (Table 1) using the HYSS speciation modelling program (16). Speciation diagrams, shown in Figure 7, compare behavior of Nd and Ho, reveal what complexes they form, and their distribution upon varying nitric acid concentration (0-0.25 M HNO_3) in the organic phase. With the introduction of nitrate, the neodymium cation rapidly shifts toward the DGA-solvated species, with over 90% of the metal bound in the $NdNO_3)_3\cdot$(DGA) complex already at 0.2 M organic phase nitric acid concentration. For holmium cation, however, the mixed complexes persist in organic phase until a higher organic phase nitrate concentration is reached. At 0.25 M NO_3^- (assuming roughly the concentration of organic nitrate equal to concentration of HNO_3 extracted to the organic titrant from 3 M HNO_3), both complexes of $Ho(HA_2)(DGA\cdot NO_3)_2$ and $Ho(DGA\cdot NO_3)_3$ coexist as the primary species present in solution.–This illustrates the effect of a larger effective cationic radius of Nd, and consequently, a bit larger effective cationic charge for Ho which favours ion-exchange complexation and stronger binding with acidic organophosphorus extractant, so it coexist with diglycoamide-nitrate solvates, while under the same extraction conditions of high nitric acid concentration the neodymium cation is fully released from the HEH[EHP] complex and exist almost exclusively as an diglycoamide-nitrate solvate.

CONCLUSIONS

The interactions of lanthanide cations with HEH[EHP] and two diglycoamides occur in the presence of nitric acid in the organic extraction phase is intricate. With the introduction of nitric acid, which provides the metal cation charge-balancing anion, the coordination of the both lanthanides is seen to shift from that of a chelating mechanism with the cation exchange

ligand HEH[EHP] to a solvating mechanism with a DGA·NO_3 adducts. Distribution studies have shown that, in combinations of HEH[EHP] with either TODGA or T2EHDGA, a minimum extraction is seen around 1 M HNO_3, suggesting a turning point in the metal complex type formed upon extraction from higher or lower nitric acid concentrations. Infrared spectroscopy confirmed that the mechanism of the solvating of metal cation with either studied diglycoamide is the same when nitrate is introduced into the organic phase by either extraction or by simple titration. UV-Vis spectrophotometric analysis of organic extraction phases was used to evaluate the relative ability of two diglycoamides in the mixture with cation-exchange ligand in the presence and absence of nitric acid to complex with neodymium and holmium. In the presence of HNO_3, TODGA presents as a more powerful metal-solvating ligand than its branched isomer T2EHDGA. The modelling of results has shown that neodymium nitrate solvates were found stronger with both DGAs than the holmium nitrate solvates.

Our future research plans are focused on behaviour of americium and other lanthanides in a wider concentration region. Diverse analytical methods, such as NMR, EXAFS, including SANS and SAXS to reveal supramolecular interactions are being applied.

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Objective 3 Stoichiometry of the metal ternary complex species:

a) Effect 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, 2016, 55 (24), pp 12675–12685; DOI: 10.1021/acs.inorgchem.6b01756*

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 organophorphoric 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 florescence 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 $Nd(HA_2)_3$ present at high HDEHP concentration and low metal loading, and a bridged, two metal species of the type $Nd_2(DEHP)_6$ 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.

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 ^{31}P NMR spectroscopy.[19] Each extractant was dissolved in n-dodecane (Acros Organics 99+%), used as delivered. Lanthanide chlorides were individually prepared by dissolving Nd_2O_3 (Sigma Aldrich, 99.9%), $Pr(NO_3)_3$ (Alfa Aesar, 99.9%), $Sm(NO_3)_3$ (Sigma Aldrich, 99.9%), Er_2O_3 (Sigma Aldrich, >99.9%) and Ho_2O_3 (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 ^{243}Am 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 ^{243}Am were determined through LSC alpha counting using an alpha-beta discriminator to prevent the interference from the beta-emitting ^{239}Np 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.

Experimental Results

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 $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ electronic transition shown in Figure 1.

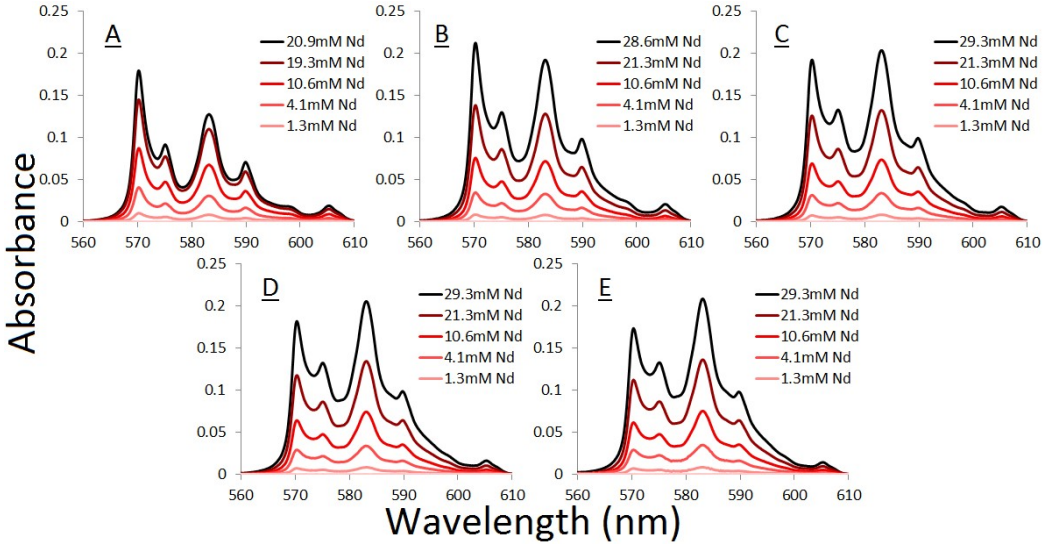


Figure 1 – Neodymium UV-Vis Spectra of Varying Metal Concentrations in (A) 0.2M HDEHP, (B) 0.5M HDEHP, (C) 1.0M HDEHP, (D) 1.5M HDEHP, and (E) 2.0M HDEHP

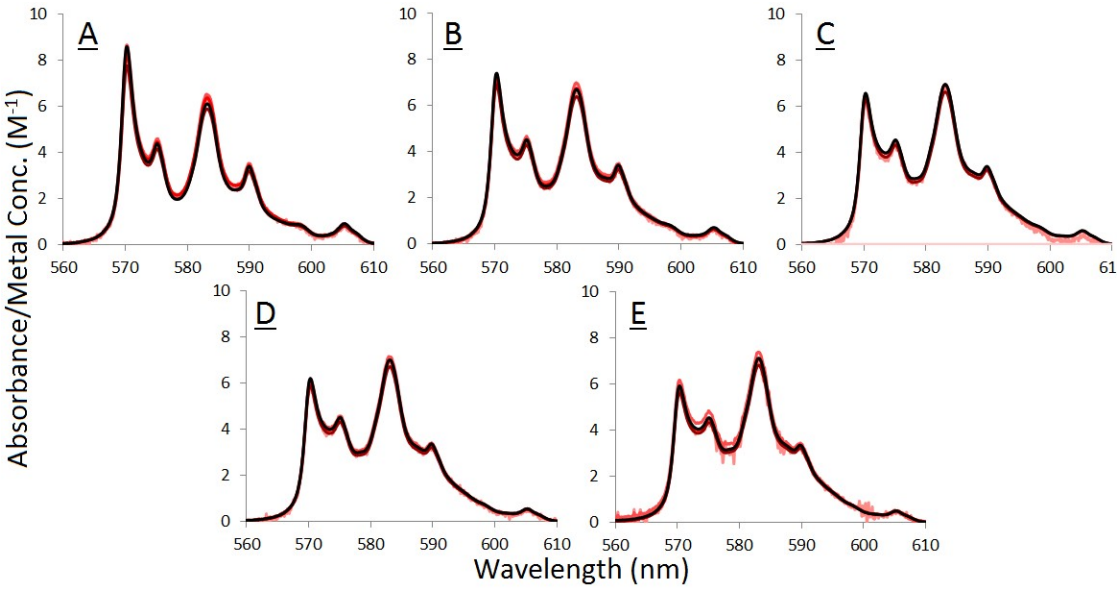


Figure 2 – Metal Concentration Corrected Spectra of Nd in (A) 0.2 M HDEHP, (B) 0.5 M HDEHP, (C) 1.0 M HDEHP, (D) 1.5 M HDEHP, and (E) 2.0 M HDEHP

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 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]

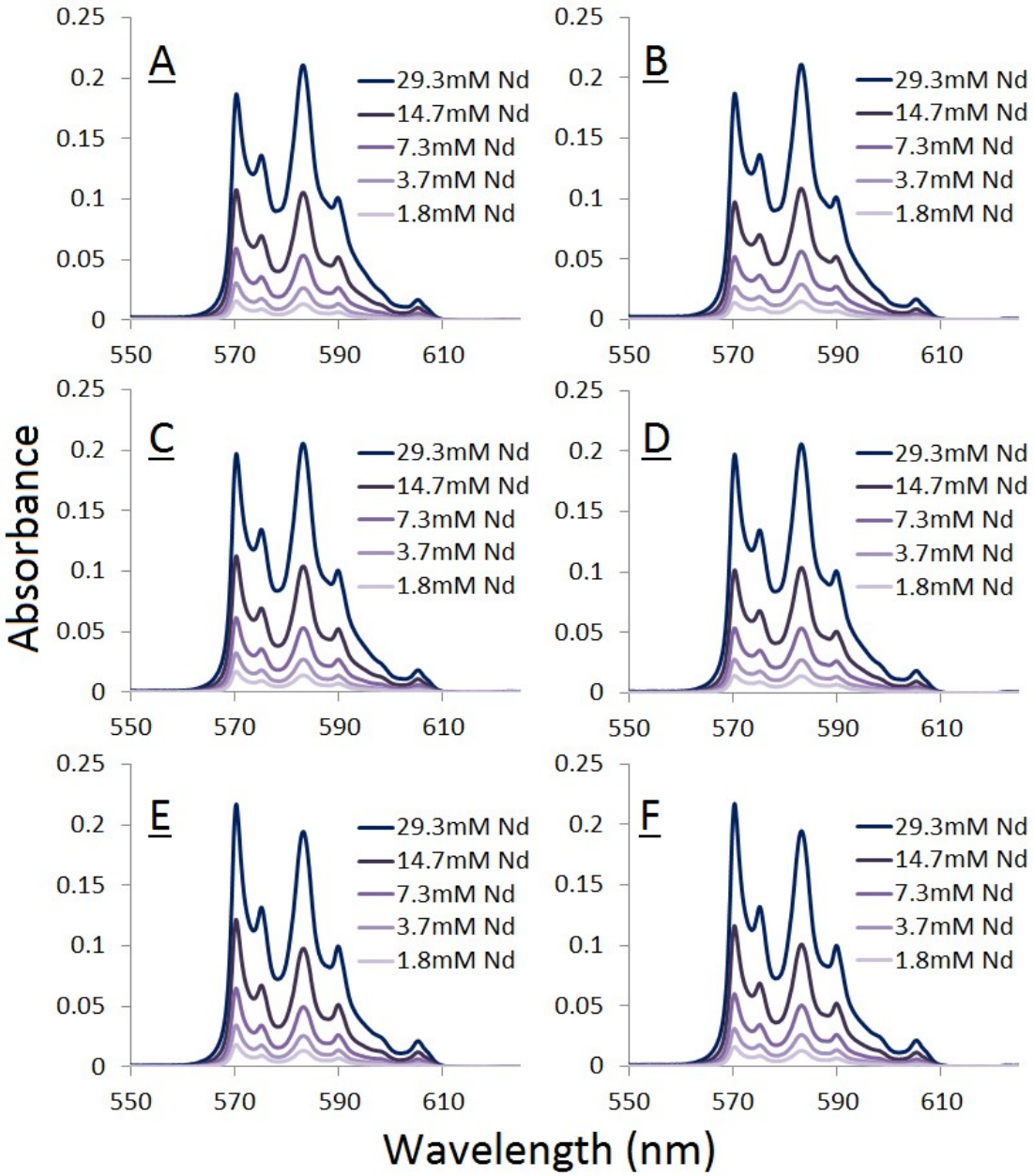


Figure 3 UV-Vis Spectra of Nd Extracted into 1.5 M HDEHP and Diluted with Non-preequilibrated (A) and Preequilibrated (B) 1.5 M HDEHP, 1 M HDEHP and Diluted with Non-preequilibrated (C) and Preequilibrated (D) 1 M HDEHP, and 0.5 M HDEHP and Diluted with Non-preequilibrated (E) and Preequilibrated (F) 0.5 M HDEHP

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, A570 is seen to decrease while the absorption band at 583 nm (A583) 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 preequilibrated organic phases resulted in no spectrum change (Figure 3).

In particular, upon dilution, A570 was seen to increase and A583 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 4.

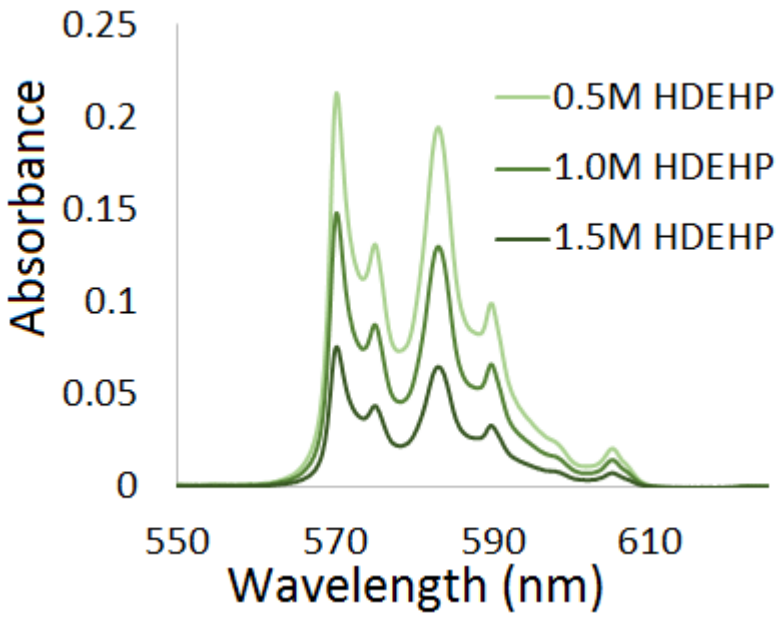


Figure 4 – Nd Extraction into 0.5M HDEHP followed by titration with 2.0M HDEHP, (increasing HDEHP concentration)

This behavior also alludes to the presence of an alternate extracted species may be causing changes in the metal complexation in these organic phases. The water concentration in post-extraction organic phases were determined by Karl Fischer titrations, as shown in Figure 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.

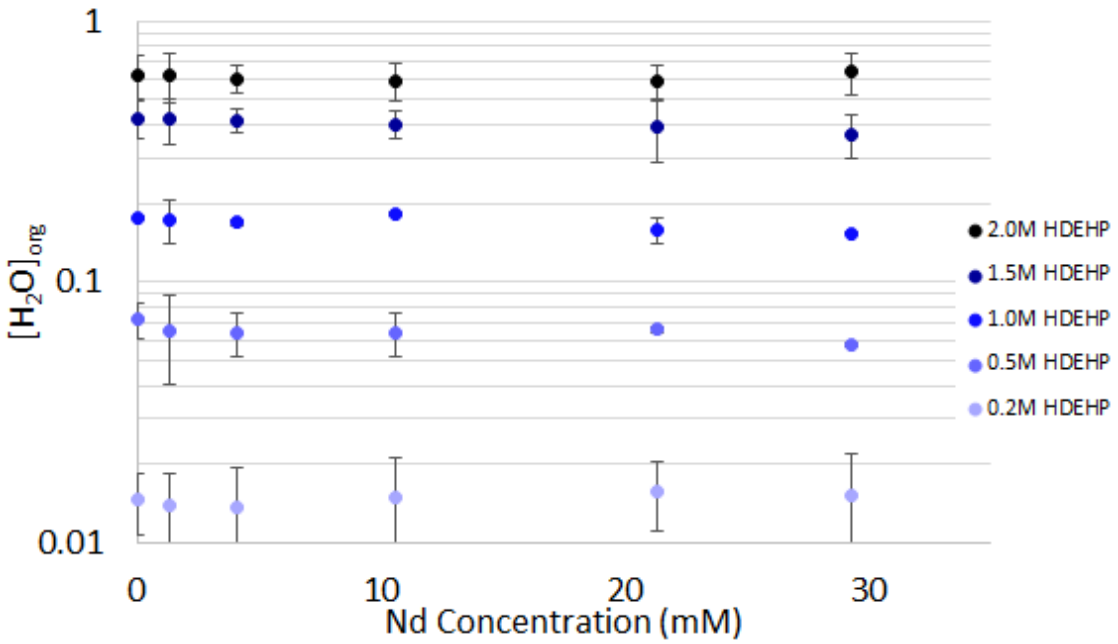


Figure 5. Water Concentration of HDEHP Organic Phases Following Extraction of Neodymium

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 6 and water content in Table 2.

Table 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
) M HEH[EHP]	0.319 +/- 0.007	0.308 +/- 0.028	0.322 +/- 0.011	0.318 +/- 0.007

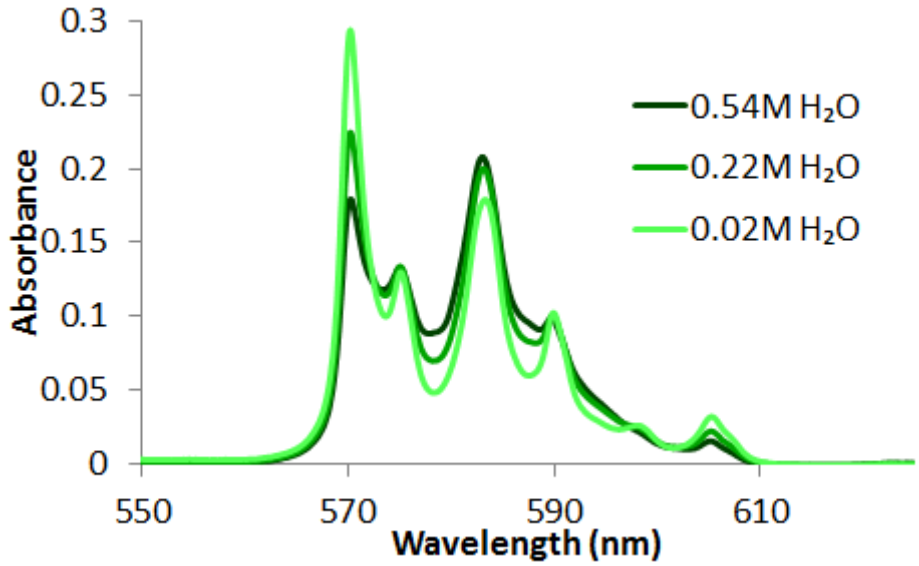


Figure 6 – UV-Vis Spectrum of 29.3 mM Nd in 2.0 M HDEHP Following Extraction and Subsequent Desiccation

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.[1]

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 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.

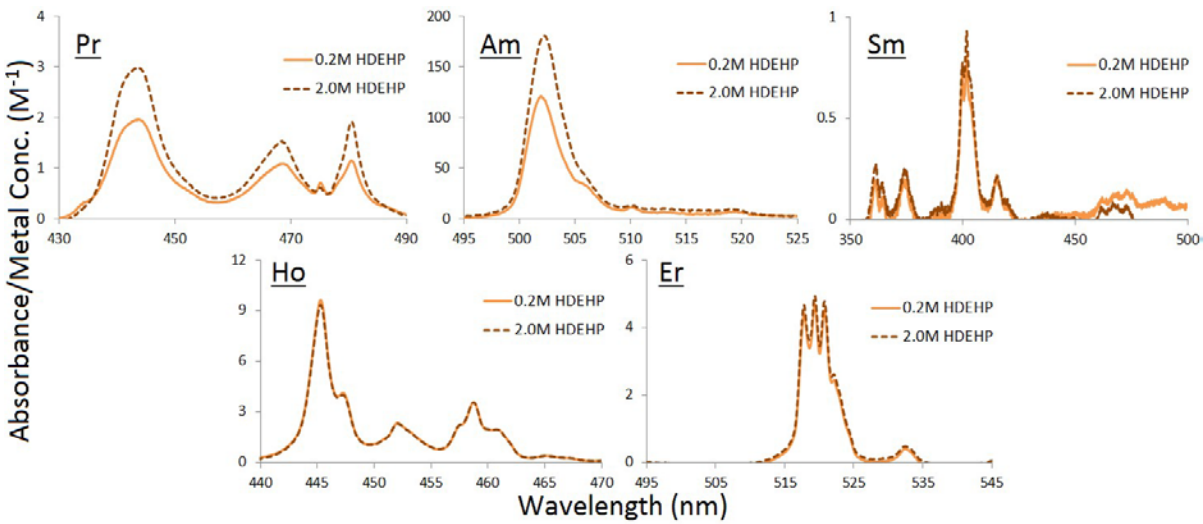
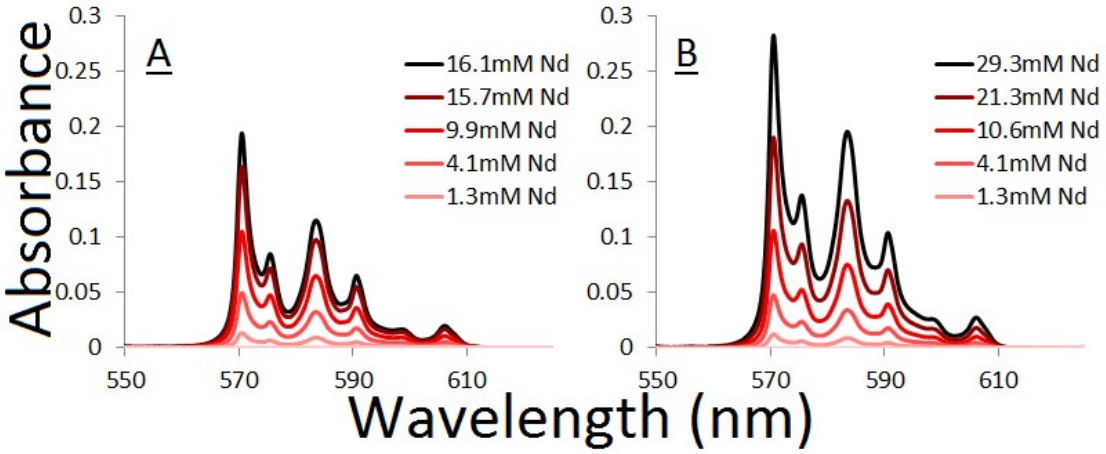


Figure 7 – UV-Vis Spectra of Praseodymium, Americium, Samarium, Holmium, and Erbium following extraction into 0.2 M HDEHP (solid line) and 2 M HDEHP (dashed line)

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 8, while Karl Fischer determination of organic phase water are shown in Figure 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.



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

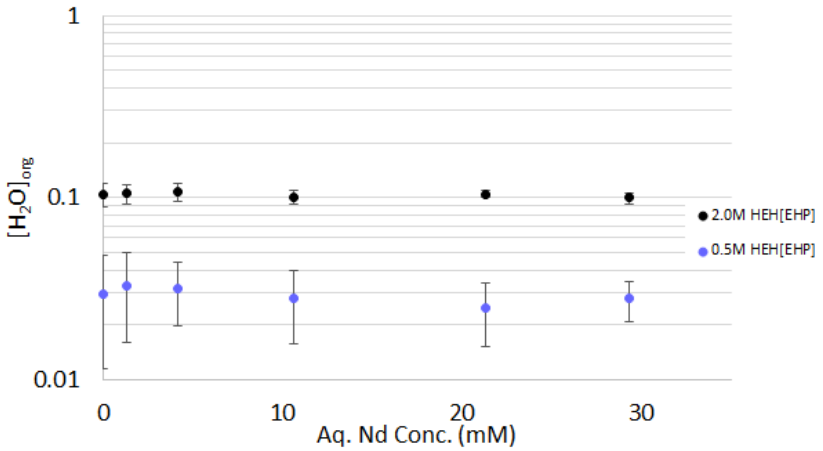


Figure 9 – Water Concentration of HEH[EHP] Organic Phases Following Extraction of Neodymium

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.

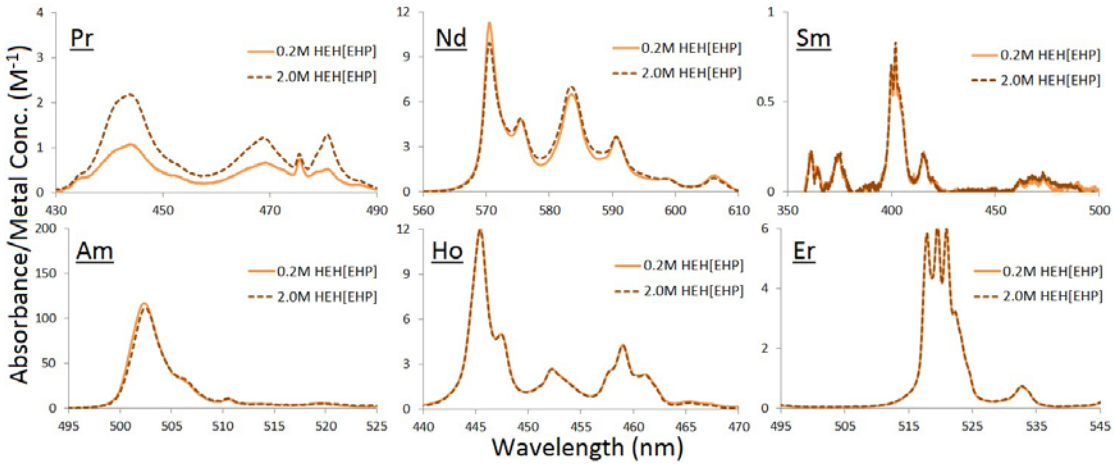


Figure 10 – UV-Vis Spectra of Praseodymium, Neodymium, Americium, Samarium, Holmium, and Erbium following extraction into 0.2 M HEH[EHP] (solid line) and 2.0 M HEH[EHP] (dashed line)

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 $Ln(H(EDHP)_2)_3(H_2O)$. 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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Objective 3b.Stoichiometry of the metal ternary complex species in the ALSEP – organic solvent

** This text is a modified version of our publication "Speciation of Select f-Elements with Lipophilic Phosphorus Acids and Diglycol Amides in the ALSEP Backward-Extraction Regime,* Brian J. Gullekson, M. Alex Brown, Alena Paulenova, and Artem V. Gelis, *Ind. Eng. Chem. Res.*, 2017, 56 (42), pp 12174–12183)

ABSTRACT

The complexation of HDEHP, HEH[EHP], T2EHDGA, TODGA and mixtures thereof in *n*-dodecane with Nd(III), Pm(III), and Am(III), extracted from pH 3 aqueous media, were investigated by distribution analysis, IR, UV-Vis, and x-ray spectroscopic methods. Appreciable adduct complex formation is seen among HDEHP with DGA components and to a lesser extent with HEH[EHP]. Adduct complex formation constants were determined by absorption spectroscopy and slope analysis. The effect of the adduct formation on the process performance and on the Ln/An selectivity is discussed. Also, extraction constants were derived for HEH[EHP] with Am and Pm as well as coordination information for Nd-HEH[EHP] and Nd-T2EHDGA.

INTRODUCTION

Used Nuclear Fuel (UNF) is a complicated chemical system comprised of nearly half of the periodic table.[i] 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 the reprocessing of the used fuel prior to geologic disposal attractive.[i,ii] Transmutation through fast neutron bombardment in nuclear reactors has been proposed as a means of actinide (An) waste treatment, but their purification from the strongly neutron absorbing fission produced lanthanides (Ln) must first be performed in order to transmute actinides efficiently. This remains one of the primary concerns of closing the nuclear fuel cycle. In particular, the minor actinides americium and curium (An(III)) have the same oxidation state and similar ionic radii to several of the more abundantly produced lanthanides, making them very chemically similar.[iii] Separations of these elements has been a major concern of 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 containing an extractant molecule in an organic diluent. The extracted metals are then typically stripped back into a suitable aqueous phase for further processing or conversion to a final waste form.[iv] The traditional approach toward partitioning An(III) and Ln is to first extract them from a PUREX (Plutonium-Uranium Redox Extraction Process) raffinate, isolating them from other fission products (in processes such as TRUEX (Transuranic Extraction) or DIAMEX (Diamide Extraction) Processes), followed by partitioning using a more sensitive process such as TALSPEAK (Trivalent Actinide Lanthanide Separation by Phosphorus Extraction from Aqueous Komplexes) or SANEX (Selective Actinide Extraction) processeses.[iii,v,vi,vii,viii] 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.[ix] Within 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 solutions is employed along with 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. However, 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.[x,xi] This makes process operations difficult to predict and scale.

Recently, several extractant molecules have been identified as potential candidates for MA(III)/Ln separations that show more favorable processing characteristics than those of their predecessors. The organophosphonic acid extractant 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP], Figure 1A) 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-ethylhexyl phosphoric acid (HDEHP, Figure 1B) traditionally used in the TALSPEAK process.[xii,xiii] HEH[EHP] has been selected for use in other mixed combined solvent extractant processes such as the TALSPEAK-MME Process.[xiv] Furthermore, the diglycolamides (collectively, DGAs) tetraoctyldiglycolamide (TODGA, Figure 1C) and tetra-2-ethylhexyldiglycolamide (T2EHDGA, Figure 1D) have been identified as viable solvating extractants due to their preferential extraction of trivalent metals from aqueous phases of high nitric acid concentration.[xv] In the Actinide Lanthanide Separation Process (ALSEP), a mixed solvent extraction system under current development, combinations of HEH[EHP] and 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.[xvi,17] A mixture of HDEHP with T2EHDGA provided lower, but sufficient An/Ln selectivity for the application, however it possessed a similar pH dependent extraction profile observed in TALSPEAK separations.[16] On the other hand, a combination of HDEHP and TODGA did not provide adequate selectivity for process consideration.[16]

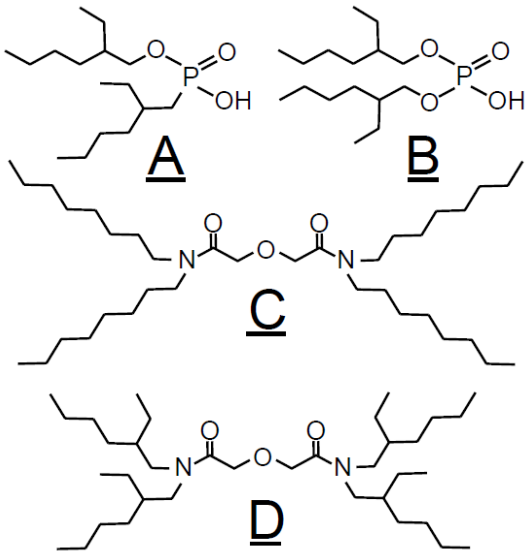

Figure 1:
Extractant Molecules Used in the ALSEP Process: (A) HEH[EHP], (B) HDEHP, (C) TODGA, and (D) T2EHDGA

In order to better understand and to possibly predict the extraction and stripping behavior of An/Ln in mixtures of extractants, any possible inter-ligand interactions must be investigated. Quantifying the ability of extractants to form inter-ligand adducts and complex with f-elements is crucial for modelling mixed extractant systems. This investigation looks into the ability of extractant combinations identified as possible choices for the ALSEP Process (HDEHP + T2EHDGA, HEH[EHP] + TODGA, or HEH[EHP] + T2EHDGA) to form ternary adduct complexes in the organic extraction phase under conditions typical to the ALSEP stripping regime.

EXPERIMENTAL METHODS

Chemical Preparation and Distribution Measurements Procedure

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.[xvii] 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.[18,xviii] 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 (≥99.0%) and TCI (98%) and used as delivered. Concentrated NH_4OH (Sigma Aldrich, ACS reagent grade) was used to dissolve DTPA and adjust pH of its solutions as checked by a pH electrode (Orion) which were calibrated by commercially available pH 3, 4, and 7 buffers. All solutions were diluted to the desired volume with deionized water (Millipore, 18.2MΩ-cm).

All distribution experiments, with concentration details described below, followed this procedure: first, organic phases were preequilibrated with an aqueous phase, which was identical to the aqueous phase in the desired extraction experiment, just the studied metal was absent. Samples were contacted in 3:1 aq:org ratio via vigorous shaking for 10 minutes using a

vortex mixer, each time with a fresh portion of aqueous phase. Finally, the pre-equilibrated organic phase was contacted with the extraction aqueous phase, now containing the studied metal (natural or radiotracer) of desired concentration, in 1:1 aq:org ratio and vortexed for 10 min. Extractions were performed in 4.5 mL polyvials followed by centrifugation for 5 minutes or until phase disengagement. The data were collected with duplicate or triplicate samples. Phases were separated using a fine tipped transfer pipet, and aliquots of each liquid phase was taken for analysis of metal concentration.

Concentrations of radiotracers were determined using gamma counters with a NaI(Tl) scintillation detector (Packard COBRA II) or semiconductor HPGe detector (Canberra) or liquid scintillation counter (Tri-carb Packard with α/β discrimination). The relative standard deviation did not exceed 3% for all the reported data.

The distribution ratio, *D*, for each metal ion M was calculated as a ratio of total metal concentrations in organic to aqueous phases: $D = \Sigma[M]_{org} / \Sigma[M]_{aq}$.

Metal Distribution Studies

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. ^{241}Am and ^{147}Pm were obtained from Argonne stocks and converted to a chloride salt in a similar technique and dissolved in the appropriate aqueous phase.

For the Job's Plot analysis, organic phases of 0.2 M total extractant concentration in n-dodecane were prepared by combining 0.2 M solutions of the individual extractants in the appropriate volumetric ratios to achieve the desired ligand mole fractions. For extraction into HDEHP + T2EHDGA solutions, 0.5 M (H^+/NH^+) citrate + 50 mM DTPA at pH = 3.36 +/- 0.05 was used for Eu extraction and 0.5 M (H^+/NH^+) citrate + 10 mM DTPA at pH = 3.36 +/- 0.05 was used for Am extraction. For extraction into HEH[EHP] + TODGA and HEH[EHP] + T2EHDGA solutions, 0.5 M (H^+/NH^+) citrate at pH = 3.17 +/- 0.05 was used for both nuclides.

For the adduct formation constant determination procedure, Am and Pm radiotracer were extracted from a 0.5M (H^+/NH_4^+) citrate + 25mM DTPA at pH = 3.15 +/- 0.05 aqueous phase into an organic phase of constant 0.5 M HDEHP and a T2EHDGA concentration from 0 – 0.1 M in n-dodecane. Extraction and quantification of concentrations were performed in the same manner as described above.

Infrared (IR) Spectroscopy 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. IR spectra were collected on a Nicolet 6700 FTIR Spectrometer using an attenuated total reflectance (ATR) diamond plate attachment.

Sequential extractions with 1 mL of a 25.2 mM Nd in pH 3 HCl aqueous phase and 1 mL of solutions of 1 M HDEHP + 200 mM T2EHDGA, 1 M HEH[EHP] + 200 mM TODGA, or 1 M HEH[EHP] + 200 mM T2EHDGA in *n*-dodecane were performed. To achieve relatively similar concentrations of metal in organic phase, adequate for observation via IR spectroscopy, a three-fold extraction with HDEHP + T2EHDGA organic phase and four-fold extractions with the HEH[EHP] + TODGA and HEH[EHP] + T2EHDGA organic phases, each time with a fresh portion of aqueous extraction phase, were completed.

Metal concentrations in organic phase were quantified as the difference between the pre-extraction and post-extraction aqueous concentration of metal; as comparison of measured absorbances with a fresh calibration line, collected with the same UV-Vis instrument.

UV-Vis Spectra Collection Procedure

Neodymium was prepared by dissolving Nd_2O_3 (Sigma Aldrich, 99.9%) in concentrated HCl (Macron, ACS grade) and evaporated. An in-house ^{243}Am stock (Oregon State University) was prepared similarly by dissolution in concentrated HCl and evaporation twice. Both were then dissolved in ~~pH3~~ 0.001M HCl prepared by dissolution of concentrated HCl with deionized water (Millipore, 18.1MΩ-cm) and diluted to 0.025 M Nd or 0.001M Am, respectively.

Table 1. Condition of the UV-Vis titration of Nd and Am, pre-extracted from 0.001M HCl aqueous solutions.

Nd	Extraction:	0.2M HDEHP	1M HEH[EHP]	1M HEH[EHP]
	Titrant:	0.2M HDEHP + 0÷41.7 mM T2EHDGA	1M HEH[EHP] + 0÷150.1mM TODGA	1M T2EHDGA + 0÷130 mM HEH[EHP]
Am	Extraction:	0.2M HDEHP	1M HEH[EHP]	1M HEH[EHP]
	Titrant:	0.2M HDEHP + 0÷25 mM T2EHDGA	1M HEH[EHP] + 0÷109.8 mM TODGA	1M T2EHDGA + 0÷129.3 mM HEH[EHP]

Table 1. Condition of the UV-Vis titration of Nd and Am, pre-extracted from 0.001M HCl aqueous solutions.

Nd	Extraction:	0.2M HDEHP	1M HEH[EHP]	1M HEH[EHP]
	Titrant:	0.2M HDEHP + 0÷42 mM T2EHDGA	1M HEH[EHP] + 0÷150mM TODGA	1M T2EHDGA + 0÷130 mM HEH[EHP]
Am	Extraction:	0.2M HDEHP	1M HEH[EHP]	1M HEH[EHP]
	Titrant:	0.2M HDEHP + 0÷25 mM T2EHDGA	1M HEH[EHP] + 0÷110 mM TODGA	1M T2EHDGA + 0÷129 mM HEH[EHP]

Extraction into 0.2 M HDEHP or 1.0 M HEH[EHP] in *n*-dodecane was performed by vortexing a 1 mL of the extracting organic phase with 1 mL of the aqueous solution of either Nd or Am. A lower concentration of HDEHP was used with the aim to achieve a similar organic phase metal concentration as with HEH[EHP]. Additionally, previous study revealed that water coextracted with Nd and Am into the organic phase complexes with the inner metal coordination sphere and affects the UV-Vis spectrum (an effect not seen with these metals extracted into HEH[EHP]).[20] Reduced concentrations of HDEHP lower organic phase water concentration, reducing this effect. Organic phase Nd concentration was determined as the difference between the aqueous phase Nd concentration before and after extraction as determined using a colorimetric technique,[21] while the Am organic phase concentration was determined using LSC counting of the post-extraction aqueous and organic phases. 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, then prior to titration with DGA, the metal-loaded organic phase was

dried over 3Å molecular sieves for 3 days to further alleviate the effects of water in the organic phase.[20] This was not done for americium to prevent excessive waste generation and to mitigate the loss of ^{243}Am.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 $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ hypersensitive transition of Nd (565 – 610 nm) and the $^7F_0 \rightarrow {}^5L_6$ transition of americium (495 – 510 nm).[xix,xx] 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 concentration conditions of titration are summarized in Table 1. The solution was vortexed for 30 seconds, and a new spectrum was collected to quantify interactions with error reported as two standard deviations of the model fit.[xxi]

XAFS Spectra Collection Procedure

Solutions of 1M HEH[EHP] or 0.1M T2EHDGA in *n*-dodecane were loaded with Nd by extraction from a 1 M or 0.001 M nitric acid solution, respectively. Nitric acid was used to promote complexation with the DGA when extracted from the higher acidity solution. The concentration of Nd-HEH[EHP] was approximately 10 mM whereas that of Nd-T2EHDGA was roughly 1 mM to combat third-phase formation. The phases were separated and the organic phases were placed into a spectrophotometric cuvette with a Kapton window. The cell window was oriented at a 45 degree angle with respect to the incident beam, while the detector was nominally positioned at 90° with respect to the incident beam in the horizontal plane. X-ray absorption fine structure (XAFS) spectra were measured on the Materials Research Collaborative Access Team (MRCAT) bending magnet beam line 10-BM at Argonne National Laboratory's Advanced Photon Source (APS). The incident energy was selected using a double-crystal Si(111) monochromator with the 2nd crystal detuned to 50% of the peak intensity. Neodymium L_3 edge spectra were measured in fluorescence mode (Nd Lα emission line) using a Vortex-ME4 4-element silicon drift detector (Hitachi High-Technologies Science America, Inc.). A minimum of two 22-minute scans were collected for each sample. The data were treated with *Athena* and *Artemis* software packages.[xxii,xxiii]

RESULTS AND DISCUSSION

IR Spectroscopy

IR spectra of organic phases in the presence of metal were collected to resolve any coordination information. Neodymium was loaded from 0.001M HCl into organic phases of 1 M cation exchange ligand and 200 mM DGA are shown in Figure 2. Under the studied aqueous extraction phase conditions, no changes in the DGA bond environment are expected, as the binding of the metal with a the cation exchange ligand is anticipated to be much stronger when extracting from these aqueous phase conditions, minimizing the metal available for DGA complexation.

Under the studied aqueous extraction phase conditions, due the higher pH, the binding of the metal with a cation exchange ligand will be promoted, minimizing the amount of metal available for DGA complexation and in the absence of extractable metal charge-compensating nitrate anion, no changes in the DGA bond environment are anticipated. However, as shown in

the Figure 2 insets, 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, infrared spectroscopy reveals that, even under backward-extraction conditions which do not favor metal complexation with DGAs in the organic phase, both the neutral and acidic ligand may be present in the metal complex. This is true for both the HDEHP+T2EHDGA and HEH[EHP]+TODGA, but does not appear to be the case for HEH[EHP]+T2EHDGA combination.

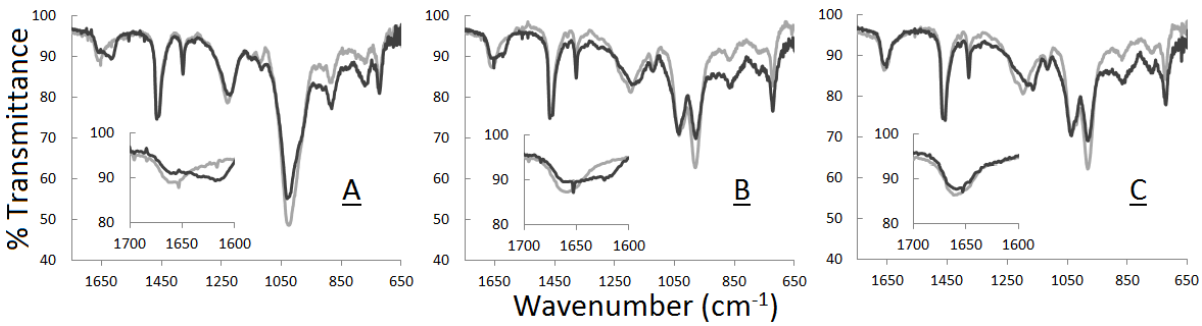

Figure 1: IR Spectra of the ALSEP Organic Solutions Prior to Extraction of Metal (Light Lines) and Following Metal Loading from a pH 2.8 HCl aqueous phase (Dark Lines). Combination are (A) 1 M HDEHP + 200 mM T2EHDGA, (B) 1 M HEH[EHP] + 200 mM TODGA, (C) 1 M HEH[EHP] + 200 mM T2EHDGA.

Stoichiometric Analysis by Job's Plot Method and Adduct Formation

Job's Plot method, or the method of continuous variation is a fundamental method in coordination chemistry for determining the approximate stoichiometry of metal complexes.[xxiv] Applied to our solvent extraction systems, the monitored value is the distribution ratio of the metal studied while varying the concentration ratio of two extracting ligands. Job's Plot method utilizes the simplified chemical equilibrium shown in Equation 1.

$$M^{n+} + nHA_{org} + mB_{org} \rightleftharpoons MA_nB_{m,org} + nH^+ \quad (1)$$

In this equation, *HA* is monomer of a cation exchange extractant, *B* is the solvating extractant, and MA_nB_m is the resulting extracted ternary species. While several species can be formed in this multicomponent system, the peak formed in the plot D vs molar fraction clearly indicates the ligand molar ratio in predominating species.

Job's plots for the extraction of americium and europium into organic solvent with 0.2 M total extractant concentration are shown in Figure 3 and Figure 4, respectively, plotted as metal distribution ratio values against the molar fraction of cation exchange ligand. For both metals extracted into HDEHP+T2EHDGA mixture as well as americium extracted into HEH[EHP] +TODGA mixture, the maximum extraction yield is seen at the molar fraction of 0.857 for cation exchange ligand and 0.143 molar fraction of neutral ligand that represents ligand ratio

of 6 molecules of organophosphorus acid and one molecule of diglycoamide. The chelate complexes of trivalent metals with those organophosphorus acids with the 6:1 metal:ligand molecular ratio due to the dimerization of the cation exchange extractant have been previously reported.[3] The observed 6:1 ligand:ligand ratio suggests that the extracted species dominating in the studied extraction mixtures also contain three cation exchange ligand dimers, somehow coordinated with a single solvating DGA molecule. Closer investigation of these features is in progress.

Almost linearly increasing D-values with increasing molar fraction of cation-exchange ligand observed for Eu with the HEH[EHP]+TODGA mixture, and for both Eu and Am with the HEH[EHP]+T2EHDGA mixture indicate that they either do not form adduct complexes with DGA under studied conditions, or their adducts with DGA are too weak to be studied by this approach.

The ternary complex formation constant K_{ad} can be calculated by expanding and rearranging the distribution ratio equation for two ligands present in organic phase, as shown in Equation 2.

$$D = \frac{\Sigma[M]_{org}}{\Sigma[M]_{aq}} = \frac{[MA]_{org}+[MAB]_{org}+[MAB^2]_{org}+\cdots}{\Sigma[M]_{aq}} = D_0 + D_0K_1[\bar{B}] + D_0K_2[\bar{B}]^2 + \cdots \quad (2)$$

In Equation 2, “M” is the extracted metal, “A” represents the extractant held constant and “B” represents the ligand of varying concentration, while “D_0” refers to the distribution ratio of metals in the absence of ligand “B”, and “K_i” refers to the equilibrium formation constant for ternary complex MAB_i. This approach assumes that if all initial aqueous and organic concentrations, except for ligand B, are held constant, the metal: ligand molar ratio M:A in the extracted species is not affected and all changes in D-values are caused only by formation of the MA adducts with molecules B. Association of ligands and coordination changes in complex have to be further investigates spectroscopically.

Rearrangement of Equation 2 allows for determination of K_i constants graphically, as shown in Equation 3.

$$\frac{D}{D_0} - 1 = K_1[\bar{B}] + K_2[\bar{B}]^2 + \cdots \quad (3)$$

This approach is illustrated in Figure 5 with Am(III) and Pm(III) radiotracers being extracted into organic phases containing a constant concentration of 0.5M HDEHP and variable T2EHDGA concentration. The first-order dependence suggests that the adduct complexes hold one T2EHDGA molecule, further confirming the stoichiometry determined from the Job’s method plot. The slopes reveal the apparent formation constants for adducts, which are listed in Table 2. Coordination environment in these complexes is discussed in this paper below, in the XAFS spectroscopy part.

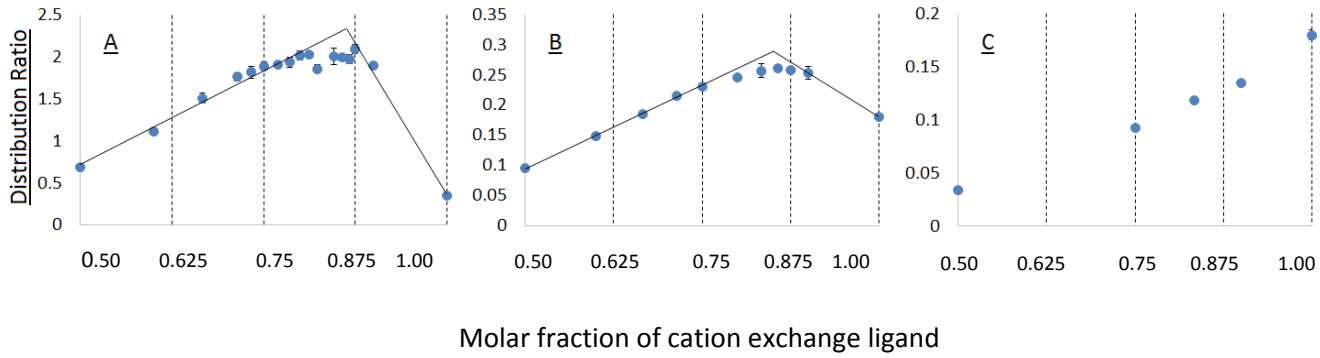

Figure 2: Job's Method Plots of Americium Distribution Ratios into 0.2M Total Extractant Organic Phases of HDEHP and T2EHDGA (A), HEH[EHP] and TODGA (B), and HEH[EHP] and T2EHDGA (C). The aqueous conditions are reported in the text.

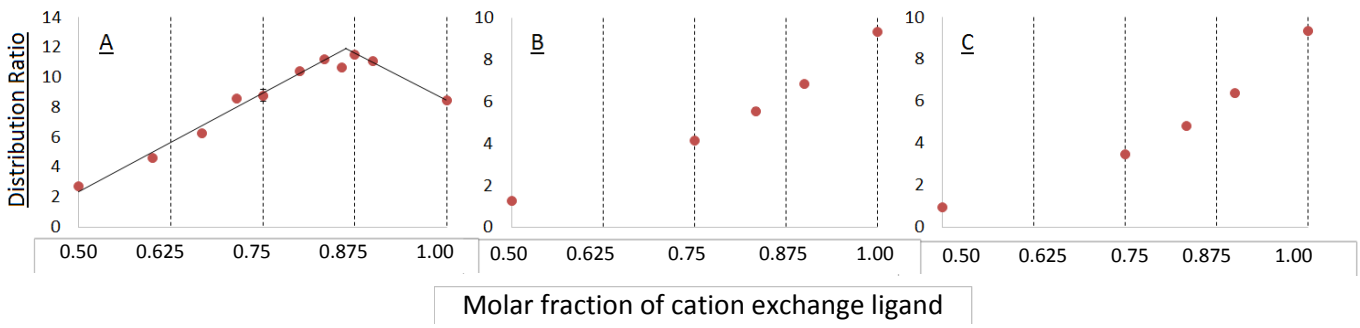

Figure 3: Job's Method Plots of Europium Distribution Ratios into 0.2M Total Extractant Organic Phases of HDEHP and T2EHDGA (A), HEH[EHP] and TODGA (B), and HEH[EHP] and T2EHDGA (C). The aqueous conditions are reported in the text.

UV-Vis Spectroscopic Titration Data

The UV-Vis spectra collected after each addition of DGA-titrant to Nd or Am, pre-extracted with one of the two cation exchange ligands, are shown in Figure 6 and Figure 7, respectively.
. Very similar results of diminishing the absorbance peak at 570 nm and greater absorbance at 583nm was observed when the Nd preextracted with HDEHP was titrated with T2EHDGA or preextracted with HEH[EHP] was titrated with TODGA. This shifting behavior resembles that of the recently reported[Error! Bookmark not defined.] increase in the coordination number of the metal in the organic phase. The spectra of Nd in the HEH[EHP]+ T2EHDGA show very little effect of the added DGA, suggesting a minimal ability of forming adduct complexes for this ligand combination.
The model generated to interpret the data, advised by the Job's plot, is shown in Equation 4.

$$\overline{M(HA_2)_3} + \overline{DGA} \rightleftharpoons \overline{M(HA_2)_3 \cdot DGA} \qquad (4)$$

.

At least 20 spectra were collected for each combined ligand system. For the determination of formation constants, the spectrophotometric data were fitted with non-linear least squares regression using the HypSpec[xxv actual #] software program, with error reported as

two standard deviations of the model fit. For americium, an increase in absorbance is seen with 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 suggests a decrease in the metal coordination symmetry. In light of the known spectral interferences in the presence of water and efforts to minimize waste, the Am absorption data was not treated to derive the extraction constants. Rather, the Am tracer data was designated to be more suitable in this regard.

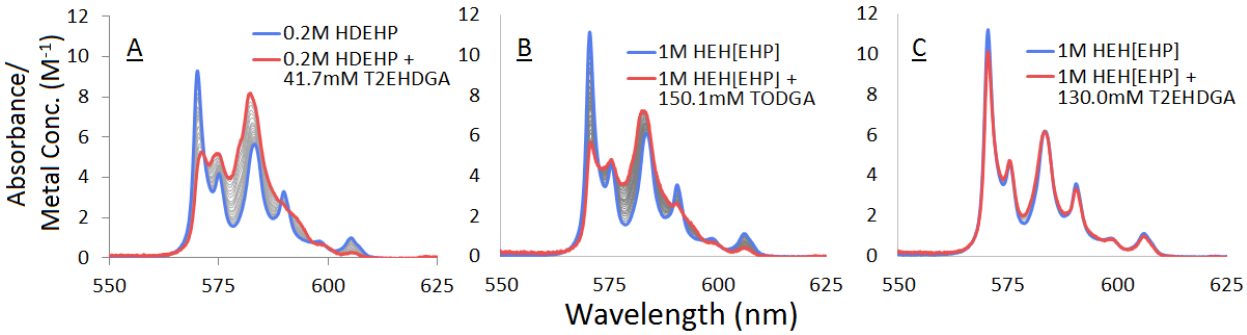

Figure 4: UV-Vis Spectra of the $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ hypersensitive transition of Nd in Organic Phases of Varying DGA Concentration with Constant Cation Exchange Ligand Concentration for (A) HDEHP – T2EHDGA, (B) HEH[EHP] – TODGA, and (C) HEH[EHP] – T2EHDGA combinations.

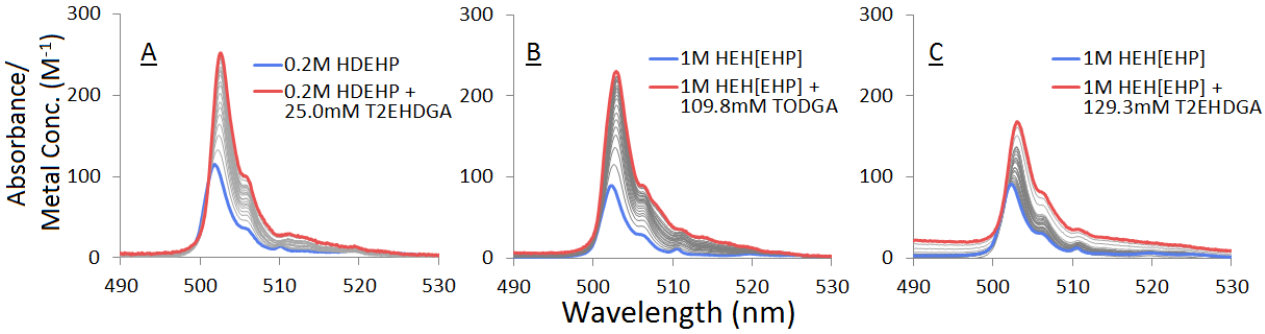

Figure 5: UV-Vis Spectra of the $^7F_0 \rightarrow {}^5L_6$ transition of Am in Organic Phases of Varying DGA Concentration with Constant Cation Exchange Ligand Concentration for (A) HDEHP – T2EHDGA, (B) HEH[EHP] – TODGA, and (C) HEH[EHP] – T2EHDGA combinations.

Of the ligand combinations proposed here, HDEHP+ T2EHDGA combination appears to possess a greater tendency to form ternary complexes with metals in the organic phase than the HEH[EHP]+ TODGA combination. The similar values of K_{ad} exhibited by Nd(III) and Am(III) are not surprising, given their near identical radii and hard ionic nature in the absence of a covalent donor.[xxvi] In comparison to the larger cation Pm(III) however, equilibrium formation constants of Nd(III) and Am(III) adduct complexes with HA-DGA are larger – which is in a stark contrast with most periodic extraction profiles in which the smaller cations exhibit higher K_{ex}. Similar trends were seen during a previous analysis of HDEHP+TODGA for a range of light and heavy Ln.[29] Interpreting these results is not necessarily conventional and would benefit greatly

from x-ray absorption and density functional theory, recently used to resolve the unorthodox lanthanide extraction profiles of DGAs.[xxvii] Nonetheless, we can only suggest that the larger coordination shells of light Ln are more inviting (less spatially occupied) to the tri-dimer HDEHP species which allows a DGA to more readily coordinate relative to the smaller, 8-coordinate heavy Ln.

The HEH[EHP]+ T2EHDGA combination however shows very little ability to form ternary complexes with neodymium based on absorption analysis. From a technological standpoint, this combination is more favourable as to avoid complicated adducts that may be difficult to simulate. As such, we concentrated our efforts on the individual extractants HEH[EHP] and T2EHDGA with respects to deriving selected equilibria and coordination information which are imperative for extraction modelling.

HEH[EHP] Extraction Constants

Extraction constants of HEH[EHP], K_{ex}, were determined for Pm(III) and Am(III) by distribution method. By varying the concentration of HEH[EHP] and stabilizing the aqueous ionic strength with the metal non-complexing perchlorate (H/$NaClO_4$) and temperature (25 °C), we are able to derive the value in terms of concentrations using this equation for both metals:

$$K_{ex} = D\frac{[H^+]^3}{[HEH[EHP]]^3} \tag{5}$$

It should be noted that in some cases the monomer concentration (instead of the dimer concentration) of the extractant is used in the calculations that adjusts Equation 5 by a factor of 8.[xxviii] The experimental results are plotted in Figure 8 and the values of extraction constants K_{ex} of HEH[EHP] with Pm(III) and Am(III) are listed in Table 3.

The relationship of each ion with HEH[EHP] at constant pH exhibits the well-known third order extractant dependence and the Pm/Am extraction ratios reflect the slightly larger ionic radii of Am(III). To our knowledge these are the first reported K_{ex} values of Am and Pm with HEH[EHP]. Consequently, any efforts to compare values with literature data are reliant mainly on interpolations of stable Ln or extrapolations from phosphoric acid relatives. Selected extraction constants of HEH[EHP] with Ln were derived from the surge in rare-earth metallurgy but were primarily focused on stable Ln.[xxix] When compared with Nd(III), our results are within the same order of magnitude regardless of the larger ionic strengths incurred from stable Ln analysis which often employ macro-quantities of tri-nitrate salts. Kosyakov and Yerin[30] investigated the extraction of Ln by HDEHP at the tracer levels using a similar approach that included Pm(III). Their extraction constant ratio K_{ex}(Pm) / K_{ex}(Am) = 5.5 is nearly identical to our value, which reflects some consistency among various phosphate-based extractants. But in absolute terms, the K_{ex} values for HEHEHP and the light Ln are roughly 2000-fold lower compared to those with HDEHP.

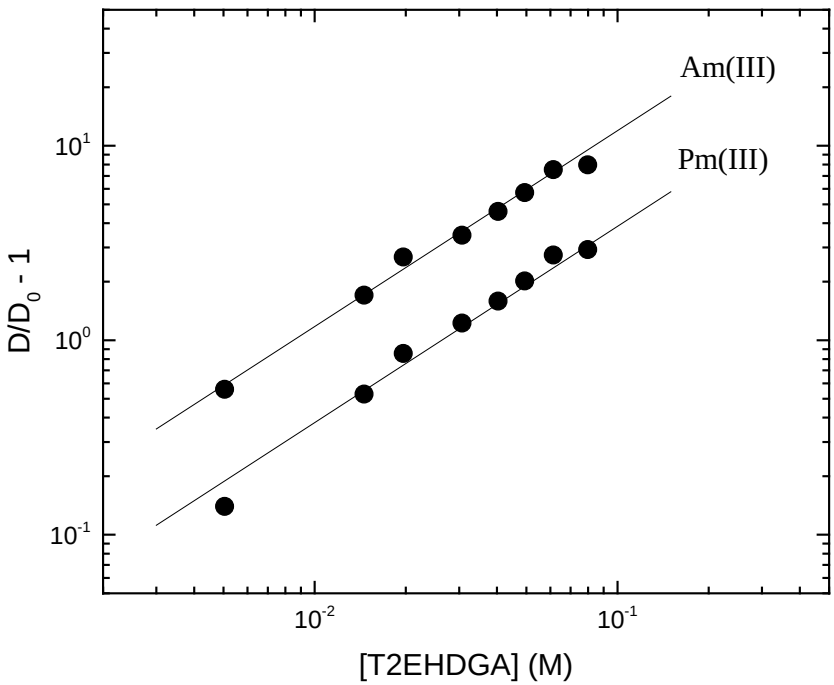

Figure 6: The distribution of Am(III) and Pm(III) into 0.5M HDEHP in *n*-dodecane as a function of T2EHDGA concentration from an aqueous solution of 0.5 M citrate, 25 mM DTPA, pH 3.1 (NO_3^-), T = 25 ±0.1 °C. The value D_0 is the distribution of the metal ion in the absence of T2EHDGA. The solid lines represent a first order dependence.

Table 2: Adduct formations constants of HDEHP and T2EHDGA (n-dodecane) with Nd(III), Pm(III), and Am(III) at 25 ± 0.1 °C. The constants for Am and Pm were determined by radiotracer methods; Nd by spectrophotometry.

Z	logK_{ad}	Method
Nd(III)	1.98 ± 0.01	Spectrophotometry
Pm(III)	1.5 ± 0.2	Tracer distribution
Am(III)	2.0 ± 0.1	Tracer distribution

Table 3: Extraction constants of HEH[EHP] with Pm(III) and Am(III) at 0.1M H/$NaClO_4$ and 25.0 ± 0.1 °C.

	logK_{ex}
Pm(III)	-1.6 ± 0.4
Am(III)	-2.4 ± 0.1

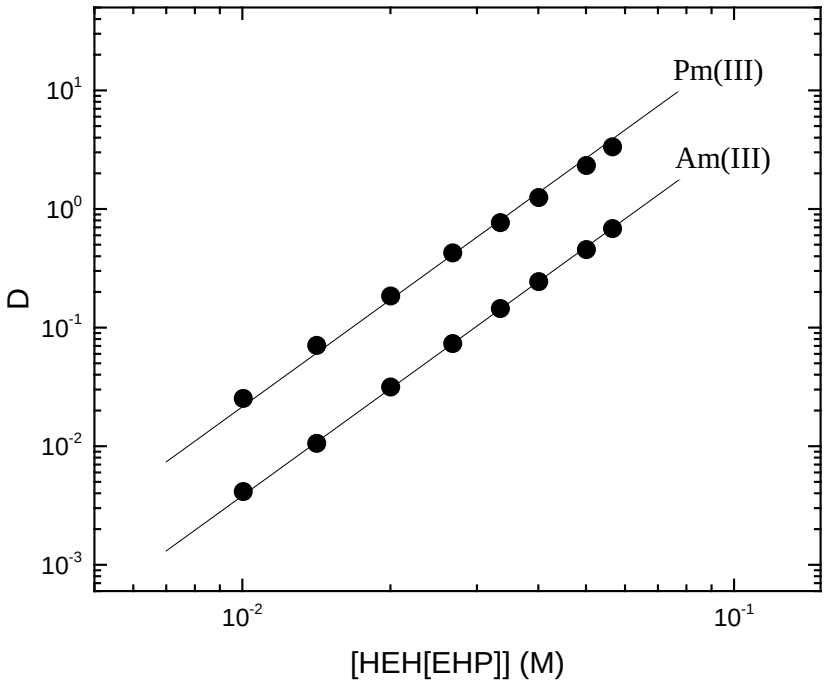

Figure 7: The distribution of Pm(III) and Am(III) into varying concentrations of HEH[EHP] in *n*-dodecane from a solution of H/$NaClO_4$ (I = 0.1M; pH = 2) at 25.0 ± 0.1 °C. The solid lines represent a third-power dependence.

XAFS Spectroscopy Results

The experimental data and the model fit for the samples Nd-HEH[EHP] and Nd-T2EHDGA are shown in Figure 9. Table 4 lists the calculated coordination numbers, bond distances, and debye-waller factors.

a) Nd(III)-HEH[EHP]

The major contributors to the Fourier Transform (FT) signal are the single-scatter Nd-O and Nd-P paths. In all cases, the dominant peak for each spectrum is the Nd-O path seen around 2.3Å. After treating the data, the calculated bond length for Nd-O was 2.33Å with a coordination number of 6.2. This is in good agreement with the literature for lanthanide(III)-dialkylphosphoric acids coordinated to three dimer extractants.[xxx,xxxi,xxxii,xxxiii] The Nd-P peak shown around 3.9Å (coordination number 6.2) is the next most prevalent signal. This scattering path length was calculated to be 3.90Å, again in good agreement with the literature. Beyond the oxygen and phosphorus potentials, there are no further features of the FT spectrum that can reveal structural information and attempts to include multiple scatter pathways generally worsened the fit.

The spectrum for the binary system Nd-HEH[EHP]+T2EHDGA extracted from 0.001M HCl (supporting information) showed a remarkable similarity to Nd-HEH[EHP] based on the

positions of the Nd-O and Nd-P peaks. However, the FT-spectrum showed appreciable fluctuations and noise past 10 $Å^{-1}$. The spectra were difficult to model coinciding with the known complications and impracticalities associated with probing binary metal-loaded extractant systems. **Error! Bookmark not defined.** In light of these complications and based on spectral interpretations, we can conclude from x-ray absorption that the majority of the Nd(III) is coordinated to HEH[EHP] within the binary solvent environment when extracted from a pH 3 0.001M mineral acid.

b) Nd(III)-T2EHDGA

The FT spectrum of Nd-T2EHDGA in Figure 9 has characteristic Nd-O peak that is slightly shifted relative to Nd-HEH[EHP]. This peak was assigned to the interactions with the two carbonyl O atoms and the single ether O atom per each T2EHDGA molecule (three coordinated O atoms per T2EHDGA). Approaching this data with the accepted extraction stoichiometry $Nd(NO_3)_3(T2EHDGA)_3$,[xxxiv] we can anticipate that more than nine oxygen atoms are coordinated to the metal on account of the charge-balancing nitrate anions. By refining the data, we calculated 10 oxygens along with the relatively high uncertainty that is typically common with XAFS fits.[xxxv] Regardless, these results are indicative of either counter ions or coordinated water molecules in the solvent. The model was unable to distinguish between the carbonyl, ether, nitrate, or water oxygen atoms, but the results revealed the average Nd-O bond length to be about 2.5 Å. Literature is relatively thin regarding Ln(III)-DGA coordination studies by XAFS, but there exists some recent work by Ellis *et al*. on Ln(III)-aliphatic malonamide extractants that are similar in structure to DGA though absent of the ether oxygen.[xxxvi,xxxvii,xxxviii] In these cases, the Ln(III)-O distances are roughly 2.4 Å. Our results indicate slightly longer Nd-O bond distances which may reflect the coordination environment of the ether backbone. It is also relevant to discuss the coordination of nitrate ions in these environments. Ellis *et al*. also investigated the coordination of nitrate on Ln(III)-micelles as a function of neutral and acidic aqueous extraction systems. Owing to hydrogen bonding activity, they found that nitrate was coordinated to the extracted Ln(III) in a mono-dentate fashion when extracted from a more acidic solution. As a result the number or coordinated oxygens should be much less than 15 as is a similar case presented here.

Beyond the Nd-O pathways, there were few structural features of significance. However, more recent literature that examined $Eu(III)(TODGA)_3(BiCl_4)_3$ by XAFS fingerprinted Eu(III)-C pathways afforded to the sp^2 and sp^3 hybridized carbons in the TODGA backbone.[29,xxxix] The same rationale was applied to our data which fit a single carbon potential at 3.6Å from the metal center; multiple carbon inputs worsened the *R*-factor statistics and were omitted. The fit yielded 8.4 carbon atoms with an unusually large uncertainty and debye-waller error which suggests that more potentials may exist in this scattering region. Larger concentrations of Nd or solid phase samples may be able to further clarify these pathways for T2EHDGA. But for the purpose of identifying Nd-DGA coordination and general solvation-extraction mechanisms, resolving the primary Nd-oxygen peak was sufficient for our analysis.

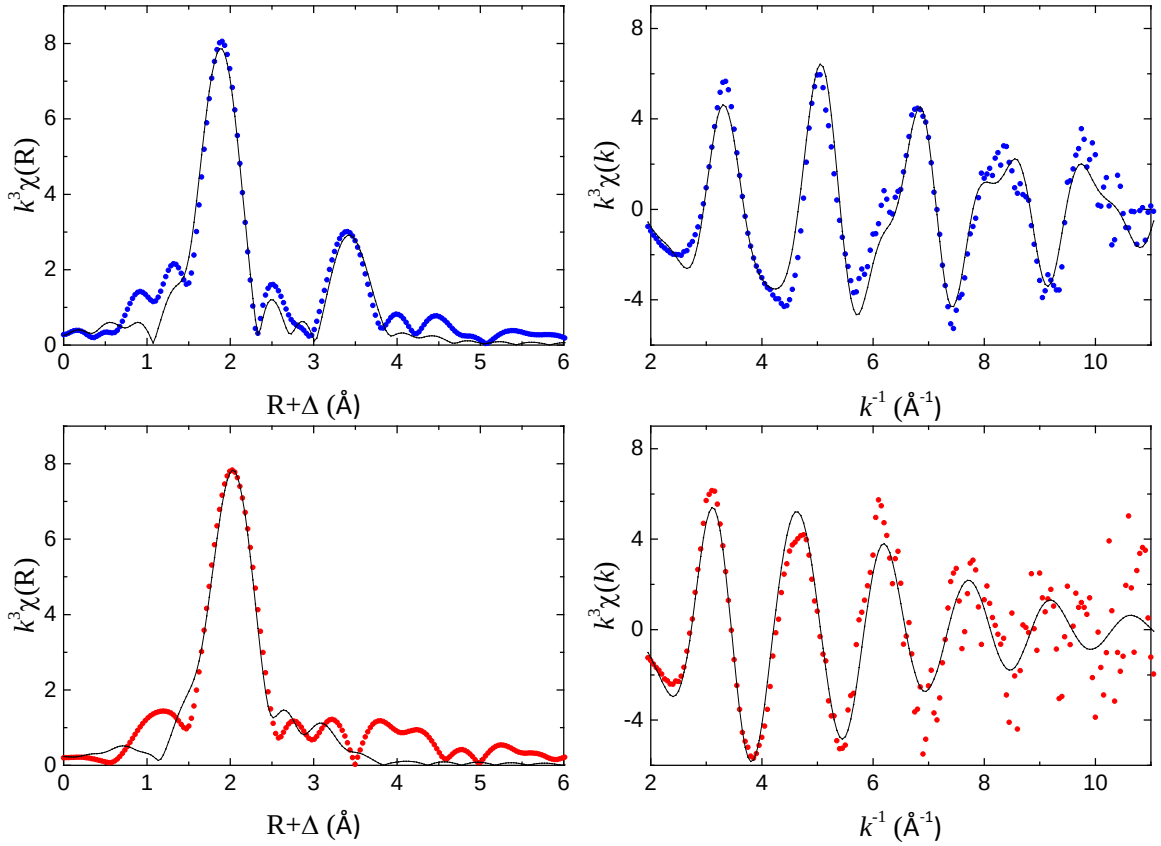

Figure 8: k^3-Weighted Fourier-transform and *k*-space Nd(III) L_3-edge XAFS spectra of (top) Nd-HEH[EHP] and (bottom) Nd-T2EHDGA in *n*-dodecane. The points represent the experimental data; the solid lines represent the model fit**.**

c) Nd(III)-HEH[EHP]-T2EHDGA

The FT spectrum of the Nd-T2EHDGA+HEH[EHP] mixture extracted from 1 M nitric acid (Figure 10) showed convincing similarities to the pure Nd-T2EHDGA data with regards to the Nd-O distance. This suggests that the mixed solvent primarily coordinates Nd via the DGA. However, there is some evidence of a Nd-P pathway in the mixture given the small signal at about 3.3 Å (uncorrected for phase-shift). Again, higher concentrations of metal or ligand may amplify the case for HEH[EHP] adduct formation here, but these results cannot rule out the possibility of relatively weak interactions between Nd-HEH[EHP]+T2EHGDA when extracted from a mildly acidic aqueous environment.

Table 4: Structural parameter results (1-σ uncertaintity) from the XAFS fits about the L_3-edge Nd(III) in the selected solvents; S_0^2 = 0.9. The *R*-factors for Nd-HEH[EHP] and Nd-T2EHDGA were 3.3% and 3.7%, respectively.

Scattering Path	*N*	*R* (Å)	$\sigma^2 \times 10^{-3}$(Å^2)	E_0
Nd-HEH[EHP]				
Nd-O	6.2 ± 0.5	2.33 ± 0.01	6 ± 2	2.6 ± 0.6
Nd-P	6.2 ± 2.2	3.90 ± 0.02	8 ± 5	
Nd-T2EHDGA				
Nd-O	10.0 ± 0.8	2.49 ± 0.01	10 ± 2	2.3 ± 0.8
Nd-C	8.4 ± 0.9?	3.63 ± 0.07	34 ± 43	

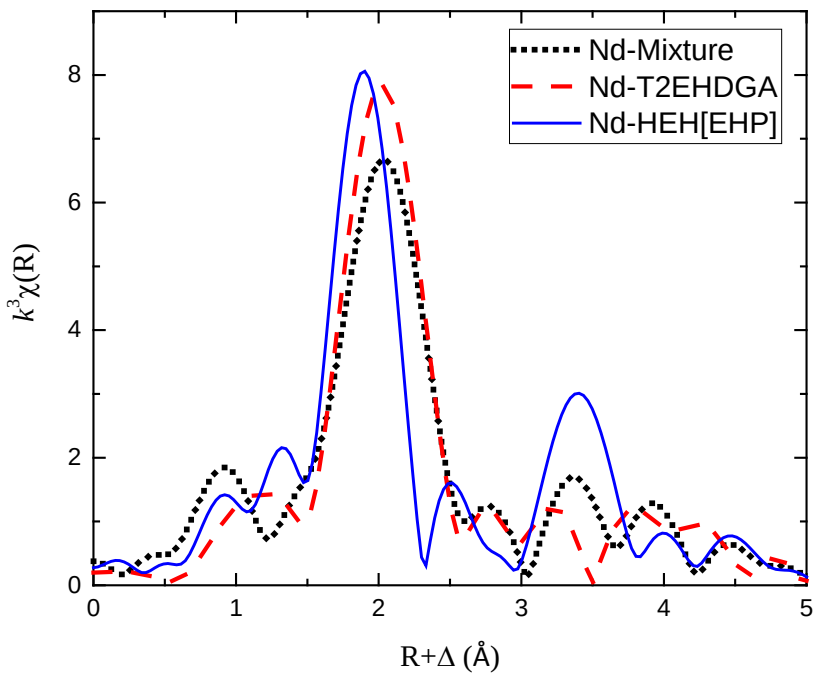

Figure 9: k^3-Weighted Fourier-transform of Nd(III) L_3-edge XAFS spectra of Nd-HEHEHP (Figure 9), Nd-T2EHDGA (Figure 9), and a mixed solvent system consisting of Nd-HEH[EHP]-T2EHDGA (labelled Nd-Mixture) in *n*-dodecane extracted from 1 M nitric acid.

CONCLUSIONS

From this work, several conclusions can be drawn about the ability of proposed ALSEP ligands to form intermolecular species - particularly how these adducts can complex with f-elements. Of the adducts investigated here based on slope analysis, HEH[EHP]+ T2EHDGA appeared to have the lowest tendency to form intermolecular adducts in the organic phase and was the least able to complex metals. For the combinations that do have a higher tendency to form adducts, however, Job's analysis revealed 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.

The UV-Vis spectra prepared for Nd and Am 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.

The XAFS investigation was able to reveal several characteristics as to the nature of metal complexation in HEH[EHP] and T2EHDGA systems. When Nd was extracted in just HEH[EHP], the metal was seen to form 6:1 HEH[EHP]:Nd complexes, similar to what has been reported previously for organophosphorus acid-based extractants. A similar coordination was seen in the combined HEH[EHP]+ T2EHDGA systems when extracted from pH 3, further suggesting that this combination does not show a great ability to form intermolecular adducts in the weakly acidic regime. When Nd has been extracted into T2EHDGA from nitric acid solutions, the metal complex formed is of the adduct type Nd(NO3)3T2EHDGA3. From a mildly acidic environment, however, the mixed-solvent shows some slight evidence of adduct formation. The conclusions drawn from combined solvents augmented our focus to a more fundamental probe of the individual extractants – HEH[EHP] and T2EHDGA – of which extractions constants and coordination information were derived.

ACKNOWLEDGEMENTS

The submitted manuscript has been created by UChicago Argonne, LLC, Operator of Argonne National Laboratory ("Argonne"). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357. The U.S. Government retains for itself, and others acting on its behalf, a paid-up nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government. This work was funded by the Department of Energy – Office of Nuclear Energy, Sigma Team for Advanced Actinide Recycle and Nuclear Energy University Programs (Award DE-NE0000720).

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