Characterization of the ALSEP Process: Investigating Equilibrium and Intermediate Complexes of the Scrub Stage

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ABSTRACT

A unique combination of real-time and conventional optical spectroscopy, off-line chemical analyses, and equilibrium solvent extraction measurements were employed to monitor progressive changes in the speciation of the organic-phase complexes of neodymium or americium in the biphasic scrub stage of the Actinide-Lanthanide Separation (ALSEP) solvent extraction process proposed for trivalent actinide/lanthanide separations. Consistent with the findings of other researchers, four unique organic-phase species are identified by three separate methods of multivariate analysis. The organic phase initially contains \( \text{M(TEHDGA)} \text{[HEH[EHP] = \( \text{H(EH[EHP]} \text{2(NO}_3\text{)}\text{3 complexes. As the ALSEP organic phase is scrubbed with an aqueous malonate buffer, the complex loses HNO}_3 \text{ to form M(TEHDGA)} \text{[HEH[EHP]} \text{2(NO}_3\text{)}\text{2 as the first organic-phase intermediate species. Further contact with the scrub aqueous phase forms a second intermediate species, M(TEHDGA)} \text{[HEH[EHP]} \text{2(NO}_3\text{), and eventually a complex containing only HEH[EHP], M(HEH[EHP]}\text{3 (where TEHDGA = N,N,N', N'-tetra(2-ethylhexyl)diglycolamide and HEH[EHP] = 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester). Similar intermediate species were also observed in equilibrium ALSEP organic phases when lower aqueous concentrations of nitric acid (e.g., 0.5 M HNO}_3 \text{ were used to extract actinides or lanthanides.}}

Introduction

The separation of long-lived minor actinides (such as americium) from lanthanides is instrumental to the deployment of advanced nuclear fuel cycles centered around the recycling of actinides from used nuclear fuel to produce additional energy. These advanced fuel cycles also propose to transmute long-lived minor actinides to shorter-lived species, thereby diminishing the burden of waste storage on geological repositories, but the similar physicochemical properties of minor actinides and lanthanides pose a challenge to optimizing the essential actinide/lanthanide separations for industrial applications.\(^{[1,2]}\)
The challenge of actinide/lanthanide separations has ignited over 60 years of research in solvent extraction separations.\textsuperscript{[3–9]} The ALSEP (Actinide Lanthanide SEParation) process – reported by Gelis and Lumetta in 2014 – simplifies the isolation of minor actinides from lanthanides by combining the partitioning of trivalent actinide (An) and lanthanide (Ln) cations from dissolved nuclear fuel and An/Ln separation processes into a single separation cycle.\textsuperscript{[10]} Advantages of the ALSEP process include direct use of PUREX raffinate solutions, fast extraction rates, and robust performance under a broad range of process conditions. The ALSEP process accomplishes this using an organic phase containing an aliphatic solvent and a mixture of two extractants: 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) and $N,N,N',N'$-tetra(2-ethylhexyl)diglycolamide (TEHDGA) (Figure 1 and Supplemental Figure S1).\textsuperscript{[10–12]} The mixture of powerful solvating and acidic extractants gives the ALSEP solvent a strong affinity for An(III) and Ln(III) at both high and low acidities, but its complexity of having two extractants that operate by different mechanisms also obscures the specific processes occurring during the different stages of the separation.

Schematically, the ALSEP’s An/Ln separation operates in three steps with a common organic phase, but three different aqueous phases (Figure 1). In the extraction step, An(III) and Ln(III) cations are extracted from 3 to 4 M HNO$_3$ in a mixed complex containing two TEHDGA molecules, one fully protonated HEH[EHP] dimer, and three nitrates (Step (1) in Figure 1).\textsuperscript{[13]} In the second step of the process – the scrub step (Step (2) in Figure 1) – the organic phase is contacted with an aqueous buffer solution, which removes minor impurities, adjusts the acidity of the organic phase, and places the An(III) and Ln(III) cations into the proper organic-phase complexes for stripping. After the scrub is complete, the actinides americium and curium are selectively stripped from the organic phase into an aqueous phase containing either of the actinide-selective aminopolycarboxylic acids: diethylenetriaminepentaacetic acid (DTPA) or $N$-(2-hydroxyethyl)ethylenediamine-$N,N',N'$-triacetic acid (HEDTA) (Step (3) in Figure 1).\textsuperscript{[14,15]}

Ultimately, our research aims to develop a kinetic model for the partitioning of americium and curium in the ALSEP strip step. However, probing the phase-transfer kinetics of this complex, multi-extractant system requires a currently unrealized level of understanding of the metal complexes present in the bulk phases at equilibrium, as these species represent the end members of the extraction processes or possible intermediate species in the phase-transfer reactions. While the ALSEP process has been studied under a variety of conditions,\textsuperscript{[12,16–19]} the scrub step has not been investigated. This work expands on our previous characterization of the organic-phase metal complexes in the ALSEP process’s extraction stage by dissecting the changes in the speciation of the organic-phase metal-complexes throughout the scrub process.
Our detailed investigation of the ALSEP acid scrub provides valuable insights into the dynamic speciation of the metal complexes observed in ALSEP under a variety of extraction acidities. Scrubbing acid from the ALSEP organic phase with an aqueous buffer solution leads the organic-phase An(III)/Ln(III) metal complexes through the same two intermediate species proposed for titrating HNO₃ equilibrated HEH[EHP]/TEHDGA mixtures into solutions of M[H(EH[EHP])₂]₃ in an n-dodecane monophase,²⁰,²¹ or varying the aqueous nitric acid concentration in equilibrium with 0.05 M TEHDGA/0.75 M HEH[EHP]/n-dodecane. We also find that the partitioning of An(III)/Ln(III) ions during the scrub does not reach the equilibrium values expected from the equilibrium extraction of organic-phase speciation.

**Experimental**

**Materials**

Chemicals were purchased from Sigma-Aldrich except where otherwise indicated. The extractant HEH[EHP] was obtained from BIOSYNTH Carbosynth (95%) and purified to ≥98% HEH[EHP] by the third-phase method,²² where the remaining 2% was confirmed as bis(2-ethylhexyl)phosphoric acid (HDEHP) by ³¹P NMR.²³ Acid-base titration in an ethanol-water mixture (80:20) confirmed the molecular weight of the purified HEH[EHP].
Stock extractant solutions were made by combining weighed amounts of TEHDGA (Eichrom Technologies, >99%) and the purified HEH[EHP] in n-dodecane (anhydrous, ≥99%) and diluting to a known volume. Aqueous phases were made from DTPA (≥99.0%), HEDTA (~98%), malonic acid (Alfa Aesar, 99.5+%), citric acid (≥99.9%), and nitric acid (Baker, ULTREX II). Acid solutions were standardized by potentiometric titration with sodium hydroxide (Fisher Chemical, 50 w/w% solution, certified) where indicated. The preparation of the neodymium nitrate stock solution was described in our previous publication.[13]

**Methods**

Experimental methods for radiotracer dependence studies can be found in a previous research publication.[13] All uncertainties have been reported at the 95% confidence level.

**Absorption spectroscopy**

Aqueous solutions of neodymium were made up to 0.02 M for the neodymium extraction from 0.5 M HNO₃, and to 0.01 M neodymium for all other experiments by diluting weighed aliquots of the metal stock solution with the relevant standardized nitric acid solutions. After preparation, organic-phase solutions were pre-equilibrated twice with twice their volume in the appropriate metal-free aqueous phase by vortexing for 1 minute, then centrifuging to separate the phases. Metal extractions were performed by vortexing equal volumes of pre-equilibrated organic phases, with aqueous phases containing neodymium at the desired nitric acid concentration for 2 minutes, followed by 2 minutes of centrifugation before the phases were separated and measured.

Spectra of both the aqueous and organic phases were obtained on either a Varian Cary 300 or Cary 5E spectrophotometer in 1.00 cm quartz cuvettes from either 550 to 620 nm or 480 to 850 nm at 0.2 nm resolution. The equilibrium concentrations of neodymium loaded into the organic phases were calculated from the total amount of neodymium in the system and the difference in the initial and final spectra of the aqueous phase.

Spectra of the ALSEP scrub were also taken in real-time while mixing the two phases in an Olis RSM 1000 spectrophotometer with CLARiTY sample cell, using a one-of-a-kind shaft immersion stirrer. The CLARiTY sample cell was designed to collect optical absorption spectra of highly scattering mixtures, enabling optical measurements on the complete biphasic system; the result is a volume-weighted average spectrum of the aqueous phase, organic phase, and interface. A hardware combination of 1200 line gratings and a 16 × 0.2 mm ScanDisk in the RSM 1000 produced spectra spanning 76 nm
with a stated resolution of 0.4 nm. The center wavelength was chosen to give a useful working range of approximately 550–620 nm to capture the Nd $^{4}I_{9/2} \rightarrow ^{4}G_{5/2}, ^{2}G_{7/2}$ hypersensitive transitions centered at approximately 580 nm. The organic phase was gently layered on top of the aqueous phase, and the phase-transfer reactions were initiated soon after by starting the stirrer at a predetermined stirring rate.

**Scrub pH, nitrate analysis, and spectroscopy**

The scrub process was monitored for changes in pH, nitrate content, and organic-phase spectra under slow stirring conditions. Slow stirring of equal volumes of the malonic acid buffered aqueous and ALSEP organic phases was interrupted at predetermined pH increments and used for nitrate and metal (where applicable) analysis. Nitrate standards diluted using nitrate-free malonic acid solution were prepared with standardized HNO$_3$. The ALSEP organic phase (0.75 M HEH[EH]/0.05 M TEHDGA/n-dodecane) pre-equilibrated overnight with twice the volume of 4 M HNO$_3$ was placed into a beaker with a nitrate-free 0.5 M malonic acid scrub solution previously adjusted to pH 3.5 using only sodium hydroxide. A ThermoOrion Ross pH electrode was inserted into the aqueous phase to monitor the pH as the reaction proceeded. At predetermined pH readings, equal aliquots were removed from each phase and centrifuged for analysis of their nitrate content. Aqueous-phase samples were diluted into the calibration range using nitrate-free malonic acid solution. Organic-phase samples were stripped of nitrate by contacting them with sufficient nitrate-free malonic acid solution to dilute the nitrate content into the calibration range.

A portion of the 4 M HNO$_3$ pre-equilibrated ALSEP organic phase was then contacted with 0.01 M Nd/4 M HNO$_3$ overnight in equal volumes. Spectra of the aqueous phases before and after extraction were collected to calculate the neodymium concentration of the loaded organic phase. Additional metal analysis was conducted on a Perkin Elmer Optima 5300 DV ICP-OES. The process described above was repeated for the scrub with neodymium. The remaining portion of each organic-phase aliquot sample was analyzed on a Cary 5E Spectrophotometer in a 1.000 cm quartz cuvette from 480 to 850 nm at 0.2 nm resolution.

All standards, diluted aqueous samples, and aqueous strip solutions were developed using a modified version of the nitration of salicylic acid method$^{[13]}$ originally described by Cataldo et al.$^{[24]}$ using adjusted reagent volumes to ensure the pH was greater than 12. Sample concentrations were determined from a standard curve measured in 1.00 cm Brand UV-cuvettes on a Varian Cary 300 at 410 nm.
**Theoretical calculations**

Gaussian 09 was used for all calculations described in this study, and the computational protocol follows previously published work on the extraction phase of ALSEP.\(^{[13,25]}\) All optimization and frequency calculations were performed at the B3LYP/6-31 G(d,p) level of theory for all second- and third-row elements,\(^{[26,27]}\) and a relativistic effective core pseudopotential and corresponding basis set were employed (Stuttgart RSC 1997 ECP, obtained from Basis Set Exchange) for treatment of the europium cation.\(^{[28-30]}\) Calculations were performed in the gas phase to limit the complexity of the ALSEP biphasic system. Optimized geometries are verified as minima due to the presence of zero imaginary frequencies. Europium complexes were prepared from truncated ligands to improve the computational cost as previously reported.\(^{[13,31]}\)

In this regard, the HEH\[EHP\] and TEHDGA coordinating ligands investigated were truncated from 2-ethylhexyl chains to ethyl chains (see Supplemental Figure S1 for the structures of the truncated ligands). Europium was used in this study to facilitate direct comparison with published results of the ALSEP extraction step and is expected to behave similarly to Nd during the ALSEP process.\(^{[13]}\) The computational protocol was validated by comparing the optimized structure of Eu(H(E[EP])\(_2\))\(_3\) (Complex [D]) with the published crystal structure of Nd(DMP)\(_3\) (DMP = dimethyl phosphate).\(^{[32]}\) While not a direct comparison, the structure of [D] optimized here matches extremely well with the crystal structure of Nd(DMP)\(_3\) as shown in Supplemental Table S1, where the Ln-O bonds and O-Ln-O angles are compared. Proposed ALSEP scrub complexes were compared by calculating complexation-free energies (difference between products and reactants of each complex). Optimized coordinates for all complexes are available in the Supplemental Materials.

**Results and discussion**

**Real-time spectroscopy of the ALSEP scrub**

Metal-ion speciation in the ALSEP system during the final scrub of the organic phase, which removes residual nitric acid from the organic phase, was monitored in real-time by optical absorption spectroscopy of equal, stirred volumes of aqueous and organic phases in an Olis CLARiTY sample cell. The organic phase initially contained 0.01 M Nd(TEHDGA)\(_2\)(HEH\[EHP\])\(_2\) (NO\(_3\))\(_3\), prepared by extraction of Nd(NO\(_3\))\(_3\) from 4 M HNO\(_3\) into 0.05 M TEHDGA/0.75 M HEH\[EHP\]/\(n\)-dodecane.\(^{[13]}\) The initial aqueous-phase composition was 0.5 M malonic acid adjusted to pH 3.5. Malonic acid was chosen as the buffer for the scrub because of its minimal tendency to strip americium and lanthanides from the organic phase.\(^{[33]}\) Recent advances in the formulation of ALSEP use ammonium citrate buffer to control pH and to
improve reaction kinetics and complexants such as acetohydroxamic acid to scrub undesired metals from the organic phase.\textsuperscript{[15,34]} Neodymium distribution values for citric acid buffered scrub solutions are equally large as in the malonic acid buffered system investigated here and would likely produce similar results. Real-time spectra collected during a typical scrub are depicted in Figure 2. As expected, the initial spectrum matches that of Nd(TEHDGA)$_2$ (HEH[EHP])$_2$(NO$_3$)$_3$, as this is the Nd complex in the starting organic phase, and no Nd is present in the aqueous phase when $t = 0$. Once the stirring of the two phases commences, the initial peak centered at 586 nm begins to decline and a new peak at 570 nm eventually begins to arise. Equilibrium, as indicated by constant absorbance values, is attained in this experiment within 700 s of stirring at 20 rps.

The effective resolution of the CLARiTY cell and the RSM 1000 rapid-scanning spectrometer is sufficient to resolve individual peaks in the $^4$I$_{9/2} \rightarrow ^4$G$_{5/2}$, $^2$G$_{7/2}$ absorption manifold and clearly distinguish between differing Nd complexes in the system. However, some peak broadening and a reduction in relative peak intensity is observed compared to the spectra obtained in this region for individual separated phases with conventional spectrophotometers operated at spectral bandwidths of 0.2 nm or better (see comparison in Supplemental Figure S2).

Post-experimental analysis of the equilibrium aqueous phase indicates that there is too little aqueous Nd to be detected by optical spectroscopy in our instrument ($D_{\text{Nd}} > 9,000$, measured instead by ICP-OES analysis). Therefore, the final equilibrium spectrum obtained is representative of the organic-phase Nd species to the exclusion of negligible concentrations of Nd complexes in the aqueous phase. The sharp band at 570 nm is characteristic of homoleptic complexes of Nd with acidic dialkylphosphorous extractants, and the similarity of the final spectrum to that of Nd extracted into concentrated solutions of HEH[EHP]\textsuperscript{[35]} or HDEHP\textsuperscript{[36]} in $n$-dodecane demonstrates that the equilibrium Nd species in the scrubbed organic phase is a neutral Nd complex containing only deprotonated HEH[EHP] extractants in the inner coordination sphere. Minor differences in the relative intensities of the peaks in the hypersensitive $^4$I$_{9/2} \rightarrow ^4$G$_{5/2}$, $^2$G$_{7/2}$ transitions have been shown to be caused by increased water uptake into organic phases containing high HEH[EHP] concentrations.\textsuperscript{[35]} Our analysis will assume that this final species of the ALSEP scrub is the idealized complex of three mono-deprotonated HEH[EHP] dimers, $\text{M}\{\text{H(HEH[EHP])}_{2}\}$, because the origin of the sub-theoretical extractant dependence slope of 2.5 for trivalent f-element extraction by HEH[EHP] in $n$-dodecane (Table 1) remains unresolved,\textsuperscript{[37,38]} and the precise extractant:metal stoichiometry of the HEH[EHP] complexes at the conclusion of the scrub is not central to understanding the nature of the scrub.
While the pre- and post-scrub spectra of the Nd-loaded ALSEP organic phase are clearly associated with previously identified Nd-containing species, the interjacent spectra suggest the presence of other complexes as the scrub progresses. The possible isosbestic point at 572.2 nm (Figure 2a) is ill-defined; some features in the intermediate spectra cannot be reproduced from linear combinations of the initial and final spectra, and following the absorbance as a function of time (for example, 590.1 nm in Figure 2b) implies the presence of a minimum of three different light-absorbing, Nd-containing species. Further analysis of the sets of collected spectra by rank reduction analysis,\textsuperscript{[39]} principal\

**Figure 2.** (a) Real-time optical absorption measurements of a mixture of 0.01 M Nd(TEHDGA)$_2$ (HEH[EHP])$_2$(NO$_3$)$_3$ in 0.05 M TEHDGA/0.75 M HEH[EHP]/$n$-dodecane scrubbed with an equal volume of a pH 3.5, 0.5 M aqueous malonic acid buffer solution over 750 s of mixing. Wavelengths corresponding to peak maxima of the initial or final spectra are indicated by vertical dashes along the upper axis. (b) Change in absorbance at wavelengths of individual maxima of the spectra in Panel (a). The model independent MCR-ALS fit of the data at each wavelength in Panel (b) is indicated by solid lines.
Table 1. Average stoichiometric coefficients for TEHDGA and (HEH[EHP])₂ in the extracted americium complexes determined from the slopes of linear regression analysis of logarithmic americium extraction data.

| Aqueous Phase | Organic Phase [TEHDGA] | Organic Phase [HEH[EHP]] | Average Stoichiometry |
|---------------|-------------------------|--------------------------|-----------------------|
| 2.0 M HNO₃ a | 0.02–0.07 M             | 0.75 M                   | 2.11 ± 0.07 TEHDGA    |
| 2.0 M HNO₃ a | 0.05 M                  | 0.005–0.075 M            | 0.9 ± 0.1 (HEH[EHP])₂ b |
| 0.5 M HNO₃ | 0.01–0.1 M              | 0.75 M                   | 1.4 ± 0.1 TEHDGA      |
| 0.5 M HNO₃ | 0.05 M                  | 0.075–0.75 M             | 0.95 ± 0.06 (HEH[EHP])₂ |
| 0.1 M HNO₃ | 0.01–0.1 M              | 0.75 M                   | 0.58 ± 0.06 TEHDGA    |
| 0.1 M HNO₃ | 0.05 M                  | 0.075–0.75 M             | 1.84 ± 0.02 (HEH[EHP])₂ |
| pH 3.75, 0.4 M Citrate, 0.25 M | 0.025–0.1 M | 0.75 M | ~0.01 ± 0.09 TEHDGA |
| HEDTA | pH 3.75, 0.4 M Citrate, 0.25 M | 0.16–0.75 M | 2.5 ± 0.1 (HEH[EHP])₂ |

aData from Reference^{13}

bFor Nd complexes, determined by spectrophotometric titration

component analysis using SixPack,^{40} and singular value decomposition using MCR-ALS GUI 2.0^{41} all report four absorbing species are required to reproduce each set of experimental spectra. These four light-absorbing Nd-containing species all exist in the organic phase during the scrub. The sampling of the aqueous phase at selected points during the scrub indicates that more than 99.99% of the Nd is retained in the organic phase throughout the process. Gullekson et al.^{12,20} and Hall et al.^{21} also report that the presence of four unique metal containing species is observed in single-phase titrations of isolated TEHDGA/HEH[EHP]/n-dodecane organic phases and that the speciation depends on the equilibrium composition of the solutions.

The variation in the distribution of Nd between these four species as the scrub progressed toward equilibrium was calculated using a model-free MCR-ALS analysis of a set of real-time absorption spectra.^{42} Unimodal and non-negative constraints were applied to the concentrations and molar absorptivities for each of the four species. The concentration profiles were further constrained by the requirement that the total Nd concentration was constant at 0.010 M throughout the scrub and only Nd-containing species with observable absorption bands were significant contributors to the solution speciation. Results of a representative run shown in Figure 3 confirm the initial disappearance of Nd(TEHDGA)₂(HEH[EHP])₂(NO₃)₃ during the scrub, driven by the sequential appearance of two intermediate Nd-containing species, followed by progressive conversion to a final, equilibrium organic-phase species, which begins to form about 120 s after the mixing starts.

Chemical analysis of the scrub process

The primary function of the ALSEP scrub stages is to reduce the acid content of the organic phase. At the outset of the scrub, the metal-loaded ALSEP organic phase contained 0.13 ± 0.01 M HNO₃ from equilibration with aqueous 4 M
HNO\textsubscript{3} in the metal loading step. Because the aqueous and organic phases of a solvent extraction system must each remain charge-neutral, protons drawn from the organic phase to react with the weak acid anions of the aqueous scrub buffer will cause an equivalent amount of NO\textsubscript{3}\textsuperscript{−} to partition from the organic phase. This is true whether the source of protons in the organic phase was previously extracted from HNO\textsubscript{3} or deprotonation of HEH[EHP]. The driving force for the sequential changes in organic-phase Nd speciation observed as the scrub progresses is the equal loss of H\textsuperscript{+} and NO\textsubscript{3}\textsuperscript{−} to the aqueous phase.

To achieve better spectral resolution over a wider wavelength range and to understand the impact of the transfer of H\textsuperscript{+} and NO\textsubscript{3}\textsuperscript{−} from the organic phase on the organic-phase Nd speciation, we performed a second set of studies where the aqueous and organic phases were sampled at intervals during the scrub. Samples of the aqueous and organic phases were taken for off-line chemical analysis of the nitrate concentration and spectrophotometric measurement of the Nd complexes in separated phases at discrete points in the scrub process. The pH of the aqueous phase was measured throughout the scrub with a pH electrode. Since no spectroscopically detectable amount of Nd reported to the aqueous phase during the strip, H\textsuperscript{+}/Nd\textsuperscript{3+} ion-exchange reactions could be neglected during the scrub, and the pH changes in the aqueous phase were attributable only to the transfer of HNO\textsubscript{3} into the aqueous phase and protonation of the buffer. Changes in the Nd absorption spectra could therefore be correlated to specific aqueous pH values and organic-phase nitrate concentrations. Selected results from these experiments are summarized in Figure 4 and Figure 5 and Supplemental Figure S3.
The relationship between the pH of the aqueous buffer (shown as a change in pH from the start), the organic-phase nitrate content (shown as a percentage of the initial organic-phase concentration), and the intermediate spectra of the organic phase are illustrated in Figure 5. The transition between the various Nd species as HNO$_3$ is scrubbed from the organic phase is readily visualized by observing changes at the wavelengths 570.4, 582.2, and 586.8 nm, represented as vertical dashed lines in each spectrum of Figure 5. While each of the absorption bands in the spectra changes continuously throughout the scrub (Supplemental Figure S3), the first noticeable spectral shift is observed at 582.2 and 586.8 nm in Spectrum (a) of Figure 5 after loss of approximately 47% of the initial organic-phase nitrate. The band centered at 582.2 nm begins to broaden, and both bands increase in intensity slightly while undergoing a hypsochromic (blue) shift. By the time 76% of the total nitrate has been scrubbed from the organic phase (Figure 5, Spectrum (b)), the hypsochromic shift of the 582.2 nm peak ceases as the intensity of the peak begins to decline. The peak at 586.8 nm continues to evolve until 85% of the nitrate is scrubbed from the organic phase (Figure 5, Spectrum (c)), where it is barely discernible. Spectrum (d), when 92% of the initial nitrate has been stripped from the organic phase, is marked by substantial broadening of the 582.2 nm peak with a bathochromic (red) shift in the $\lambda_{\text{max}}$ to 582.6 nm, as well as the first appearance of a 570.4 nm peak attributable to the homoleptic Nd-HEH[EHP] complex as a weak shoulder. Finally, at 96% loss of nitrate from the organic phase (Figure 5, Spectrum (e)) the 570.4 nm peak is clearly visible.
The evolution of the Nd spectra is consistent with observations from real-time spectroscopic measurements, and they also qualitatively suggest the presence of at least four different spectroscopically significant Nd-containing species. Further analysis of the set of collected spectra over the wavelength range of 490–850 nm (Supplemental Figure S3) by singular value decomposition with MCR-ALS again reveals the presence of four light-absorbing Nd-containing species under these experimental conditions. A model-free MCR-ALS analysis was used to fit the experimental absorption spectra under the same constraints used for the analysis of the real-time spectra. The MCR-ALS analysis yielded spectra for each of the four unique Nd species (Supplemental Figure S3 and Figure S4) and the concentration of each Nd-containing species for every sampled condition of the scrub (Figure 6). The agreement between the experimental and MCR-ALS fit spectra is excellent, as demonstrated in Figure 4.

As in the real-time scrub measurements, the initial spectrum of the organic phase represents the first of the four Nd-containing species, and it matches the spectrum of Nd in the equilibrium ALSEP loading stage where
Nd(TEHDGA)₂(HEH[EHP])₂(NO₃)₃ is the dominant organic-phase species.\textsuperscript{[13]} The formulation of the starting Nd-containing species is further supported by the initial organic-phase nitrate concentration determined in these experiments. After correction for HNO₃ extraction by uncomplexed extractant,\textsuperscript{[13]} 2.7 ± 0.4 NO₃⁻ are found to be associated with each Nd in the organic phase when the mixing of the organic and aqueous phases begins. The final spectrum, obtained when there was less than 0.04 NO₃⁻ per Nd in the organic phase, matches that of Nd–HEH[EHP] complexes containing no nitrate, namely Nd{H(EH[EHP])₂}₃.

Compared to the speciation as a function of time determined from the \textit{operando} real-time spectroscopic experiments (Figure 3), the speciation determined as a function of organic-phase nitrate concentration (Figure 6) displays a similar distribution of species. However, the much slower stirring in the off-line chemical analysis experiments allows substantially higher concentrations of Intermediate 1 to build up before Intermediate 2 begins to form, which eventually achieves concentrations for Intermediate 2 similar to those observed in real-time experiments. The discrepancy in the fractional quantities of Intermediate 1 and Intermediate 2 across Figure 3 and Figure 6 is likely a by-product of the aforementioned differences in experimental design. Experiments in the CLARiTY cell begin when stirring is initiated, and the stirring speed remains constant throughout the experiment until

![Figure 6. Changes in the Nd speciation of 0.00929 M Nd(TEHDGA)₂(HEH[EHP])₂(NO₃)₃ in 0.05 M TEHDGA/0.75 M HEH[EHP]/n-dodecane while being scrubbed by an equal volume of pH 3.5 0.5 M aqueous malonic acid buffer as calculated from the spectra in Supplemental Figure S3 using MCR-ALS; (■) Nd(TEHDGA)₂(HEH[EHP])₂(NO₃)₃, (○) Intermediate species 1, (▲) Intermediate species 2, (▽) Equilibrium Nd-HEH[EHP] only species. Solution conditions identified in Figure 5 are noted by the appropriate letter code.](image-url)
equilibrium is reached. Conversely, the experiment behind Figure 6 requires variable and interrupted stirring to provide adequate time to reach predetermined pH values and collect samples for analysis. Stir speeds for Olis CLARiTY cell experiments are chosen to be slow enough to resolve sufficient detail between the initial and final spectra within 50–100 spectra before equilibrium is reached, but fast enough to complete a reaction in under 30 min.

When stir rates for the scrub reaction were tested, it was observed that insufficient stirring produced a kinetic bottleneck in the Intermediate 1 spectrum. Quite a few studies have described the rate-limiting kinetic reactions of simple HEH[EHP]/buffer systems as interfacial processes occurring in the diffusion regime,\textsuperscript{[43,44]} meaning that fast-enough stirring can diminish the observable quantities of optically active intermediate species and thus their overall contribution to the linear combination of species that creates the organic-phase spectrum is diminished.

While the initial and final organic-phase Nd species can be identified by fingerprinting the component spectra calculated by the MCR-ALS algorithm against known spectra, model-free MCR-ALS can only produce the spectra of the two intermediate Nd-containing species. It cannot, by itself, identify the species. Nevertheless, the MCR-ALS results hold important clues to the identities of the intermediates. First, the end-members of the series of Nd complexes in the scrub constrain the likely chemical steps involved in the scrub. The overall reaction sequence for Nd in the organic phase of the ALSEP scrub is

\[
Nd(\text{TEHDGA})_2(\text{HEH}[\text{EHP}])_2(\text{NO}_3)_3 \rightarrow \text{Intermediate 1} \rightarrow \\
\text{Intermediate 2} \rightarrow Nd\{H(\text{EH}[\text{EHP}])_2\}_3
\]

with the overall net reaction being

\[
\text{Nd(TEHDGA)}_2(\text{HEH}[\text{EHP}])_2(\text{NO}_3)_3 + 2(\text{HEH}[\text{EHP}])_2 \rightleftharpoons \\
\text{Nd}\{H(\text{EH}[\text{EHP}])_2\}_3 + 2 \text{TEHDGA} + 3\text{HNO}_3
\]

where the overbars indicate species in the organic phase. In three steps, the initial Nd complex needs to lose hydrogen from a HEH[EHP] dimer, lose three nitrate anions, and replace two coordinated TEHDGA molecules with two other monodeprotonated HEH[EHP] dimers.

The spectra of the intermediate species hold a second set of clues to the likely stoichiometries of the intermediate species. The spectrum of the first intermediate species (Supplemental Figure S5) resembles the spectrum of its progenitor, Nd(TEHDGA)_2(HEH[EHP])_2(NO_3)_3, suggesting that the core coordination environment of the Nd ions in Intermediate 1 undergoes relatively small changes when it forms from Nd(TEHDGA)_2(HEH[EHP])_2(NO_3)_3. Like each
of the three other scrub species, Intermediate 1 also displays a 575.4 nm peak (Supplemental Figure S5), which is a defining distinction between the spectra of Nd(TEHDGA)₂(HEH[EHP])₂(NO₃)₃ and Nd(TEHDGA)₃(NO₃)₃.¹³ Together, these facts suggest Intermediate 1 has the composition Nd(TEHDGA)₂(H(HEH[EHP])₂)(NO₃)₂, resulting from the loss of HNO₃ from the parent complex. The spectrum of Intermediate 2, on the other hand, is unique among the spectra of the scrub species, indicating a larger change in the coordination environment likely due to the displacement of one TEHDGA molecule and one NO₃⁻ from the organic-phase complex by one H(HEH[EHP])₂⁻ anion. This would give Intermediate 2 the formula: Nd(TEHDGA)(H(HEH[EHP])₂)₂(NO₃). The final equilibrium species could then be formed from Intermediate 2 by a second displacement of another TEHDGA molecule and NO₃⁻ anion by another H(HEH[EHP])₂⁻ anion (or an EH[EHP]⁻ anion if the final average stoichiometry is Nd(H(HEH[EHP])₂)₂). Furthermore, substantial broadening of the hypersensitive manifold occurs only after the transition from Intermediate 2 to the six-coordinate, homoleptic Nd-HEH[EHP] complex, which supports the suggestion by Hall et al.²¹ that TEHDGA remains in the inner coordination sphere of the complex deep into the lower acid portion of the moderate acid regime.⁴⁵ The overall scrub reaction depicted in Equation 2 would thus be broken down into three reactions,

\[
\text{Nd(TEHDGA)₂(HEH[EHP])₂(NO₃)₃} \rightleftharpoons \text{Nd(TEHDGA)₂(H(HEH[EHP])₂)(NO₃)₂ + HNO₃} \tag{3}
\]

\[
\text{Nd(TEHDGA)₂(H(HEH[EHP])₂)(NO₃)₂ + (HEH[EHP])₂} \rightleftharpoons \text{Nd(TEHDGA)(H(HEH[EHP])₂)₂(NO₃) + TEHDGA + HNO₃} \tag{4}
\]

and

\[
\text{Nd(TEHDGA)(H(HEH[EHP])₂)₂(NO₃) + (HEH[EHP])₂} \rightleftharpoons \text{Nd\{H(HEH[EHP])₂\}₃ + TEHDGA + HNO₃} \tag{5}
\]

In the scrub, these reactions would be driven by the comparatively low concentration of HNO₃ in the aqueous phase and rapid consumption of H⁺ in the aqueous phase by the buffer anions. The two intermediate species suggested by this set of equations – Nd(TEHDGA)₂(H(HEH[EHP])₂)(NO₃)₂ and Nd(TEHDGA)(H(HEH[EHP])₂)₂(NO₃) – have been previously postulated by both Gullekson et al.²⁰ and Hall et al.²¹ to explain the equilibria linking the four metal-containing species observed in their single-phase equilibrium titrations of the ALSEP organic phase.
Liquid-liquid extraction equilibria of ALSEP at low acidity

A third clue to the identity of the intermediate species also emerges from the discrete sampling of the ALSEP scrub. The spectrum of the Nd containing scrub organic phase in contact with the aqueous scrub at \( \Delta \text{pH} = -0.752 \) (Figure 5, Spectrum (b)) is strikingly similar to the equilibrium organic-phase species formed when Nd is extracted from 0.5 M HNO\(_3\) into the 0.05 M TEHDGA/0.75 M HEH[EHP]/n-dodecane (Supplemental Figure S6). Given the compositions of the two intermediate species suggested by the spectroscopic measurements above, we studied the equilibrium species formed by extraction of Am at low nitric acid concentrations in an attempt to correlate the equilibrium acid-dependent organic-phase metal speciation with the non-equilibrium organic-phase speciation during the acid-reducing scrub.

The partitioning behavior of Am\(^{3+}\) between aqueous solutions of nitric acid or an ALSEP strip solution and organic phases composed of TEHDGA, HEH[EHP], and n-dodecane was quantified by equilibrium distribution ratio measurements. Slope analysis by linear regression was used to derive the average stoichiometries of TEHDGA and (HEH[EHP])\(_2\) in the equilibrium extracted complexes when the ALSEP solvent is contacted with low-acid solutions (Table 1 and Supplemental Figure S7). The stoichiometries derived from the slope analysis are generally non-integral and indicate mixtures of complexes of different stoichiometries containing between zero and two molecules of TEHDGA and between one and three (HEH[EHP])\(_2\) in the organic phase under these conditions. In general, lowering the concentration of H\(^+\) and NO\(_3^-\) in the system decreases the importance of the solvating extractant TEHDGA in the extracted complexes and increases the importance of the acidic extractant HEH[EHP] in the extraction process. The H(HEH[EHP])\(_2\)^- anion progressively displaces TEHDGA and NO\(_3^-\) from the extracted Am complexes as was suggested for Nd partitioning in the spectroscopic studies discussed above. Under conditions representative of the completion of the strip step (HEDTA/citrate buffered aqueous phase at pH 3.75), the TEHDGA extraction dependence, 0.0 ± 0.2 TEHDGA:Am implies Am is only complexed by HEH[EHP] in the organic phase. This finding agrees with Hall et al.’s spectroscopic titrations,\(^{[21]}\) and Gullekson et al.’s distribution-ratio measurement,\(^{[20]}\) which both imply no involvement of TEHDGA in the extracted complexes under these conditions.

Nitric acid dependence

To further quantify the influence of HNO\(_3\) on metal speciation in the organic phase and better connect the equilibrium distribution ratio measurements to the real-time ALSEP scrub, the nitric acid dependence of Am extraction was
measured for equilibrium aqueous acidities between 0.02 and 5 M HNO₃. The resulting Am distribution ratios, corrected for variations in the aqueous activity coefficient Am³⁺ and the formation of aqueous Am(NO₃)²⁺ and Am(NO₃)₂⁺ complexes, are depicted in Figure 7. We applied a thermodynamic Am–ALSEP extraction model[13] modified to include multiple extracted Am species for modeling the extraction data (Supplemental Material). Systematically testing sets of extraction equilibria to find the model that best reproduced the experimental nitric acid dependence demonstrated that extracted complexes with four different Am:nitrate stoichiometries matching the four complexes proposed in Equations 3–5 were necessary to fully fit the americium extraction data (Supplemental Table S3, Supplemental Figure S9). The resulting extraction constants (Table 2) and distribution ratios were used to construct a speciation diagram for Am under these extracting conditions (Figure 8 and Supplemental Figure S8).

The most notable difference between the speciation diagrams produced from the scrub data (Figure 3 and Figure 6) and the speciation diagram derived from the extraction data in Figure 8b is the presence of aqueous Am in the buffer-free system. With an aqueous buffer, the distribution ratios of Nd remain high throughout the ALSEP scrub, with negligible amounts of metal reporting to the aqueous phase even temporarily. In the absence of buffer, though, metal rapidly reports to the aqueous phase at the lower acidities supporting formation of the intermediate species M(TEHDGA)₂(H(EH[EHP]₂)(NO₃)₂ and M(TEHDGA)(H(EH[EHP]₂)₃(NO₃) (Figures 8b and S8). The presence of a buffer in the ALSEP scrub is central to understanding this difference across

Figure 7. Dependence of Am extraction on the aqueous-phase activity of NO₃⁻ or H⁺. The corresponding concentrations of nitric acid are indicated along the top axis. (○) Am distribution ratios corrected for variations in the activity coefficient of Am³⁺ and the formation of aqueous Am-nitrate complexes, (−) best fit of the data to a four species extraction model.
Table 2. Extraction constants derived from the nitric acid dependence of Am extraction from aqueous nitric acid into 0.05 M TEHDSA/0.75 M HEH[EHP]/n-dodecane. The general extraction equilibrium connected to each value of $K_{ex}$ is discussed in the Supplemental Material.

| Extracted species                          | log $K_{ex}$  |
|--------------------------------------------|---------------|
| Am(TEHDSA)$_2$(HEH[EHP])$_2$(NO$_3$)$_3$   | 4.35 ± 0.05   |
| Am(TEHDSA)$_2$(H(EH[EHP])$_2$(NO$_3$)$_2$ | 3.61 ± 0.17   |
| Am(TEHDSA)(H(EH[EHP])$_2$(NO$_3$)$_2$     | 1.54 ± 0.18   |
| Am(H(EH[EHP])$_2$(NO$_3$)$_3$             | -1.28 ± 0.13  |

*If the final species is Am(H(EH[EHP])$_2$(NO$_3$)$_3$ instead, log $K_{ex} = -1.49 ± 0.15$ for Am(H(EH[EHP])$_2$(NO$_3$)$_3$ with no change in the other three parameters or $K_{ex}$.*

the two conditions. From beginning to end, the scrub aqueous phase absorbs 98% of the nitric acid present in the organic phase from its initial equilibration with 4 M HNO$_3$ (roughly 0.14 M HNO$_3$).\[13\] Normally, an organic phase in equilibrium with that concentration of aqueous nitric acid would produce a mixture of Intermediate 2, M(TEHDSA)(H(EH[EHP])$_2$(NO$_3$)$_3$), and the homoleptic metal-HEH[EHP] complex (Figure 8b), rather than only the homoleptic metal-HEH[EHP] complex as observed when the scrub reaches equilibrium. However, unlike a buffer-free nitric acid system where the aqueous concentrations of free H$^+$ and NO$_3^-$ would be equal, the malonic acid buffer lowers the amount of free H$^+$ in the aqueous phase and the concentrations of free H$^+$ and NO$_3^-$ are no longer equal. Therefore, the lower concentration of HNO$_3$ in the buffer system disfavors the formation of the initial ternary complex, M(TEHDSA)$_2$(HEH[EHP])$_2$(NO$_3$)$_3$ while a higher NO$_3^-$:H$^+$ ratio favors and stabilizes the formation of Intermediate 1, M(TEHDSA)$_2$(H(EH[EHP])$_2$(NO$_3$)$_2$. Further evidence of this effect was seen where the Intermediate 1 complex’s spectrum was observed by contacting a Nd-ALSEP organic phase with aqueous phases containing lower acid and higher nitrate conditions such as 0.1 M HNO$_3$/1.9 M NaNO$_3$.

An additional kinetic effect on the metal partitioning is observed when comparing the speciation of the scrub experiments in Figure 3 with that of the slow scrub experiments (Figure 6). Slowing the scrub down in the latter experiment allows substantially more of both Intermediate 1 and Intermediate 2 to form during the scrub. However, the specific nature and mechanism of this kinetic hindrance is a topic for further investigation.

The speciation diagrams for Am extraction show that the minimum in the Am extraction (Figure 8a and Figure S8) corresponds to the point where all four organic-phase species coexist. This region is also between where the maximum fraction of the intermediate species Am(TEHDSA)$_2$(H(EH[EHP])$_2$(NO$_3$)$_2$(Intermediate 1) and Am(TEHDSA)(H(EH[EHP])$_2$(NO$_3$)$_2$(Intermediate 2) occurs in the organic phase. Further verification of the extraction model can be obtained from the
average TEHDGA:Am and (HEH[EHP])$_2$:Am ratios for the organic-phase complexes calculated from the stoichiometry and the fraction of each complex present at a given acidity. The speciation thereby calculated from the thermodynamic extraction model can be checked against the average extractant stoichiometries derived from the slope analysis of the extractant dependence of the distribution ratios given in Table 1. At an equilibrium aqueous acidity of 2 M HNO$_3$, the speciation model depicted in Figure 8 predicts a TEHDGA:Am stoichiometry of 2.00 ± 0.01 and a (HEH[EHP])$_2$:Am stoichiometry of 1.00 ± 0.01, which are in excellent agreement with the average stoichiometries derived from slope analysis of the extractant dependencies, 2.11 ± 0.07 and 0.9 ± 0.1, respectively. For 0.5 M HNO$_3$, the predicted TEHDGA:Am ratio is 1.76 ± 0.06 and that for (HEH[EHP])$_2$:Am is 1.22 ± 0.06, which are both somewhat higher than the value expected from the slope analysis, at 1.4 ± 0.1
and 0.95 ± 0.06, respectively. At 0.1 M HNO₃, the model predicts a TEHDGA:Am ratio of 0.4 ± 0.1 and a (HEH[EHP])₂:Am ratio of 2.26 ± 0.05, while the experimentally observed slopes give average stoichiometries of 0.58 ± 0.06 and 1.84 ± 0.02, respectively. Although this suggests some polydispersity in the number of coordinated extractants, the general agreement of the extractant stoichiometries derived from the equilibrium extraction model based on the nitric acid dependence of the Am extraction support the importance of Equilibria 3–5 in the dynamic ALSEP scrub step.

**Computational studies**

To gain further insight into the inner coordination environment of trivalent f-element cations and assess the energetic nature of the ASLEP scrub reaction sequence, chemical computations were performed on the four proposed scrub complexes (*vide supra*). The calculations were performed using trivalent europium and extractants composed of truncated alkyl chains for consistency with our previous analysis of the ALSEP extraction phase. As described in the Methods section, the 2-ethylhexyl chains of TEHDGA and HEH[EHP] were replaced with ethyl chains to reduce the computational cost. As such, this computational analysis will describe TEDGA and HE[EP] rather than TEHDGA and HEH[EHP], respectively (see Supplemental Figure S1 for structures of the truncated extractants). As shown in Figure 9, four Eu complexes were investigated beginning with the dominant complex after ALSEP metal loading, [A] Eu(TEDGA)₂(HE[EP])₂·3NO₃, the two proposed intermediate complexes, [B] Eu(TEDGA)₂(H(E[EP])₂)·2NO₃ and [C] Eu(TEDGA)(H(E[EP])₂)·NO₃, and the final organic-phase complex, [D] Eu(H(E[EP])₂)₃.

![Figure 9. Proposed ALSEP scrub complexation sequence beginning from ALSEP extraction complex [A]. Complexation energies are presented in kcal/mol and normalized to complex [A]. Europium is teal, oxygen atoms are red, nitrogen atoms are blue, carbon atoms are gray, phosphorus atoms are yellow, and hydrogen atoms are white. Dashed lines from Eu highlight the chelating oxygen in every complex.](image-url)
Complex [A] corresponds to Eu coordinated with two tridentate TEDGA extractants and one HE[EP] dimer, resulting in an eight-coordinated complex with three outer-sphere nitrate anions. One of the outer-sphere nitrate anions closely interacts with the proton of the HE[EP] dimer. The interactions within complex [A] suggest a simple mechanism for the formation of complex [B] as the acidity is decreased during the scrub process; one H⁺ from the HE[EP] dimer and the NO₃⁻ hydrogen-bonded to it of complex [A] form HNO₃, which then reports to the aqueous phase. The change in stoichiometry (formation and loss of HNO₃) results in complex [B] which possesses a higher complexation energy compared to [A]. Although the difference in the complexation energies of [A] and [B] is unfavorable (+11.6 kcal/mol), the analysis does not consider the overall energy balance of the reaction, which includes a favorable energy of transfer of HNO₃ into the aqueous phase at lower aqueous acidity and the protonation of the malonate anions, which are the key driving forces of the ALSEP scrub. In contrast, by itself complex [C] is energetically favorable (–7.8 kcal/mol) compared to the initial structure and is formed from [B] by replacing TEDGA with H(E[EP])₂⁻ and forming HNO₃. Complex [C] maintains the eight-coordinate complex as observed with complexes [A] and [B] as the one remaining nitrate anion is directly coordinated with Eu. This relocation of the nitrate anion from the outer sphere is a result of the free space created by replacing TEDGA with an anionic HE[EP] dimer, and the elimination of the cleft between coordinated TEDGA molecules that readily accommodates nitrate or chloride anions in the outer coordination sphere. This rearrangement also explains the minimal change to the average Eu–O coordination distance observed between complexes [B] and [C] (Supplemental Table S4). Lastly, the final scrub complex [D] is formed by another sequential replacement of TEDGA with H(E[EP])₂ and loss of HNO₃ forming the complex with the lowest complexation energy of the series, Eu{H(E[EP])₂}₃. The last transformation requires a change in Eu coordination from eight to six and results in shortening the average Eu–O bond length as more free space around the Eu cation becomes available, as shown in Supplemental Table S4.

The initial mono-deprotonation of (HE[EP])₂ with release of HNO₃ is the only reaction requiring energy. However, the favorable energies of transfer of HNO₃ to the aqueous phase and the protonation of the malonic acid buffer are sufficient to drive the formation of complex [B]. Subsequent reactions where the solvating extractant TEDGA and a nitrate are sequentially replaced by the mono-deprotonated extractant dimer H(E[EP])₂⁻ are each exergonic in themselves, supporting the experimental observations of discrete intermediate species and the final ALSEP scrub complex being Eu{H(E[EP])₂}₃.
Conclusions

In this study, we introduce a powerful tool for probing biphasic speciation in real-time. When coupled with an off-line analysis using a model-free MCR-ALS analysis, the series of spectra of the combined ALSEP aqueous and organic phases collected in an Olis Inc. CLARiTY sample cell during mixing of neodymium-containing solutions became a window into the speciation transitions in ALSEP. Using straightforward constraints within the MCR-ALS program, we were able to obtain spectra for the intermediate species and recognize the similarity of the first intermediate species observed in the ALSEP scrub to a spectrum obtained under equilibrium extracting conditions in the absence of buffer. This link suggests that the transitory organic-phase species encountered in the ALSEP scrub are the same species observed at equilibrium as the aqueous nitric acid concentration is varied.

The high metal distribution ratios observed under scrub conditions are not ideal for obtaining data on the stoichiometry of organic-phase complexes from radiotracer slope analysis. However, the observation that the spectra of the organic-phase species being formed during the scrub match those of species obtained at lower nitric acid concentrations allowed us to identify the average stoichiometries for the intermediate species through extractant dependencies at fixed nitric acid concentrations under conditions where the organic-phase spectra match those of the intermediate species. Using clues from the scrub data and radiotracer dependencies to solidify the transitional species stoichiometries, this approach can also be expanded to model the equilibrium nitric acid dependence curve for ALSEP extraction conditions. This is possible mainly because interference by the weakly complexing malonic acid buffer is not observed. Were a buffer such as lactic acid employed, it is unlikely that the organic-phase complexes would be the same in the presence and absence of the buffer.

Our study also correlates the spectra of organic-phase neodymium complexes to specific aqueous pH’s and organic-phase nitrate conditions. The computational values, experimental data and observation, and modeling in this manuscript support our previous findings of a fully solvated ternary metal complex as the primary extracting complex at high acidities. These findings also suggest the importance of future detailed studies of the effects of HNO₃ vs. NO₃⁻ on the organic-phase speciation, as this could be important for future iterations of ALSEP employing alternative aqueous complexants that operate under different acid regimes.

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