

Extraction Behavior of Ln(III) Ions by T2EHDGA/*n*-Dodecane from Nitric Acid and Sodium Nitrate Solutions

Emily Campbell, Vanessa E. Holfeltz, Gabriel B. Hall, Kenneth L. Nash, Gregg J. Lumetta & Tatiana G. Levitskaia

To cite this article: Emily Campbell, Vanessa E. Holfeltz, Gabriel B. Hall, Kenneth L. Nash, Gregg J. Lumetta & Tatiana G. Levitskaia (2018) Extraction Behavior of Ln(III) Ions by T2EHDGA/*n*-Dodecane from Nitric Acid and Sodium Nitrate Solutions, Solvent Extraction and Ion Exchange, 36:4, 331-346, DOI: [10.1080/07366299.2018.1447261](https://doi.org/10.1080/07366299.2018.1447261)

To link to this article: <https://doi.org/10.1080/07366299.2018.1447261>



Published online: 18 Jun 2018.



Submit your article to this journal [↗](#)



Article views: 583



View related articles [↗](#)



View Crossmark data [↗](#)



Citing articles: 15 View citing articles [↗](#)



Extraction Behavior of Ln(III) Ions by T2EHDGA/*n*-Dodecane from Nitric Acid and Sodium Nitrate Solutions

Emily Campbell ^{a,b}, Vanessa E. Holfeltz ^{a,c}, Gabriel B. Hall ^a, Kenneth L. Nash^b,
Gregg J. Lumetta ^a, and Tatiana G. Levitskaia ^a

^aActinide Science Team, Pacific Northwest National Laboratory, Richland, Washington; ^bChemistry Department, Washington State University, Pullman, Washington; ^cSchool of Nuclear Science and Engineering, Oregon State University, Corvallis, OR

ABSTRACT

The diglycolamide extractant T2EHDGA has proven to be promising for the separation of lanthanides and minor actinides in high-level nuclear waste reprocessing. This neutral extractant has shown significant extraction capacity for HNO₃ into the nonpolar organic phase, along with hyper-stoichiometric nitrate dependence on extraction of trivalent *f*-elements. The transport behavior of T2EHDGA/*n*-dodecane toward trivalent lanthanides is not well understood. This work found a significant increase in distribution ratios for Eu(III) extracted from aqueous HNO₃ media compared with that from NaNO₃. The extraction of Eu(III) from HNO₃ results in a different thermodynamic product than predicted by classic solvent extraction of 3:1 ligand–metal complex as observed with NaNO₃ in FTIR and UV-vis spectroscopy. Experimental distribution measurements in conjunction with mass-action modeling using the solvent extraction modeling program SXLSQI suggest participation of 1 to 2 HNO₃ molecules in the Eu(III)/T2EHDGA complex upon extraction from HNO₃ media, indicative of a mechanism change responsible for the enhanced extraction behavior toward lanthanides in the presence of HNO₃.

KEYWORDS

ALSEP; T2EHDGA; speciation model; trivalent actinides and lanthanides; extraction constant

Introduction

A major challenge that persists in closing the nuclear fuel cycle is the safe management of high-level waste generated from the Plutonium Uranium Reduction Extraction (PUREX) process for the recovery of uranium and plutonium. There has been significant interest in developing an extraction scheme to separate the lanthanides (Ln) from minor actinides (MAs) (primarily americium and curium) in order to enable MA transmutation, which would improve geological repository efficiency by reducing the radiolytic heat generated by the waste, and decrease the long-term radiotoxicity of the material disposed of geologically.^[1] The MAs are the primary contributors to the thermal load and long-term radiotoxicity of intact used nuclear fuel from 200 to 4000 years after discharge from a reactor.^[2] Partitioning and transmutation of these elements to burn as fuel in a fast breeder reactor has been proposed as a method for high-level waste management in conjunction with a geological repository for the relatively short-lived fission products and lanthanides.^[3,4]

Separation of the trivalent Ln and MA has proven a difficult technical challenge for more than 60 years.^[5] The Ln³⁺ and MA³⁺ have very similar ionic radii, and both act as classic hard-acid cations.^[6] Some separation schemes have found success in taking advantage of the slightly “softer” nature of the

CONTACT Tatiana G. Levitskaia  tatiana.levitskaia@pnnl.gov

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/LSEI.

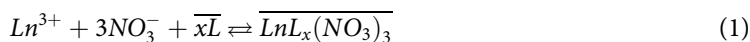
This article was originally published with errors. This version has been corrected/amended. Please see Erratum (<http://dx.doi.org/10.1080/07366299.2018.1511313>)

This material is published by permission of the Pacific Northwest National Laboratory (PNNL), operated by Battelle Memorial Institute for the US Department of Energy under Contract No. DE-AC05-76RLO 1830. The US Government retains for itself, and others acting on its behalf, a paid-up, non-exclusive, and irrevocable worldwide licence 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.

actinide cations along with the fact that the actinide 5*f* orbitals exhibit slightly more covalency than the lanthanide 4*f* orbitals.^[2] Ligands with donor atoms less electronegative than oxygen, such as sulfur or nitrogen, exhibit preferential bonding to actinides over lanthanides.^[7–9] As a result, these ligand functionalities have been found to be advantageous for separating the trivalent *f*-elements.^[10]

A significant effort has been put forth to develop and test new extractants for actinide partitioning. Diamide-based extractants have gained considerable interest, as they are completely incinerable and capable of extracting tri-, tetra-, and hexavalent actinides from nitric acid solutions with better backward extraction of MA compared to phosphorus-based extractants.^[11–13] Within this class of extractants, diglycolamide (DGA) extractants—containing an ether oxygen between the two amide groups—have proven to have advantageous Ln and MA extraction characteristics compared to malonamides.^[12] *N,N,N',N'*-tetraoctyldiglycolamide (TODGA) was found to be promising for fuel reprocessing applications due to its high solubility in paraffinic solvents, low solubility in the aqueous phase, and significantly higher distribution ratios for Am(III) from moderate nitric acid concentrations.^[13] The branched derivative, *N,N,N',N'*-tetra-2-ethylhexyl diglycolamide (T2EHDGA), exhibits poorer extraction affinity toward Am(III) compared to TODGA due to steric hindrance, but it has also proven useful in actinide partitioning studies.^[12,14]

Extraction of trivalent Ln from nitrate media with a neutral extractant is usually represented by the following equation:



where the charged metal ion requires three nitrate counter anions to create the charge neutral metal–ligand complex capable of interfacial transfer to the organic phase. Crystal structures of aqueous-soluble DGA ligands, such as *N,N,N',N'*-tetraethyldiglycolamide, have shown tris-tridentate behavior, suggesting that the number of ligands (*n*) is equal to three for the DGA class of extractants in aqueous media.^[15] The extraction mechanism of the neutral DGA extractant TODGA toward trivalent *f*-element ions has been the subject of a significant research effort. Solvent extraction studies have suggested participation of three to four TODGA molecules in the extracted complex of trivalent actinides and lanthanides from moderate nitric acid concentrations.^[11,16–19] Coordination of three to four tridentate DGA extractants, along with three nitrate ligands, in the first coordination sphere does not seem plausible, given the restricted coordination sites of these *f*-elements. Small-angle X-ray and neutron scattering (SAXS and SANS) studies of metal and acid-loaded TODGA solutions have suggested that aggregation is responsible for the unusual extraction behavior of the straight-chain DGA.^[11,17,18,20] Literature information describing aggregation of the branched derivative T2EHDGA and subsequent extraction behavior toward trivalent Ln and MA is scarce.

Previous studies on the permeation of Am(III) across supported liquid membranes with TODGA provided interesting observations regarding the source of nitrate present in the aqueous phase. Extraction and transport of Am(III) was suppressed in the presence of NaNO₃ compared to HNO₃.^[21] This suggested that H⁺ plays a significant role in the extraction of the metal ion. Subsequent SANS experiments of TODGA and T2EHDGA in contact with HNO₃ and NaNO₃ indicate that the aggregation phenomenon is only observed when the neutral extractants are contacted with HNO₃, and no aggregation is observed after contact with aqueous NaNO₃.^[17] The same study also stated that T2EHDGA has less tendency to form aggregates in the organic phase than TODGA, but a stronger tendency for organic-phase splitting, resulting in third-phase formation.

Previous studies on the extraction of HNO₃ by T2EHDGA in *n*-dodecane diluent determined that extraction of HNO₃ can be adequately described by the formation of two organic species, HNO₃·T2EHDGA and (HNO₃)₂·T2EHDGA.^[22] Characterization using fourier transform infrared spectroscopy (FTIR), ¹³C, ¹H, and ¹⁵N nuclear magnetic resonance (NMR) spectroscopies provides strong evidence of interaction of HNO₃ through the T2EHDGA carbonyl oxygen atom. Third-phase formation was determined to be dependent on both extractant concentration and aqueous acidity, as the extractant was observed to be >80% loaded as aqueous acidity exceeded 3 M HNO₃. Thermodynamic extraction constants for the extraction of HNO₃ were determined using SXLSQI,

and the values were used in the development of the model discussed in the text. The present work seeks to better understand the extraction mechanism(s) responsible for the Ln extraction behavior with T2EHDGA/*n*-dodecane from nitrate media.

Experimental

Materials

T2EHDGA was purchased from Eichrom Technologies (Lisle, Illinois, US) and purified by column chromatography using a dichloromethane/diethyl ether gradient elution. The purified product was characterized by ^1H -NMR, ^{13}C -NMR, FTIR, UV-vis, and electrospray ionization mass spectrometry (ESI-MS).

All aqueous solutions were prepared using distilled water deionized to $>18.2\text{ M}\Omega$ (DIW). Nitric acid solutions were made from TraceSELECT HNO_3 (Fluka Chemicals, Inc.) diluted with DIW and standardized by titration against NaOH using a Titrand Metrohm 905 Automatic Titrator. High-purity NaNO_3 , 99.995%, metals basis, was purchased from Sigma-Aldrich (St. Louis, Missouri, US) and used as received. $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%) was purchased from Alfa Aesar (Tewksbury, Massachusetts, US) and $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%) was purchased from Aldrich Chemical Company (Milwaukee, Wisconsin, US). Normal-dodecane, 99+%, was obtained from Alfa Aesar and used as received. Reagents not specifically mentioned were of analytical grade and used as received.

$^{152/154}\text{Eu}$ was purchased from Eckert & Ziegler (Valencia, California, US) as EuCl_3 in 0.5 M HCl. Distribution studies with Eu(III) contained a non-radioactive carrier concentration of 0.3 mM Eu (NO_3) $_3$ with the concentration of HCl in the samples accounted for during data analysis.

Solvent extraction experiments

Stock solutions of the extractant were made by weighing the appropriate mass of T2EHDGA in a volumetric flask and diluting with *n*-dodecane. Aqueous solutions of HNO_3 or NaNO_3 were spiked with radiotracer prior to contact with the organic phase. To determine the effect of HNO_3 on Eu(III) extraction, samples of 0.1 M T2EHDGA in *n*-dodecane were contacted with equal volumes of aqueous 0.07–3 M HNO_3 on a shaker table at 300 rpm for 1 h at 25°C. Temperature was maintained within $\pm 1^\circ\text{C}$ using a temperature-controlled box to house the shaker table. The samples were centrifuged after mixing, and an aliquot from each phase was removed for analysis. The distribution ratios of Eu(III) were determined by measuring the radioactivity of each phase using an automated gamma counter equipped with a NaI(Tl) scintillation detector. The distribution ratio, D_{Eu} , defined as:

$$D_{\text{Eu}} = \frac{[\text{Eu}^{3+}]_{\text{organic}}}{[\text{Eu}^{3+}]_{\text{aqueous}}} \quad (2)$$

was calculated as the radioactivity in the organic phase divided by the radioactivity in the aqueous phase.

Eu(III) extraction from variable concentration T2EHDGA in *n*-dodecane was studied at 25°C using the method described above. The extractant concentration was varied from 0.03 to 0.2 M T2EHDGA in *n*-dodecane with aqueous-phase acid concentration of 0.5 M HNO_3 and 0.004–0.15 M T2EHDGA with aqueous 2.5 M HNO_3 . Investigation of Eu(III) extraction from 2 M NaNO_3 media with variable T2EHDGA concentrations from 0.03 to 0.15 M was also included for comparison with the HNO_3 distribution measurements.

Solvent extraction studies of Eu(III) from NaNO_3 media were performed with 0.1 M T2EHDGA in *n*-dodecane at 25°C. The concentrations of NaNO_3 ranged from 1 to 3 M NaNO_3 . In control experiments, extraction of NaNO_3 into 0.1 M T2EHDGA in *n*-dodecane was investigated using a ^{22}Na tracer with aqueous-phase composition in the range of 0.1–4 M NaNO_3 . Equal volumes of aqueous and organic phase were contacted at 25°C for 1 h. After centrifugation and separation, the distribution ratio of ^{22}Na was determined by sampling both the organic and aqueous phases and measuring the relative

radioactivity of each phase using an automated gamma counter equipped with a NaI(Tl) scintillation detector. In these experiments, D_{Na} was found to be below detection limit and is estimated at 10^{-4} .

Duplicate experiments were performed for every data point. For proper weighting of the data in SXLSQI modeling (see below), experimental precision for each data point was taken to be $\pm 5\%$, unless otherwise noted, as estimated from a combination of replicate determinations, volumetric error, and precision of radiometric analysis.

Extraction data treatment

The solvent extraction modeling program SXLSQI was used to facilitate thermodynamic analysis of europium distribution data at 25°C .^[23] Modeling parameter inputs for SXLSQI are summarized in Table 1. Comparison of calculated distribution ratios to the experimental distribution data using refined extraction constants reports an agreement factor that reflects the goodness of fit.^[24]

Solvent extraction studies of Eu(III) from variable T2EHDGA with both HNO_3 and NaNO_3 media, along with 0.1 M T2EHDGA contacted with variable concentration of HNO_3 were used as input to the solvent extraction modeling program. Pitzer parameters for $\text{Eu}(\text{NO}_3)_3$ and HNO_3 at 25°C were supplied in order to calculate nonideality effects in the aqueous phase along with Masson coefficients to convert molar concentration into the molality scale.^[25,26] The solubility parameter of T2EHDGA was calculated using group contributions as outlined elsewhere to account for activity effects in the organic phase.^[27] Thermodynamic extraction constants for HNO_3 -T2EHDGA and

Table 1. Parameters used in SXLSQI modeling.

| Masson Coefficients ^a | | | | |
|---|--|------------------|---|-----|
| ion | V ₀ (cm ³ mol ⁻¹) | | Sv* (cm ³ L ^{1/2} mol ^{-3/2}) | |
| Eu ³⁺ | 21.34 | | 1.91 | |
| NO ₃ ⁻ | 29.33 | | 0.543 | |
| Pitzer Parameters ^{[25,45]b} | | | | |
| interaction | β ⁽⁰⁾ | β ⁽¹⁾ | Cφ | α |
| H ⁺ —NO ₃ ⁻ | 0.1168 | 0.3546 | -0.00539 | 2.0 |
| H ⁺ —Cl ⁻ | 0.1775 | 0.2945 | 0.00080 | 2.0 |
| Na ⁺ —NO ₃ ⁻ | 0.0068 | 0.1783 | -0.00072 | 2.0 |
| Na ⁺ —Cl ⁻ | 0.0765 | 0.2664 | 0.00127 | 2.0 |
| Eu ³⁺ —NO ₃ ⁻ | 0.4547 | 5.3266 | -0.03887 | 2.0 |
| Eu ³⁺ —Cl ⁻ | 0.60733 | 5.6000 | -0.02078 | 2.0 |
| Other Parameters | | | | |
| species | V ₀ ^c (cm ³ mol ⁻¹) | | δ(J ^{1/2} cm ^{-3/2}) | |
| n-dodecane | 228.6 ^d | | 16.1 ^d | |
| T2EHDGA | 606.6 ^e | | 19.15 ^e | |
| HNO ₃ ·T2EHDGA | - | | 22.54 ^f | |
| (HNO ₃) ₂ ·T2EHDGA | - | | 21.91 ^f | |
| Eu(NO ₃) ₃ (T2EHDGA) ₃ | - | | 20.55 ^g | |
| Eu(NO ₃) ₃ (T2EHDGA) ₃ (HNO ₃) | - | | 20.62 ^g | |
| Eu(NO ₃) ₃ (T2EHDGA) ₃ (HNO ₃) ₂ | - | | 21.96 ^g | |
| Nitrate formation constants ^[46] | β ₁ | | β ₂ | |
| Eu | 1.86 | | 0.43 | |

^aMasson coefficients allow molality-molarity interconversions. Values taken from ref 26.

^bPitzer parameters allow aqueous-phase ionic activity coefficients to be estimated. Values were taken from ref 25, except $\text{Eu}^{3+} - \text{NO}_3^-$ was taken from ref 44.

^cMolar volumes of the species in the organic phase. Values for the inorganic ions were taken to be approximately equal to V_0 .

^dTaken from ref 27.

^eValues estimated according to group contributions as described in ref 27.

^fTaken from ref 22.

^gThe solubility parameter of the complex was refined in this work.

(HNO_3)₂·T2EHDGA, determined to be the species responsible for HNO_3 extraction from T2EHDGA in the absence of metal, were included in the model.^[22]

An extraction model consisting of three organic-phase species, $\text{Eu}(\text{NO}_3)_3(\text{T2EHDGA})_3$, $\text{Eu}(\text{NO}_3)_3(\text{T2EHDGA})_3(\text{HNO}_3)$, and $\text{Eu}(\text{NO}_3)_3(\text{T2EHDGA})_3(\text{HNO}_3)_2$, was used based on the results from UV-vis and FTIR spectroscopy. The refinement of corresponding extraction constants was determined via SXLSQI based on input of experimental data.

Spectroscopic methods

FTIR measurements of metal–ligand complexes under various aqueous conditions were examined on a Bruker ALPHA Platinum ATR module with a single-reflection diamond cell at room temperature ($23 \pm 1^\circ\text{C}$). Organic liquids were measured by placing a drop directly on the diamond plate. All spectra were collected between 400 and 4000 cm^{-1} with a minimum of 24 scans averaged and 4 cm^{-1} resolution. Background measurements of air (or *n*-dodecane where specified) were taken between every sample after cleaning with an appropriate solvent.

Samples of T2EHDGA were prepared *via* solvent extraction from NaNO_3 or HNO_3 media. Pristine 0.1 M T2EHDGA/*n*-dodecane was contacted with 3 M NaNO_3 or 3 M HNO_3 for reference. Structural information of organic-phase Eu/T2EHDGA species was investigated by contacting 0.1 M T2EHDGA/*n*-dodecane with 2 mM $\text{Eu}(\text{NO}_3)_3$ in 3 M HNO_3 , 30 mM $\text{Eu}(\text{NO}_3)_3$ in 1 M HNO_3 , and 15 mM $\text{Eu}(\text{NO}_3)_3$ in 3 M NaNO_3 . The concentration of Eu(III) in the organic phase was determined from the distribution ratio of $^{152/154}\text{Eu}$ as found in a parallel radiotracer experiment prepared with aqueous and organic solutions used in the FTIR analysis.

Increasing the concentration of $\text{Eu}(\text{NO}_3)_3$ to 10 mM in 2.5 M HNO_3 and 20 mM $\text{Eu}(\text{NO}_3)_3$ in 4 M NaNO_3 resulted in third-phase formation. This viscous third phase was placed directly on the diamond ATR plate, referenced against air, and compared to pristine T2EHDGA.

To probe the effect of HNO_3 on metal coordination in the T2EHDGA/*n*-dodecane solvent, a UV-vis titration experiment was performed using $\text{Nd}(\text{NO}_3)_3$. Absorbance spectra of Nd(III) were collected on a Cary Bio 50 Spectrophotometer using a 10-mm semi-micro quartz cuvette with 0.1 M T2EHDGA/*n*-dodecane as the solvent. The experimental setup utilized automatic background subtraction with a medium scan rate (300 nm/min). The spectral window was 200–800 nm measured in 0.5 nm increments.

A spectrophotometric titration of Nd(III) loaded into 0.1 M T2EHDGA/*n*-dodecane from 15 mM $\text{Nd}(\text{NO}_3)_3$ in 3 M NaNO_3 was collected in a 10-mm quartz cuvette. To load 0.1 M T2EHDGA/*n*-dodecane, 800 μL of each phase was contacted on a shaker table for >30 min. The sample was centrifuged and 750 μL of the organic phase was transferred to the cuvette. Pre-equilibrated 0.1 M T2EHDGA/*n*-dodecane with 3 M HNO_3 was added incrementally to the Nd(III)/ NaNO_3 -loaded organic phase. A total volume of 1600 μL of acid-loaded T2EHDGA was added. A secondary titration experiment was performed in the same manner, with 0.1 M T2EHDGA/*n*-dodecane pre-equilibrated with >18.2 MΩ DIW instead of HNO_3 .

The distribution ratio of Nd(III) was determined by analysis of the post-contact aqueous phase. The maximum intensity of the hypersensitive $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2} + ^2\text{G}_{7/2}$ band at 578 nm was plotted against a calibration curve generated from 1 to 20 mM $\text{Nd}(\text{NO}_3)_3$ in a 3 M NaNO_3 matrix to determine the aqueous Nd(III) concentration. Extraction of Nd(III) into 0.1 M T2EHDGA/*n*-dodecane from 3 mM $\text{Nd}(\text{NO}_3)_3$ in 3 M HNO_3 was quantitative.

Results and discussion

Eu(III) distribution studies

Distribution ratios of Eu(III) extracted from variable concentrations of T2EHDGA in *n*-dodecane at 0.5 M HNO_3 , 2.5 M HNO_3 , and 2 M NaNO_3 are shown in Fig. 1A. The linear relationship between D_{Eu} and variable T2EHDGA concentrations is observed for all aqueous systems studied. The distribution ratios for extraction of Eu(III) from 0.5 M HNO_3 are significantly less than the

Eu(III) extraction from 2.5 M HNO_3 even taking into account the significant quantities of HNO_3 extracted by the ligand at 2.5 M HNO_3 . More interestingly, the distribution ratios of Eu(III) with variable T2EHDGA drop by more than two orders of magnitude by switching the source of counter anion to 2 M NaNO_3 rather than 2.5 M HNO_3 .

The D values for extraction of Eu(III) from variable HNO_3 concentrations by T2EHDGA in n -dodecane at 25°C are presented in Fig. 1B as a function of initial HNO_3 concentration. At low HNO_3 concentrations, the extraction of Eu(III) is low with D_{Eu} values less than 10^{-2} . As the HNO_3 concentration increases, Eu(III) extraction is markedly enhanced as indicated by the steep increase in distribution ratios as aqueous acidity exceeds 1 M HNO_3 . Additionally, the steep dependence of D_{Eu} on HNO_3 concentration is observed for 0.05 M T2EHDGA in n -dodecane contacted with 1–3 M HNO_3 at 25°C.

Assuming that T2EHDGA behaves according to the mechanism described by Eq. (1) for Eu(III) extraction, the neutral extractant should not be selective toward the source of NO_3^- in the system. In fact, one may expect the distribution ratio of Eu(III) to be suppressed in the presence of HNO_3 due to the formation of $(\text{HNO}_3)_n\cdot\text{T2EHDGA}$ ($n = 1, 2$) adducts that decrease the amount of free ligand available to participate in the extracted complex.^[22] The significant enhancement in D_{Eu} from HNO_3 compared to NaNO_3 suggests that HNO_3 participates in the extracted complex and/or facilitates the pre-organization of a supramolecular structure responsible for enhanced Eu(III) extraction. SXLSQI computer modeling program was used to elucidate the organic-phase species responsible for the significant increase in Eu(III) extraction from HNO_3 media.

Experimental distribution measurements for Eu(III) extraction by 0.1 M T2EHDGA as a function of HNO_3 concentration were combined with D_{Eu} data obtained as a function of the T2EHDGA concentration at 25°C (Fig. 1A) from 0.5 and 2.5 M HNO_3 and 2 M NaNO_3 and subsequently supplied to the SXLSQI modeling program. Previous investigation of HNO_3 extraction into T2EHDGA/ n -dodecane indicates two organic species responsible for the extraction of HNO_3 , namely, $\text{HNO}_3\cdot\text{T2EHDGA}$ and $(\text{HNO}_3)_2\cdot\text{T2EHDGA}$, with log K values of -0.76 ± 0.03 and -2.0 ± 0.1 , respectively.^[22] These extraction constants, along with aqueous stability constants

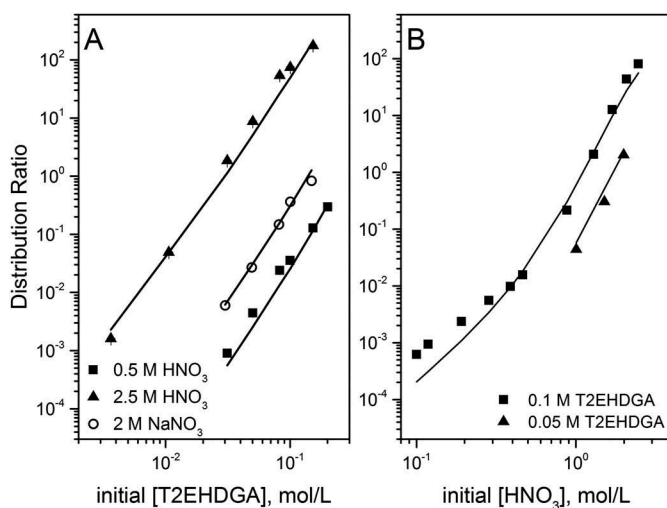
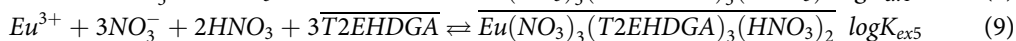
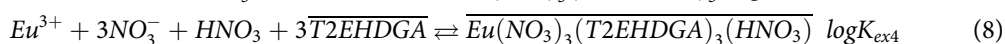
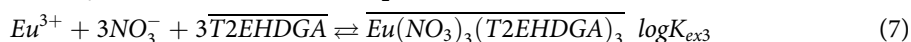
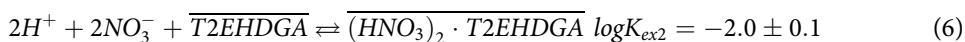
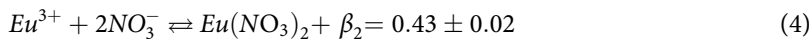
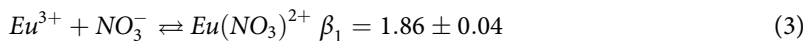


Figure 1. Extraction of Eu(III) by (A) variable concentrations of T2EHDGA in n -dodecane contacted with (■) 0.5 M, (▲) 2.5 M HNO_3 , and (○) 2 M NaNO_3 at 25°C. (B) D_{Eu} from (▲) 0.05 M and (■) 0.1 M T2EHDGA in n -dodecane contacted with variable concentrations of HNO_3 at 25°C. All data points were obtained in at least duplicate. The black lines represent calculated values based on the model described in the text.

for $\text{Eu}(\text{NO}_3)_3^{2+}$ and $\text{Eu}(\text{NO}_3)_2^+$, were used as part of the SXLSQI model to refine thermodynamic extractant constants for the organic-phase Eu(III) complexes. The best SXLSQI fit to the Eu(III) extraction data, shown by the solid line in Fig. 1, was obtained using the following equilibrium reactions:



The extraction behavior of Eu(III) by T2EHDGA in *n*-dodecane from HNO_3 and NaNO_3 solutions was modeled using Eqs. (7–9). Three organic-phase species are justified by restriction of only the $\text{Eu}(\text{NO}_3)_3(\text{T2EHDGA})_3$ species extracted from aqueous NaNO_3 media, along with the two different extraction regimes observed for D_{Eu} by 0.1 M T2EHDGA with variable HNO_3 . The change in mechanism for Eu(III) extraction with variable HNO_3 occurs around 1 M HNO_3 , after which there is a steep increase in the extraction of Eu(III).^[22] At low HNO_3 concentrations, the HNO_3 in the organic phase significantly exceeds the concentration of extracted Eu(III), justifying the addition of the $\text{Eu}(\text{NO}_3)_3(\text{T2EHDGA})_3(\text{HNO}_3)$ species. At HNO_3 concentrations greater than 1 M, a super-stoichiometric nitrate dependence is observed on extracted Eu(III), which warrants inclusion of the $\text{Eu}(\text{NO}_3)_3(\text{T2EHDGA})_3(\text{HNO}_3)_2$ species. Modeling attempts excluding the $\text{Eu}(\text{NO}_3)_3(\text{T2EHDGA})_3(\text{HNO}_3)_2$ species failed to predict the moderate (1–3 M HNO_3) regime. This is in agreement with literature studies of the non-branched DGA derivative, TODGA, where slopes observed for the extraction of Am(III) and Eu(III) in *n*-dodecane indicated the presence of zero to two molecules of HNO_3 in the extracted complex.^[16]

The model generated using Eqs. (7–9) predicts D_{Eu} very well across variable T2EHDGA concentrations from both HNO_3 and NaNO_3 media as represented by the solid lines in Fig. 1A. Refinement of the equilibrium constants for Eqs. (7–9) using the nonideality parameters listed in Table 1 yielded $\log K$ values of 3.29 ± 0.04 , 4.24 ± 0.10 , and 4.17 ± 0.06 for $\log K_{\text{ex3}}$, $\log K_{\text{ex4}}$, and $\log K_{\text{ex5}}$, respectively, with a goodness of fit of 5.30.

Prediction of D_{Eu} over the entire HNO_3 regime in Fig. 1B is indicated by the solid black line. The model predicts moderate HNO_3 concentrations very well for both 0.1 M and 0.05 M T2EHDGA, but slightly underpredicts the extraction of Eu(III) at low nitric acid concentrations with 0.1 M T2EHDGA/*n*-dodecane for D values below 10^{-2} consistent with HNO_3 concentrations below 0.4 M. One possible explanation for the underprediction of D_{Eu} at low HNO_3 concentrations is potential dissociation of the organic $\text{Eu}(\text{NO}_3)_3(\text{T2EHDGA})_3$ species; however, inclusion of the corresponding species into the SXLSQI model did not improve the overall fit increasing the goodness of fit to 6.3. Another potential reason for the underprediction of D_{Eu} is the lack of the Pitzer parameters for the aqueous-phase species, $\text{Eu}(\text{NO}_3)_2^+$ and $\text{Eu}(\text{NO}_3)_3^{2+}$. These values are not reported in the literature, so the Pitzer parameters of the ions were used for model development.

A speciation diagram of the extracted Eu(III) complexes as a function of HNO_3 concentration, generated using the SXLSQI model parameters at low metal loading conditions (2 mM $\text{Eu}(\text{NO}_3)_3$), is shown in Fig. 2. In the absence of HNO_3 , the Eu(III) complex exists as the classic $\text{Eu}(\text{NO}_3)_3(\text{T2EHDGA})_3$ species. This species is also observed at low HNO_3 concentrations (below 0.5 M HNO_3) but decreases rapidly with the ingrowth of the $\text{Eu}(\text{NO}_3)_3(\text{T2EHDGA})_3(\text{HNO}_3)$ species. The $\text{Eu}(\text{NO}_3)_3(\text{T2EHDGA})_3(\text{HNO}_3)$ species reaches a maximum near 0.8 M HNO_3 , after which point the $\text{Eu}(\text{NO}_3)_3(\text{T2EHDGA})_3(\text{HNO}_3)_2$ species begins to increase steadily before becoming the dominant

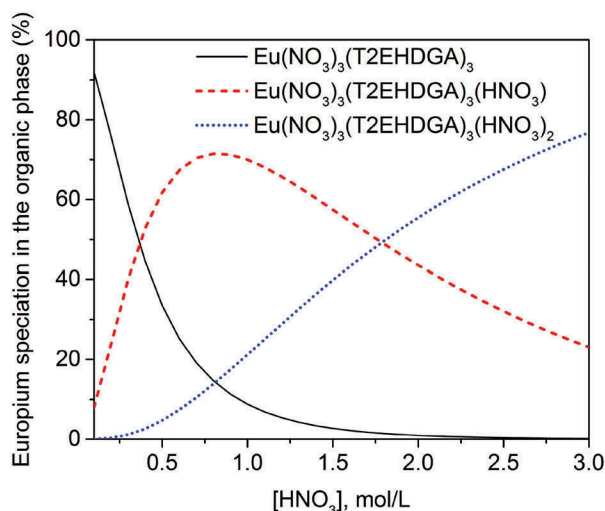


Figure 2. Speciation diagram of organic-phase Eu(III) complexes, as a function of HNO₃ concentration, extracted from 0.1 M T2EHDGA in *n*-dodecane. The initial aqueous Eu(NO₃)₃ concentration was 2 mM to achieve low metal loading of T2EHDGA. Concentrations of each species were calculated using the refined extraction constants generated from the three-species model in SXLSQL.

species at 1.8 M HNO₃. This correlates well with the mechanism change observed for D_{Eu} with 0.1 M T2EHDGA in *n*-dodecane at 1 M HNO₃ where the maximum concentration of Eu(NO₃)₃(T2EHDGA)₃(HNO₃) is present before a steep increase in the Eu(NO₃)₃(T2EHDGA)₃(HNO₃)₂ species is observed. The preorganization of the (HNO₃)_{*n*}·T2EHDGA (*n* = 1, 2) adducts is likely responsible for the enhanced Eu(III) extraction observed in the presence of HNO₃.

Limiting organic concentration

The strong tendency toward third-phase formation at moderate acid concentrations, as reported in the literature, warranted a limiting organic concentration (LOC) experiment prior to spectroscopic studies to determine experimentally limiting conditions.^[28] Metal dependence of Eu(III) extraction can be deduced from a plot of the equilibrium organic concentration of europium versus initial aqueous concentration of europium.^[29] Organic and aqueous europium concentrations were calculated from distribution ratios determined radiometrically in *n*-dodecane solvent with 0.1 M and 0.05 M T2EHDGA and Eu(NO₃)₃ concentrations of 0.3 to 30 mM in 1, 2, and 3 M HNO₃. The Eu(III) organic concentration increases linearly as shown in Fig. 3 until a maximum is observed, indicative of splitting the organic phase into the light and heavy (third) phase.

Results of the LOC experiment with 0.05 and 0.1 M T2EHDGA/*n*-dodecane show that phase splitting does not occur at 1 M HNO₃, even up to aqueous concentrations of 30 mM Eu(NO₃)₃, as shown in Fig. 3. Increasing aqueous acidity to 2 and 3 M HNO₃ with 50 mM T2EHDGA/*n*-dodecane results in an LOC of 1.75 and 1.48 mM Eu(III), respectively. Doubling the ligand concentration increases the LOC of Eu(III) to 4.05 and 2.45 mM for 2 and 3 M HNO₃, respectively. The solubility of the 3:1 ligand–metal complex in the organic phase is likely not the driving force of third-phase formation for this system, as 5.7 mM Eu(III) can be loaded into 0.1 M T2EHDGA/*n*-dodecane at aqueous 1 M HNO₃. Rather, progressive loading/aggregation of the organic phase due to (HNO₃) T2EHDGA and (HNO₃)₂T2EHDGA species is the probable explanation for phase splitting.

Third phases for TODGA and T2EHDGA have been reported in the literature even in the absence of metal, where 0.2 M T2EHDGA/*n*-dodecane forms third phase after contact with the aqueous phases

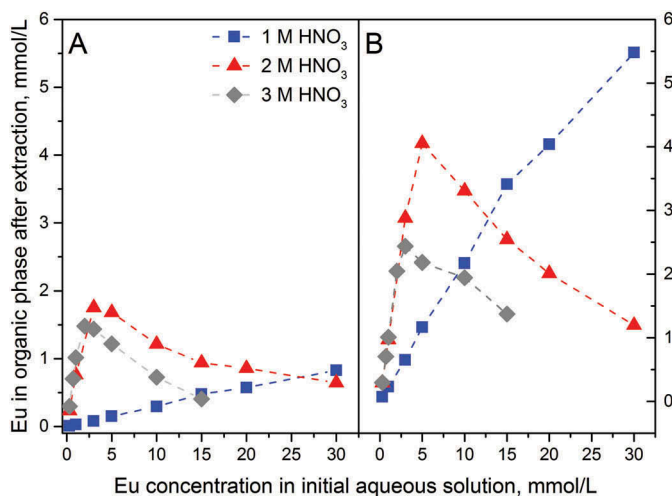


Figure 3. Limiting organic concentration (LOC) of Eu(III) with (A) 0.05 M and (B) 0.1 M T2EHDGA/*n*-dodecane from 1, 2, and 3 M HNO₃ at 25°C determined radiometrically with ^{152/154}Eu.

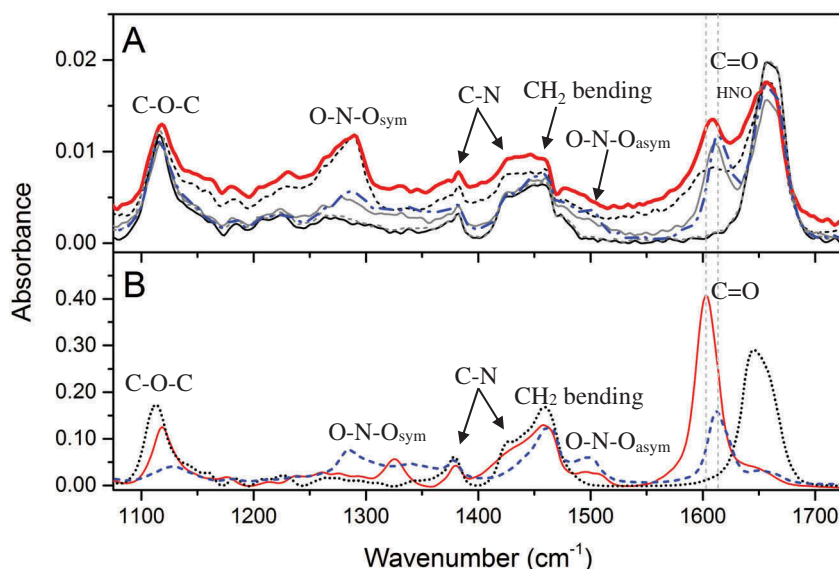
containing HNO₃ at 3.9 M or greater and 0.1 M T2EHDGA/*n*-dodecane forms visible third phase as aqueous HNO₃ concentration approaches 5 M.^[28] TODGA, the straight-chain DGA, does not form a third phase until the aqueous nitric acid concentrations exceeds 6 M.^[30] In the case of TODGA, third-phase behavior can be explained by attractive interactions of the aggregates as a result of van der Waals attraction and steric stabilization of aggregates by diluent molecules.^[31] Steric stabilization can be increased with longer extractant chains and/or branched diluents, which explains why the branched DGA, T2EHDGA, forms third phase at lower nitric acid concentrations to those observed by the longer, straight-chain DGA isomer, TODGA.^[17]

FTIR characterization of extracted Eu(III)-T2EHDGA complexes

The FTIR spectrum of pristine T2EHDGA in *n*-dodecane is shown in Fig. 4A (black trace) along with assignment of the observed vibrations. The vibrational bands of pristine DGA have been assigned as the ether C–O–C stretch at 1118 cm^{−1} and the amide functionality with C = O (1660 cm^{−1}) and C–N (1380 and 1426 cm^{−1}).^[16,32–37] All of the spectra in Fig. 4A were referenced against *n*-dodecane.

FTIR measurements of 0.1 M T2EHDGA/*n*-dodecane contacted with 2 mM Eu(NO₃)₃ in 3 M HNO₃, 30 mM Eu(NO₃)₃ in 1 M HNO₃, and 15 mM Eu(NO₃)₃ in 3 M NaNO₃ are shown in Fig. 4A. The concentrations of Eu(III) and HNO₃ were chosen based on LOC experimental results to load the maximum concentration of Eu(III) into the organic phase without interference of third phase. There are no distinct differences in the FTIR spectra of 0.1 M T2EHDGA/*n*-dodecane before and after contact with 3 M NaNO₃ (gray dashed line, Fig. 4A) as expected due to the lack of nitrate extraction by the neutral ligand as confirmed in radiotracer experiments with ²²Na. However, significant spectral changes are observed in the FTIR spectra upon equilibration with HNO₃ and the addition of Eu(III).

The carbonyl absorbance of T2EHDGA at 1660 cm^{−1} has been assigned as a combination of the free carbonyl on the DGA and the carbonyl participating in the extraction of the 1:1 HNO₃·T2EHDGA adduct, as discussed elsewhere.^[22] The appearance of a new carbonyl stretch at 1604 cm^{−1} and subsequent decrease in the 1660 cm^{−1} stretch upon contact with 3 M HNO₃ (black dash, Fig. 4A) has been assigned to the higher-order (HNO₃)₂·T2EHDGA species responsible for



| C | Initial aqueous phase conditions | | | |
|---|--|--|---|--------------------------------------|
| | 30 mM Eu(NO ₃) ₃ 1 M HNO ₃ (grey) | 2 mM Eu(NO ₃) ₃ 3 M HNO ₃ (red) | 15 mM Eu(NO ₃) ₃ 3 M NaNO ₃ (blue) | 3 M HNO ₃ (black dash) |
| Concentration of equilibrium aqueous phase species calculated using SXLSQI model parameters | | | | |
| Eu(III) ^a , mM | 22.3 | 0.04 | 8.69 | - |
| HNO ₃ , M | 0.988 | 2.90 | - | 2.90 |
| NaNO ₃ , M - - 3.0 - | | | | |
| Concentration of organic phase species calculated using SXLSQI model parameters, mM | | | | |
| HNO ₃ ·T2EHDGA | 10.6 | 53.7 | - | 57.2 |
| (HNO ₃) ₂ ·T2EHDGA | 0.29 | 19.8 | - | 21.2 |
| Eu(NO ₃) ₃ (T2EHDGA) ₃ | 0.59 | < 10 ⁻³ | 6.31 | - |
| Eu(NO ₃) ₃ (T2EHDGA) ₃ (HNO ₃) | 5.44 | 0.45 | - | - |
| Eu(NO ₃) ₃ (T2EHDGA) ₃ (HNO ₃) ₂ | 1.64 | 1.50 | - | - |

^aTotal Eu(III) concentration in the aqueous phase composed of hydrated, mono- and di-nitrato Eu(III) complexes.

Figure 4. FTIR spectra of (A) 0.1 M T2EHDGA/*n*-dodecane (black), after contact with 2 mM Eu(NO₃)₃ in 3 M HNO₃ (red), 30 mM Eu(NO₃)₃ in 1 M HNO₃ (grey), 15 mM Eu(NO₃)₃ in 3 M NaNO₃ (blue), and 0.1 M T2EHDGA loaded with 3 M HNO₃ (black dash) and after contact with 3 M NaNO₃ (gray dash). (B) Spectral overlay of pristine T2EHDGA (black) with heavy Eu(III)/(H,Na)NO₃/T2EHDGA organic phase resulting upon contact of 0.1 M T2EHDGA/*n*-dodecane with 10 mM Eu(NO₃)₃ in 2.5 M HNO₃ (red) and 20 mM Eu(NO₃)₃ in 4 M NaNO₃ (blue). (C) Concentration of organic-phase species in (A) predicted using SXLSQI model parameters along with equilibrium aqueous conditions.

super-stoichiometric HNO₃ extraction into 0.1 M T2EHDGA/*n*-dodecane. There is additional evidence of extracted HNO₃ in the IR spectra indicated by the presence of the O–N–O symmetric stretch centered about 1295 cm^{-1} .

Addition of Eu(III) to the system results in a decrease of the free carbonyl stretching band on T2EHDGA and a corresponding shift of europium-bound carbonyl to 1614 or 1608 cm^{-1} from NaNO₃ or HNO₃ media, respectively. Upon contact of 0.1 M T2EHDGA/*n*-dodecane with 15 mM Eu(NO₃)₃ in 3 M NaNO₃, the concentration of Eu(III) in the organic phase was found to be 6.6 mM as determined by

distribution data from radiotracer experiments. The appearance of the O–N–O symmetric stretch centered below 1300 cm^{-1} appears in the NaNO_3 system only in the presence of Eu(III) . A new peak at 1500 cm^{-1} appears for Eu(III) extracted from NaNO_3 corresponding to the O–N–O asymmetric stretch. According to the literature, the separation of the symmetric and asymmetric O–N–O stretching frequencies ($\Delta\nu$) can be used to determine the coordination mode of the nitrate.^[38,39] A difference in wavenumber of greater than 186 cm^{-1} is indicative of bidentate nitrate coordination, whereas a $\Delta\nu$ less than 115 cm^{-1} indicates monodentate coordination of the nitrate.^[40] The difference in stretching frequencies ($\Delta\nu$) of the symmetric and asymmetric O–N–O vibrations was calculated to be 206 cm^{-1} in the NaNO_3 system with metal extraction, which indicates nitrate is coordinated bidentate to Eu(III) after extraction into 0.1 M T2EHDGA/*n*-dodecane.

Eu(III) extracted from $30\text{ mM Eu(NO}_3)_3/1\text{ M HNO}_3$ and $2\text{ mM Eu(NO}_3)_3/3\text{ M HNO}_3$ show similar spectral features in Fig. 4A as indicated by the gray and red traces, respectively, with the Eu(III) -bound carbonyl stretch observed at 1608 cm^{-1} . The increased intensity of the O–N–O symmetric stretch for Eu(III) extracted from 3 M HNO_3 can be attributed to the enhanced extraction of HNO_3 by the predominant $(\text{HNO}_3)_2\cdot\text{T2EHDGA}$ species at 3 M HNO_3 , as indicated by the black dashed trace. Quantitative extraction of Eu(III) from $2\text{ mM Eu(NO}_3)_3$ in 3 M HNO_3 was observed, whereas the concentration of Eu(III) extracted from $30\text{ mM Eu(NO}_3)_3$ in 1 M HNO_3 was determined radiometrically as 5.7 mM . The decrease in the carbonyl stretch at 1660 cm^{-1} for $30\text{ mM Eu(NO}_3)_3$ in 1 M HNO_3 can be attributed to the $\sim 18\text{ mM}$ T2EHDGA bound to the $\sim 6\text{ mM}$ Eu(III) extracted assuming the 1:3 metal–ligand complex. However, the intensity of the 1660 cm^{-1} stretch cannot be directly compared to free DGA concentration due to the contribution of multiple species in this region, including the 1:1 $\text{HNO}_3\cdot\text{T2EHDGA}$ species.

The slightly greater peak shift for Eu(III) extracted from HNO_3 media indicates that the $\text{Eu(III)}/\text{T2EHDGA}/\text{HNO}_3$ complex(es) have greater bond strength between the oxygen of the carbonyl group and the Eu(III) ion, which can be correlated to the enhanced D_{Eu} for the HNO_3 system.^[41]

Third-phase formation can be observed upon contacting 0.1 M T2EHDGA/*n*-dodecane with $10\text{ mM Eu(NO}_3)_3$ in 2.5 M HNO_3 and $20\text{ mM Eu(NO}_3)_3$ in 4 M NaNO_3 as shown in Fig. 4B. The vibrations observed for pristine DGA can be assigned as C=O (1645 cm^{-1}), C–N (1380 and 1425 cm^{-1}), CH_2 bending, and the C–O–C stretch (1117 cm^{-1}). There is a significant shift in the free carbonyl of neat T2EHDGA and the Eu(III) -bound carbonyl from both HNO_3 and NaNO_3 media. The heavy organic phase resulting from $\text{Eu(III)}/\text{HNO}_3/\text{T2EHDGA}$ shifts to 1603 cm^{-1} compared to the $\text{Eu(III)}/\text{NaNO}_3/\text{T2EHDGA}$ heavy organic phase, with a shift to 1618 cm^{-1} . More importantly, the positions of the O–N–O symmetric stretches from HNO_3 and NaNO_3 media are significantly shifted from one another, with the O–N–O symmetric stretch from the $\text{Eu}/\text{HNO}_3/\text{T2EHDGA}$ observed at 1328 cm^{-1} but shifted to 1290 cm^{-1} for $\text{Eu}/\text{NaNO}_3/\text{T2EHDGA}$. This shift in the O–N–O symmetric stretch is diagnostic of the nitrate environment within the extracted complex. The stretch observed at 1328 cm^{-1} for the $\text{Eu}/(\text{HNO}_3)_{1-2}/\text{T2EHDGA}$ heavy phase is indicative of HNO_3 , likely participating in the outer coordination sphere.^[42] However, the O–N–O symmetric stretch at 1290 cm^{-1} for Eu/NaNO_3 species is indicative of nitrate chelated to metal.^[42] The combined FTIR observations in the light and heavy organic phase are indicative of different thermodynamic product species as a result of extraction from HNO_3 or NaNO_3 .

Absorbance spectra of Nd(III)

Insight into the coordination environment of extracted lanthanide–ligand complexes is often accessible via UV–visible spectroscopy, by probing the electronic structure of the extracted metal. Neodymium was chosen for the analysis due to its spectroscopic properties. Figure 5 shows representative spectrophotometric absorbance spectra of Nd(III) complexed in the organic phase by T2EHDGA after extraction from an aqueous phase of NaNO_3 or HNO_3 . The absorbance of the hypersensitive $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2} + ^2\text{G}_{7/2}$ transition of $\text{Nd(NO}_3)_3(\text{T2EHDGA})_3$ compared to $\text{Nd(NO}_3)_3(\text{T2EHDGA})_3(\text{HNO}_3)_{1-2}$ is observed at $580\text{--}600\text{ nm}$ in Fig. 5 by a change in the peak shape and intensity.^[43] These spectra were

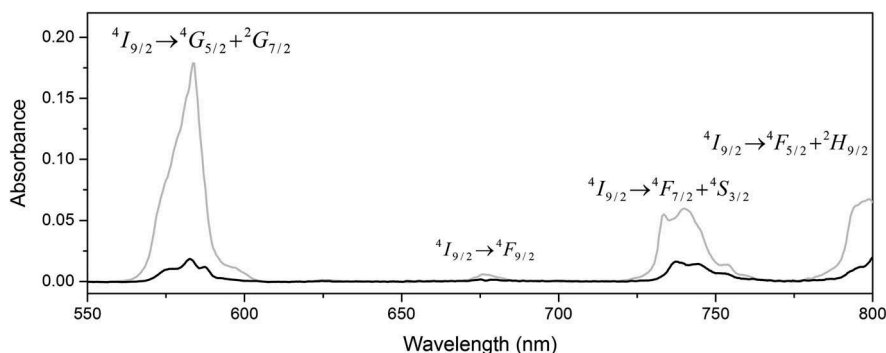


Figure 5. Absorbance spectra of Nd(III) complexes with 0.1 M T2EHDGA in *n*-dodecane extracted from 3 M NaNO₃ (gray) and 3 M HNO₃ (black). Concentration of Nd(III) in the organic phase is 8.6 and 3 mM for NaNO₃ and HNO₃, respectively.^[43,44]

collected under limiting experimental conditions to avoid the formation of third phase for HNO₃ extractions; as such, the metal concentrations in the organic phases are not equivalent.

Spectrophotometric titrations of the loaded organic phase were performed using 0.1 M T2EHDGA/*n*-dodecane conditioned by either water washing or precontacting with 3 M HNO₃ as shown in the dilution-corrected figures below. Figure 6 A and B shows no change in either the hypersensitive transition $^4I_{9/2} \rightarrow ^4G_{5/2} + ^2G_{7/2}$ nor the $^4I_{9/2} \rightarrow ^4F_{7/2} + ^4S_{3/2}$ transition with the addition of water-contacted extractant, indicating no change in neodymium speciation upon addition of organic-phase water.

However, when the extractant is titrated with preconditioned 3 M HNO₃, drastic changes to Nd (III) electronic structure are observed as shown in Fig. 6 C and D. Upon addition of the HNO₃·T2EHDGA and (HNO₃)₂·T2EHDGA species, the band at 584 nm broadens and decreases in intensity, coupled by a slight blue shift. The more interesting transition affected by the addition of HNO₃ is the peak centered around 745 nm. An isosbestic point is observed at 735 nm, indicating the presence of at least two absorbing species.

The hypersensitive band with maximum at 585 nm is very sensitive to metal complexation environment and exhibits enhanced absorbance (1) as the number of coordinated ligands around the metal increases and (2) a decrease in metal–ligand bond distance.^[44] The dilution-corrected titration spectra show a decrease in the intensity of the hypersensitive band upon addition of organic-phase HNO₃, but more significantly, an enhancement of the non-hypersensitive transition at 740 nm. Non-hypersensitive bands are affected by the presence of a center of symmetry in the coordination sphere; namely, the presence of increased symmetry about the metal causes a decrease in intensity of the non-hypersensitive bands.^[44] The opposite effect is observed with extraction of Nd (III) from HNO₃ where there is a loss of symmetry about the metal, coupled with a decrease in the number of coordinated ligands as extrapolated from the drop in absorbance of the hypersensitive band. The spectral changes are consistent with a loss of symmetry about the metal center, indicating a decrease in the number of coordinated ligands. This is likely a result of the partial dissociation of the DGA from the metal coordination sphere to accommodate an HNO₃·DGA adduct into the extracted complex as HNO₃ is titrated into the organic phase.

Conclusions

Investigation of T2EHDGA extraction behavior toward trivalent lanthanides indicates that both complexation and extraction behavior of Ln(III) are steeply dependent on NaNO₃ and HNO₃ conditions. Structural characterization using FTIR and UV-vis spectroscopies, in conjunction with SXLSQI modeling of distribution measurements, suggests that three organic-phase species are

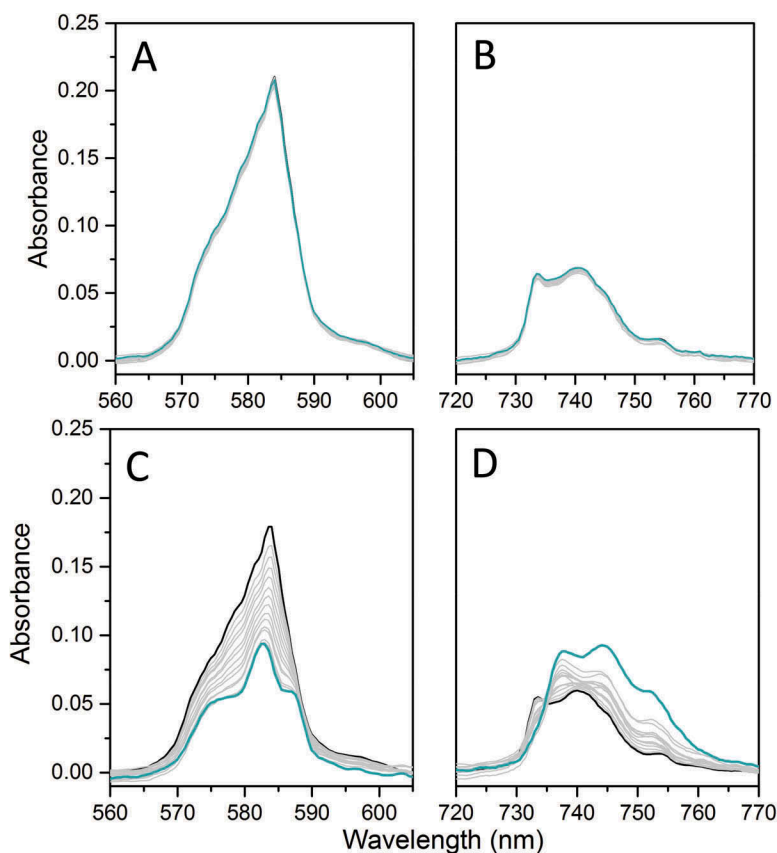


Figure 6. Dilution-corrected UV-vis spectrophotometric titration of 0.1 M T2EHDGA/*n*-dodecane after contact with 15 mM $\text{Nd}(\text{NO}_3)_3$ in 3 M NaNO_3 titrated with 0.1 M T2EHDGA/*n*-dodecane equilibrated with DI H_2O (A, B) or 3 M HNO_3 (C, D).

necessary to adequately describe the extraction of Eu(III) by T2EHDGA in *n*-dodecane from NaNO_3 and HNO_3 . Lanthanides with the coordination number of 8 or 9, as seen for Eu(III), cannot accommodate bound HNO_3 , bidentate nitrate, and bi- or tri-dentate binding of the neutral DGA in the first coordination sphere. The ligand is therefore likely to be coordinated both in the inner and in the outer coordination sphere of Eu(III).^[16] The HNO_3 in the extracted complex is likely hydrogen-bound through one of the carbonyls on the DGA, which removes one of the available oxygens for metal complexation.^[11,20] It is difficult to ascertain how the ligand is bound to the metal center, but it is apparent that the inner coordination spheres for Eu(III) extracted from NaNO_3 and HNO_3 are undeniably different and that extractant modification by the $(\text{HNO}_3)_n\text{-T2EHDGA}$ ($n = 1, 2$) adducts is responsible for enhanced extraction of Eu(III).

Acknowledgments

This work was supported by U.S. Department of Energy, Office of Nuclear Energy, through the Nuclear Technology Research and Development Program. Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC05-76RL01830.

Funding

This work was supported by U.S. Department of Energy, Office of Nuclear Energy, through the Nuclear Technology Research and Development Program.

ORCID

Emily Campbell  <http://orcid.org/0000-0002-8069-2160>
 Vanessa E. Holfeltz  <http://orcid.org/0000-0002-8938-0323>
 Gabriel B. Hall  <http://orcid.org/0000-0002-4193-7807>
 Gregg J. Lumetta  <http://orcid.org/0000-0002-0216-8515>
 Tatiana G. Levitskaia  <http://orcid.org/0000-0002-6217-3105>

References

- [1] Wigeland, R. A.; Bauer, T. H.; Fanning, T. H.; Morris, E. E. Spent Nuclear Fuel Separations and Transmutation Criteria for Benefit to a Geologic Repository. *Proceedings of Waste Management, Tuscon, Arizona, 2004*.
- [2] Nash, K. L.; The Chemistry of TALSPEAK: A Review of the Science. *Solvent Extr. Ion Exch.* **2015**, 33(1), 1–55. DOI: [10.1080/07366299.2014.985912](https://doi.org/10.1080/07366299.2014.985912).
- [3] Tachimori, S.; Morita, Y. Overview of Solvent Extraction Chemistry for Reprocessing. In *Ion Exchange and Solvent Extraction*, Vol. 19; Moyer B. A., Ed.; CRC Press: Boca Raton, **2010**; pp 1–63.
- [4] IAEA. Implication of Partitioning and Transmutation in Radioactive Waste Management. *Tech. Reports Ser.* **2004**, 435, 4–7, STI/DOC/010/435.
- [5] Weaver, B.; Kappelmann, F. A. *TALSPEAK: A New Method of Separating Americium and Curium from the Lanthanides by Extraction from an Aqueous Solution of an Aminopolyacetic Acid Complex with a Monoacidic Organophosphate or Phosphonate*; Oak Ridge, **1964**.
- [6] Pearson, G.; Hard and Soft Acids and Bases. *J. Am. Chem. Soc.* **1963**, 85(22), 3533–3539. DOI: [10.1021/ja00905a001](https://doi.org/10.1021/ja00905a001).
- [7] Clark, D. L.; The Chemical Complexities of Plutonium. *Los Alamos Sci.* **2000**, 26, 364–381.
- [8] Seaborg, G. T.; Loveland, W. D. *The Elements beyond Uranium*; Wiley & Sons: New York, **1990**.
- [9] Jensen, M. P.; Chiarizia, R.; Ulicki, J. S.; Spindler, B. D.; Murphy, D. J.; Hossain, M. M.; Roca-Sabio, A.; De Blas, A.; Rodríguez-Blas, T. Solvent Extraction Separation of Trivalent Americium from Curium and the Lanthanides. *Solvent Extr. Ion Exch.* **2015**, 33(4), 329–345. DOI: [10.1080/07366299.2015.1046292](https://doi.org/10.1080/07366299.2015.1046292).
- [10] Rydberg, J.; Cox, M.; Musikas, C.; Choppin, G. R. *Solvent Extraction Principles and Practice*, 2nd ed.; Marcel Dekker: New York, **2004**.
- [11] Yaita, T.; Herlinger, A. W.; Thiagarajan, P.; Jensen, M. P. Influence of Extractant Aggregation on the Extraction of Trivalent f-Element Cations by a Tetraalkyldiglycolamide. *Solvent Extr. Ion Exch.* **2004**, 22(4), 553–571. DOI: [10.1081/SEI-120039640](https://doi.org/10.1081/SEI-120039640).
- [12] Gujar, R. B.; Ansari, S. A.; Mohapatra, P. K.; Manchanda, V. K. Development of T2EHDGA Based Process for Actinide Partitioning. Part I: Batch Studies for Process Optimization. *Solvent Extr. Ion Exch.* **2010**, 28(3), 350–366. DOI: [10.1080/07366291003685383](https://doi.org/10.1080/07366291003685383).
- [13] Ansari, S. A.; Pathak, P.; Mohapatra, P. K.; Manchanda, V. K. Chemistry of Diglycolamides: Promising Extractants for Actinide Partitioning. *Chem. Rev.* **2012**, 112(3), 1751–1772. DOI: [10.1021/cr200002f](https://doi.org/10.1021/cr200002f).
- [14] Gelis, A. V.; Lumetta, G. J. Actinide Lanthanide Separation Process - ALSEP. *Ind. Eng. Chem. Res.* **2014**, 53(4), 1624–1631. DOI: [10.1021/ie403569e](https://doi.org/10.1021/ie403569e).
- [15] Kawasaki, T.; Okumura, S.; Sasaki, Y.; Ikeda, Y. Crystal Structures of Ln(III) (Ln = La, Pr, Nd, Sm, Eu, and Gd) Complexes with N,N,N',N'-Tetraethyldiglycolamide Associated with Homoleptic [Ln(No³)₆]³⁻. *Bull. Chem. Soc. Jpn.* **2014**, 87(2), 294–300. DOI: [10.1246/bcsj.20130259](https://doi.org/10.1246/bcsj.20130259).
- [16] Sasaki, Y.; Rapold, P.; Arisaka, M.; Hirata, M.; Kimura, T.; Hill, C.; Cote, G. An Additional Insight into the Correlation between the Distribution Ratios and the Aqueous Acidity of the TODGA System. *Solvent Extr. Ion Exch.* **2007**, 25(2), 187–204. DOI: [10.1080/07366290601169345](https://doi.org/10.1080/07366290601169345).
- [17] Pathak, P. N.; Ansari, S. A.; Mohapatra, P. K.; Manchanda, V. K.; Patra, A. K.; Aswal, V. K. Role of Alkyl Chain Branching on Aggregation Behavior of Two Symmetrical Diglycolamides: Small Angle Neutron Scattering Studies. *J. Colloid Interface Sci.* **2013**, 393(1), 347–351. DOI: [10.1016/j.jcis.2012.10.023](https://doi.org/10.1016/j.jcis.2012.10.023).
- [18] Jensen, M. P.; Yaita, T.; Chiarizia, R. Reverse-Micelle Formation in the Partitioning of Trivalent F-Element Cations by Biphasic Systems Containing a Tetraalkyldiglycolamide. *Langmuir*. **2007**, 23(9), 4765–4774. DOI: [10.1021/la0631926](https://doi.org/10.1021/la0631926).
- [19] Antonio, M. R.; McAlister, D. R.; Horwitz, E. P. An Europium(III) Diglycolamide Complex: Insights into the Coordination Chemistry of Lanthanides in Solvent Extraction. *Dalton Trans.* **2015**, 44(2), 515–521. DOI: [10.1039/C4DT01775G](https://doi.org/10.1039/C4DT01775G).

- [20] Nave, S.; Modolo, G.; Madic, C.; Testard, F. Aggregation Properties of *N, N, N', N'*-Tetraoctyl-3-oxapentane-diamide (TODGA) in *n*-Dodecane. *Solvent Extr. Ion Exch.* **2004**, *22*(4), 527–551. DOI: [10.1081/SEI-120039721](https://doi.org/10.1081/SEI-120039721).
- [21] Ansari, S. A.; Mohapatra, P. K.; Prabhu, D. R.; Manchanda, V. K. Transport of Americium(III) through a Supported Liquid Membrane Containing *N,N,N',N'*-tetraoctyl-3-Oxapentane Diamide (TODGA) in *N*-Dodecane as the Carrier. *J. Memb. Sci.* **2006**, *282*(1–2), 133–141. DOI: [10.1016/j.memsci.2006.05.013](https://doi.org/10.1016/j.memsci.2006.05.013).
- [22] Campbell, E. L.; Holfeltz, V. E.; Hall, G.; Nash, K. L.; Lumetta, G. J.; Levitskaia, T. G. Nitric Acid and Water Extraction by T2EHDGA in *n*-Dodecane. *Solvent Extr. Ion Exch.* **2017**, *35*(7), 586–603. DOI: [10.1080/07366299.2017.1400161](https://doi.org/10.1080/07366299.2017.1400161).
- [23] Baes, C. F.; *SXLSQL, A Program for Modeling Solvent Extraction Systems*; ORNL/TM-13604, Oak Ridge National Laboratory: Oak Ridge, TN, **1998**.
- [24] Herbst, R. S.; Peterman, D. R.; Zalupski, P. R.; Nash, K. L.; Tillotson, R. D.; Delmau, L. H. Thermodynamics of Cesium Extraction from Acidic Media by HCCD and PEG. *Solvent Extr. Ion Exch.* **2010**, *28*(5), 563–578. DOI: [10.1080/07366299.2010.502865](https://doi.org/10.1080/07366299.2010.502865).
- [25] Pitzer, K.; *Activity Coefficients in Electrolyte Solutions*, 2nd ed.; Pitzer K. S., Ed.; CRC Press: Boca Raton, **1991**.
- [26] Millero, F. J.; *Water and Aqueous Solutions*; Horne, R. A., Ed.; Wiley-Interscience: New York, **1971**.
- [27] Barton, A. F. M.; *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC Press: Boca Raton, **1991**.
- [28] Deepika, P.; Sabharwal, K. N.; Srinivasan, T. G.; Vasudeva Rao, P. R. Studies on the Use of *N, N, N', N'*-Tetra(2-Ethylhexyl) Diglycolamide (TEHDGA) for Actinide Partitioning II: Investigation on Radiolytic Stability. *Solvent Extr. Ion Exch.* **2011**, *29*(2), 230–246. DOI: [10.1080/07366299.2011.539145](https://doi.org/10.1080/07366299.2011.539145).
- [29] Sasaki, Y.; Sugo, Y.; Suzuki, S.; Kimura, T. A Method for the Determination of Extraction Capacity and Its Application to *N,N,N',N'*-Tetraalkylderivatives of Diglycolamide-Monoamide/*n*-Dodecane Media. *Anal. Chim. Acta.* **2005**, *543*(1–2), 31–37. DOI: [10.1016/j.aca.2005.04.061](https://doi.org/10.1016/j.aca.2005.04.061).
- [30] Gujar, R. B.; Ansari, S. A.; Murali, M. S.; Mohapatra, P. K.; Manchanda, V. K. Comparative Evaluation of Two Substituted Diglycolamide Extractants for “Actinide Partitioning.”. *J. Radioanal. Nucl. Chem.* **2010**, *284*(2), 377–385. DOI: [10.1007/s10967-010-0467-y](https://doi.org/10.1007/s10967-010-0467-y).
- [31] Berthon, L.; Martinet, L.; Testard, F.; Madic, C.; Zemb, T. Solvent Penetration and Sterical Stabilization of Reverse Aggregates Based on the DIAMEX Process Extracting Molecules: Consequences for the Third Phase Formation. *Solvent Extr. Ion Exch.* **2007**, *25*, 545–576. DOI: [10.1080/07366290701512576](https://doi.org/10.1080/07366290701512576).
- [32] Ravi, J.; Venkatesan, K. A.; Antony, M. P.; Srinivasan, T. G.; Vasudeva Rao, P. R. Tuning the Diglycolamides for Modifier-Free Minor Actinide Partitioning. *J. Radioanal. Nucl. Chem.* **2013**, *295*(2), 1283–1292. DOI: [10.1007/s10967-012-1905-9](https://doi.org/10.1007/s10967-012-1905-9).
- [33] Reilly, S. D.; Gaunt, A. J.; Scott, B. L.; Modolo, G.; Iqbal, M.; Verboom, W.; Sarsfield, M. J. Plutonium(IV) Complexation by Diglycolamide Ligands—Coordination Chemistry Insight into TODGA-Based Actinide Separations. *Chem. Commun.* **2012**, *48*(78), 9732. DOI: [10.1039/c2cc34967a](https://doi.org/10.1039/c2cc34967a).
- [34] Mowafy, E. A.; Mohamed, D. Extraction of Rare Earth Elements from Nitrate Solution Using Novel Unsymmetrical Diglycolamide. *Sep. Sci. Technol.* **2017**, *52*(6), 1006–1014. DOI: [10.1080/01496395.2016.1274760](https://doi.org/10.1080/01496395.2016.1274760).
- [35] Mowafy, E. A.; Aly, H. F. Extraction Behaviours of Nd(III), Eu(III), La(III), Am(III), and U(VI) with Some Substituted Malonamides from Nitrate Medium. *Solvent Extr. Ion Exch.* **2002**, *20*(2), 177–194. DOI: [10.1081/SEI-120003020](https://doi.org/10.1081/SEI-120003020).
- [36] Mowafy, E. A.; Mohamed, D. Extraction and Separation of Nd(III), Sm(III), Dy(III), Fe(III), Ni(II), and Cs(I) from Concentrated Chloride Solutions with *N,N,N',N'*-tetra(2-Ethylhexyl) Diglycolamide as New Extractant. *J. Rare Earths.* **2015**, *33*(4), 432–438. DOI: [10.1016/S1002-0721\(14\)60437-3](https://doi.org/10.1016/S1002-0721(14)60437-3).
- [37] Mowafy, E. A.; Mohamed, D. Extraction Behavior of Trivalent Lanthanides from Nitric Acid Medium by Selected Structurally Related Diglycolamides as Novel Extractants. *Sep. Purif. Technol.* **2014**, *128*, 18–24. DOI: [10.1016/j.seppur.2014.03.005](https://doi.org/10.1016/j.seppur.2014.03.005).
- [38] Curtis, N. F.; Curtis, Y. M. Some Nitrate-Amine Nickel(II) Compounds with Monodentate and Bidentate Nitrate Ions. *Inorg. Chem.* **1965**, *4*(6), 804–809. DOI: [10.1021/ic50028a007](https://doi.org/10.1021/ic50028a007).
- [39] Gatehouse, B. B. M.; Nyholm, R. S. Gatehouse, Livingstone, and Nyholm : Infrared Spectra of Some Nitrate-Co-Ordination Complexes. *J. Chem. Soc.* **1956**, *4222*, 4222–4225.
- [40] Chiarizia, R.; Jensen, M. P.; Borkowski, M.; Ferraro, J. R.; Thiyagarajan, P.; Littrell, K. C. Third Phase Formation Revisited: The U(VI), HNO₃–TBP, *n*-Dodecane System. *Solvent Extr. Ion Exch.* **2003**, *21*(1), 1–27. DOI: [10.1081/SEI-120017545](https://doi.org/10.1081/SEI-120017545).
- [41] Narita, H.; Yaita, T.; Tamura, K.; Tachimori, S. Study on the Extraction of Trivalent Lanthanide Ions with *N, N'*-dimethyl-*N, N'*-diphenyl-Malonamide and -Diglycolamide. *J. Radioanal. Nucl. Chem.* **1999**, *239*(2), 38–41. DOI: [10.1007/BF02349516](https://doi.org/10.1007/BF02349516).
- [42] Borkowski, M.; Ferraro, J. R.; Chiarizia, R.; McAlister, D. R. FT-IR Study of Third Phase Formation in the U(VI) or Th(IV)/HNO₃, TBP/Alkane Systems. *Solvent Extr. Ion Exch.* **2002**, *20*(3), 313–330. DOI: [10.1081/SEI-120004807](https://doi.org/10.1081/SEI-120004807).

- [43] Song, X.-Q.; Liu, W.-S.; Dou, W.; Zheng, J.-R.; Tang, X.-L.; Zhang, H.-R.; Wang, D.-Q. Tuning the Self-Assembly and Luminescence Properties of Lanthanide Coordination Polymers by Ligand Design. *Dalton Trans.* **2008**, 27, 3582–3591. DOI: [10.1039/b800217g](https://doi.org/10.1039/b800217g).
- [44] Henrie, D. E.; Fellows, R. L.; Choppin, G. R. Hypersensitivity in the Electronic Transitions of Lanthanide and Actinide Complexes. *Coord. Chem. Rev.* **1976**, 18(2), 199–224. DOI: [10.1016/S0010-8545\(00\)82044-5](https://doi.org/10.1016/S0010-8545(00)82044-5).
- [45] Chatterjee, S.; Campbell, E. L.; Neiner, D.; Pence, N. K.; Robinson, T. A.; Levitskaia, T. G. Aqueous Binary Lanthanide(III) Nitrate $\text{Ln}(\text{NO}_3)_3$ Electrolytes Revisited: Extended Pitzer and Bromley Treatments. *J. Chem. Eng. Data.* **2015**, 60(10), 2974–2988. DOI: [10.1021/acs.jced.5b00392](https://doi.org/10.1021/acs.jced.5b00392).
- [46] Andersson, S.; Eberhardt, K.; Ekberg, C.; Liljenzin, J. O.; Nilsson, M.; Skarnemark, G. Determination of Stability Constants of Lanthanide Nitrate Complex Formation Using a Solvent Extraction Technique. *Radiochim. Acta.* **2006**, 94, 469–474.