

Influence of Aqueous Phase Acidity on Ln(III) Coordination by *N,N,N',N'*-Tetraoctyldiglycolamide

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ABSTRACT: This study highlights the importance of combining distribution ratio measurements with multiple spectroscopic techniques to provide a more comprehensive understanding of organic phase Ln coordination chemistry. Solvent extraction investigations with *N,N,N',N'*-tetraoctyldiglycolamide (TODGA) in *n*-heptane reveal the sensitivity of Ln complexation to the HNO₃ concentration. Distribution ratio measurements in tandem with UV–Vis demonstrated that increasing the concentration of HNO₃ above 0.5 M with a constant NO₃[−] of 1 M increases the number of coordinating TODGA molecules, from a 1:2 to a 1:3 Ln:TODGA complex. At each concentration of HNO₃ considered herein (from 0.01 to 1 M), Eu lifetime analysis demonstrated no evidence of H₂O coordination. Results from Fourier transform infrared investigations suggest the presence of inner-sphere NO₃[−] under low concentrations of HNO₃ when the 1:2 Ln:TODGA complex is present. Increasing the HNO₃ concentration above 0.5 M increases the propensity for outer-sphere interactions by removing the coordinated NO₃[−] and saturating the Ln coordination sphere with three TODGA molecules, resulting in the well-established cationic, trischelate homoleptic [Ln(TODGA)₃]³⁺ complex. This work demonstrates the importance in considering the NO₃[−] source for solvent extraction systems. In particular, for systems with an affinity for outer-sphere interactions with molar concentrations of HNO₃, changing the NO₃[−] source can change the inner-sphere coordination of the Ln complex, which, in turn, affects the separation efficacy.

The urgent need to enhance intralanthanide separations is driven by the emerging clean energy, digital technology, and medical isotopes industries, which demand high purity of individual lanthanides (Ln).^{1,2} Recent studies have identified diglycolamides, particularly *N,N,N',N'*-tetraoctyldiglycolamide (TODGA), as a promising extractant for Ln separations.^{3,4} Understanding Ln complexation in extraction conditions is crucial for improving separations, but investigating organic phase coordination chemistry, especially with neutral extractants like TODGA, can be challenging.^{5,6} Complex speciation resulting from large amounts of H₂O and HNO₃ in addition to Ln being extracted poses difficulties, necessitating the use of a combination of analytical techniques to gain a comprehensive understanding of organic phase chemistry.

Previous work has focused on investigating Ln coordination in TODGA systems from extraction from high HNO₃ concentrations. Under these conditions, multiple spectroscopic techniques have been utilized [i.e., extended X-ray absorption fine structure, Fourier transform infrared (FT-IR), and time-resolved laser-induced fluorescence spectroscopy (TRLIFS)] in tandem with distribution ratio extractant dependence to determine Ln coordination in nonpolar paraffinic organic phases.^{4,7–12} These studies demonstrated that Ln are extracted by TODGA in a cationic, trischelate homoleptic complex, [Ln(TODGA)₃]³⁺, with outer-sphere NO₃[−] located in the clefts between TODGA alkyl tails.¹³ Sasaki et al. proposed that extraction of significant amounts of HNO₃ along with the Ln facilitates formation of the 1:3 [Ln(TODGA)₃]³⁺ complex.¹⁴ A standard method for studying Ln coordination in intricate solvent extraction organic phases involves substituting HNO₃ with a related NO₃[−] salt like LiNO₃ or NaNO₃.^{15,16} It is

essential to grasp the significance of using HNO₃ versus LiNO₃ in these investigations.

In this study, we investigate the impact of varying aqueous phase HNO₃ concentrations on the extracted Ln complex in TODGA with *n*-heptane organic phases. The role of HNO₃ was systematically examined by adjusting its concentration from 0.01 to 1 M, while keeping the NO₃[−] concentration constant at 1 M with LiNO₃. Distribution ratios were measured at different TODGA concentrations to evaluate the number of TODGA molecules coordinating to Ln under varying HNO₃ levels. UV–Vis, TRLIFS, and FT-IR spectroscopic methods were employed to analyze changes in the Ln coordination sphere and study the complexation of H₂O and NO₃[−] with specific Ln. Combining distribution ratio measurements with spectroscopic analysis offers a comprehensive exploration of how Ln complexes evolve in response to HNO₃ concentrations.

To evaluate the role of HNO₃ on the complexation of Ln by TODGA, a slope dependence study was conducted where the concentration of TODGA was varied from 0.03 to 0.2 M in *n*-heptane with a constant aqueous phase of either 0.01 M HNO₃ + 0.99 M LiNO₃ or 1 M HNO₃ (Figure 1). The linear relationship between log *D*_{Ln} and log [TODGA] is dependent

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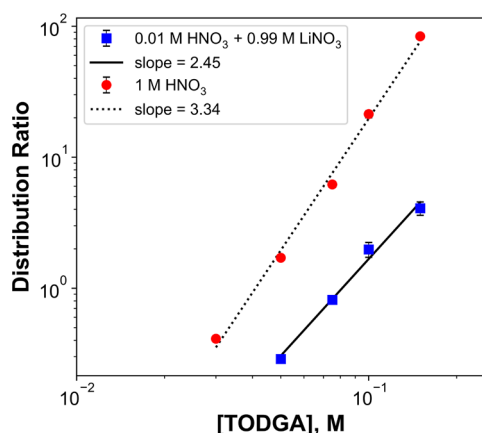


Figure 1. TODGA dependence on D_{Nd} from 0.01 M HNO_3 (blue squares) and 1 M HNO_3 (red circles), with a constant $[\text{NO}_3^-]$ of 1 M.

on the concentration of HNO_3 , resulting in a slope of 2.45 for 0.01 M HNO_3 + 0.99 M LiNO_3 and a slope of 3.34 for 1 M HNO_3 . The values obtained for the TODGA dependence with 1 M HNO_3 reported herein are consistent with the literature for Ln extraction from molar concentrations of HNO_3 in diglycolamide systems.⁸ However, it is important to note that the TODGA dependence for 0.01 M HNO_3 + 0.99 M LiNO_3 significantly decreases for Ln complexes in *n*-alkane solutions, which was not previously observed. Changes in the extractant slope dependence are generally considered to be a product of changing the number of coordinating extractant molecules to the selected metal. This suggests the formation of 1:2 Ln:TODGA complexes with 0.01 M HNO_3 + 0.99 M LiNO_3 and 1:3 complexes for 1 M of HNO_3 . However, a change in the organic phase composition impacting activity or the relative concentration of free TODGA monomers (TODGA not protonated by HNO_3) with increasing TODGA are potential explanations for deviations in the extractant dependence. Because it is ambiguous from the slope analysis alone whether the TODGA stoichiometry varies between the aqueous acidities considered, we now perform a spectroscopic investigation of the Ln complexes.

The combination of the extractant slope dependence with spectroscopic investigations, such as UV–Vis, enables determination of whether the change in the slope is a product of changing the Ln inner-sphere complexation. Select Ln that exhibit hypersensitive absorption bands (such as Nd) enable

utilization of UV–Vis spectroscopy to determine whether the inner-sphere complex is changing.¹⁹ Absorption spectra after Nd extraction by 0.2 M TODGA in *n*-heptane were collected as a function of the HNO_3 concentration (Figure 2). Under dilute concentrations of HNO_3 , the Nd spectra exhibit peaks at 515, 525, and 584 nm, with two shoulders observed at 575 and 588 nm. Tracking the peak evolution with an increase in HNO_3 involved analysis of the changes in the molar absorptivity at 575 and 588 nm (Figure 3b). Increasing the concentration of HNO_3 increases the 588 peak, while decreasing the 575 peak. The spectral transition from a maximum peak at 584 nm with two shoulders to the appearance of three distinct peaks at 575, 584, and 588 nm is consistent with lowering the symmetry of Nd as a result of increasing the ligand coordination.¹¹

Sengupta et al. performed a spectrophotometric titration of TODGA in a Nd/methanol solution with 0.01 M tetramethylammonium nitrate to identify the Nd UV–Vis spectra corresponding to the 1:2 and 1:3 Nd:TODGA complexes.²⁰ The Nd UV–Vis spectrum reported herein at 0.01 M HNO_3 + 0.99 M LiNO_3 and 1 M HNO_3 is consistent with the spectra corresponding to 1:2 and 1:3 Nd:TODGA complexes, respectively. Increasing $[\text{LiNO}_3]$ from 1 to 3 M did not result in a change in the Nd absorption spectrum (Figure S1). Therefore, higher NO_3^- concentrations do not change the extracted Nd complex or result in the 1:3 complex formed at sufficient HNO_3 concentration. Meanwhile, increasing the HNO_3 concentration from 1 to 3 M resulted in small spectral differences that do not indicate a new complex but could instead be explained by an increased fraction of 1:3 complexes or the influence of outer-sphere hydrogen-bonding interactions stabilizing the M:L complex.^{11,17,18,21} The results from both solvent extraction and UV–Vis absorption spectra suggest that increasing the concentration of HNO_3 above 0.5 M increases the number of coordinating TODGA molecules, where a transition from 1:2 and 1:3 Nd:TODGA complexes is observed. A different Nd spectrum in either NaNO_3 or LiNO_3 has previously been reported in comparison to HNO_3 .^{11,15} However, the link between the different spectra and the corresponding Nd:TODGA complexes was not discussed.

The impact of HNO_3 concentrations on D_{Nd} for an organic phase of 0.2 M TODGA in *n*-heptane is reported in Figure 3a. Increasing the concentration of HNO_3 from 0.01 to 0.3 M slightly increases D_{Nd} , until the HNO_3 concentration exceeds 0.5 M, where D_{Nd} increases by an order of magnitude between

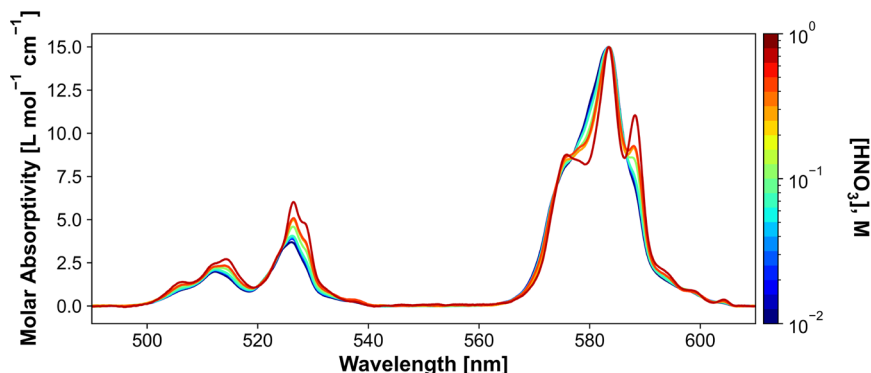


Figure 2. Evolution of the Nd absorption spectra as a function of increasing HNO_3 concentration from 0.01 to 1 M, while maintaining a constant $[\text{NO}_3^-]$ of 1 M. The organic phase consisted of 0.2 M TODGA in *n*-heptane.

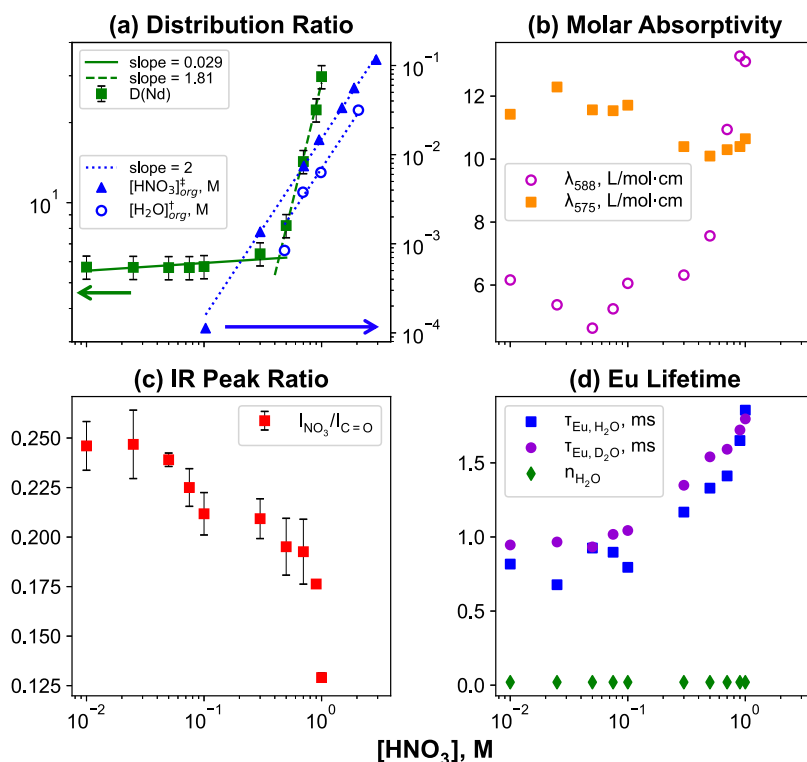


Figure 3. (a) Distribution ratios (this work). $^{\dagger}\text{H}_2\text{O}$ extraction from Jensen et al.¹⁷ with additional background water content correction (see text). $^{\ddagger}\text{HNO}_3$ extraction from Campbell et al.¹⁸ (b) Nd hypersensitive peak intensities, (c) IR peak ratios, and (d) Eu lifetimes as a function of the initial HNO_3 concentration with a constant $[\text{NO}_3^-]$ of 1 M. Organic phase: 0.2 M TODGA in *n*-heptane.

0.5 and 1 M HNO_3 . The shape of the dependence of D_{Nd} on $[\text{HNO}_3]$, where crossover is observed between power laws, suggests multiple extracted species. The obtained D_{Nd} values were compared to refit the literature values for HNO_3 ¹⁸ and H_2O ¹⁷ extraction in the absence of metals (Figure 3a). (For the acid concentration dependence of water extraction, we subtract the background water content (0.018 M) that is extracted by DGA in the absence of acid.) The extracted HNO_3 and H_2O concentrations show power law behavior as a function of $[\text{HNO}_3]$ with consistent slopes across all of $[\text{HNO}_3]$, suggesting that the extraction mechanism does not depend on the acid concentration. Because the Nd concentration is small compared to HNO_3 and H_2O , except at the smallest acid concentrations, we do not expect acid and water speciation to depend strongly on the amount of Nd extracted. While the total NO_3^- concentration is fixed, the transition from a slope (for D_{Nd} on the HNO_3 concentration) of nearly 0 to a slope of ~ 2 reveals the onset of a complex, including, presumably, additional associated nitric acid molecules. This finding is consistent with the literature where the role of HNO_3 on D_{Ln} has been emphasized, particularly for molar concentrations of HNO_3 .^{14,22} The onset of the 1:3 Nd:TODGA complex at the same HNO_3 concentration, noted above from the UV–Vis spectra, suggests that the inclusion of additional nitric acid and H_2O in the complex stabilizes—or is stabilized by—the 1:3 complex over the 1:2 complex.

Because the maximum coordination number of TODGA is 3, through each oxygen atom, the formation of 1:2 complexes at most would result in a Ln coordination number of 6, allowing for NO_3^- and/or H_2O coordination. To investigate NO_3^- coordination under these systems, FT-IR spectra were

measured on organic phases after HNO_3 and Nd extraction. Differences between these spectra are indicative of changes within the organic phase coordination and, more importantly, can provide insight if NO_3^- are coordinating to Ln.^{16,23,24} A comparison of the results obtained after Ln extraction to those after HNO_3 extraction (Figure S2) demonstrates several changes. The first occurs at 1650 cm^{-1} , associated with the TODGA C=O vibrational stretch, which after Ln extraction red-shifts to 1608 cm^{-1} . This red shift by approximately 50 cm^{-1} suggests coordination of the C=O moiety to Ln.

While the coordination of TODGA C=O moieties is expected, the appearance of multiple peaks from 700 to 1400 cm^{-1} suggests coordination of NO_3^- to Ln as well.^{16,23,24} The location of the NO_3^- peak can be used to determine the denticity of NO_3^- to Ln. Monodentate nitrate ($\text{K}^1\text{-NO}_3$) has signature peaks at 818 , 1325 , and 1460 cm^{-1} , whereas bidentate nitrate ($\text{K}^2\text{-NO}_3$) has peaks at 818 , 1291 , and 1504 cm^{-1} .^{23,24} The appearance of both monodentate and bidentate NO_3^- is evident from the appearance of peaks at 1325 and 1510 cm^{-1} . Through a comparison of the intensities of the NO_3^- peak at 1325 cm^{-1} to the associated Ln–O=C vibrational stretch at 1608 cm^{-1} , the trend in Ln– NO_3^- coordination with increasing HNO_3 can be approximated (Figure 3c). Increasing the concentration of HNO_3 decreases the relative peak ratios of Ln– NO_3^- to Ln–O=C. This suggests that increasing the concentration of HNO_3 decreases the propensity for Ln– NO_3^- coordination. A comparison of the FT-IR results to those obtained by UV–Vis and TODGA dependence indicates that increasing the concentration of HNO_3 at a constant NO_3^- of 1 M increases the number of TODGA molecules coordinating while decreasing NO_3^- coordination.

The final piece to understanding organic phase Ln complexation in TODGA systems is to determine whether H₂O is coordinating to Ln. This involves conducting organic phase TRLIFS lifetime measurements after Eu extraction from both H₂O and D₂O (Figure S3), where observed differences are related to the number of coordination H₂O molecules through eq S2. The obtained Eu lifetimes (milliseconds) from H₂O and D₂O with 0.01–1 M HNO₃ and the number of coordinating H₂O molecules are reported in Figure 3d and Table S1. Lifetime analysis demonstrated that from 0.01 to 1 M HNO₃, zero H₂O molecules coordinate to Eu. It should be pointed out that while the number of coordinating H₂O molecules is not changing, the Eu lifetimes increase from 0.82 to 1.86 ms with increasing HNO₃ (Figure 3d). An increase in lifetime when the number of H₂O is not changing has previously been attributed to an increase in the number of coordinating ligands.²⁵

This study has demonstrated the sensitivity of organic phase Ln complexes to the HNO₃ concentration at fixed [NO₃[−]] in TODGA/*n*-heptane systems. Extraction of Ln with low acid (0.01–0.1 M HNO₃) results in a decreased number of coordinating TODGA molecules along with coordinating NO₃[−]. Increasing the concentration of HNO₃ above 0.5 M increases the number of coordinating TODGA and decreases the number of coordinating NO₃[−]. The conditions studied herein resulted in zero coordinating H₂O molecules to Ln. Leveraging the combination of distribution ratio measurements with spectroscopic techniques demonstrated an effective approach for determining inner-sphere Ln coordination in complex organic phases. This work emphasizes the importance of considering a NO₃[−] source when conducting solvent extraction experiments because it can change the inner-sphere Ln coordination. Particularly for systems like diglycolamides with a propensity for outer-sphere interactions, the NO₃[−] source impacts the separation efficacy.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.4c01006>.

Experimental procedures and additional characterization of organic phases by TRLIFS and FT-IR spectroscopy (PDF)

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Notes

The authors declare no competing financial interest.

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