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 sensitivity of Ln complexation to HNO_3 concentration. Distribution ratio measurements in tandem with UV-Vis demonstrated that increasing the concentration of HNO_3 above 0.5 M with constant NO_3^- 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 HNO_3 considered herein (from 0.01 to 1 M), Eu lifetime analysis demonstrated no evidence of H_2O coordination. Results from FT-IR investigations suggest the presence of inner-sphere NO_3^- under low concentrations of HNO_3, when the 1:2 Ln:TODGA complex is present. Increasing the HNO_3 concentration above 0.5 M, increases the propensity for outer-sphere interactions by removing the coordinated NO_3^- and saturating the Ln coordination sphere with 3 TODGA molecules resulting in the well-established cationic, trischelate homoleptic $[Ln(TODGA)_3]^{3+}$ complex. This work demonstrates the importance in considering NO_3^- source for solvent extraction systems. In particular, for systems with an affinity for outer-sphere interactions with molar concentrations of HNO_3, changing the NO_3^- source can change the inner-sphere coordination of the Ln complex, which in turn affects the separations efficacy.

The urgent need to enhance intra-lanthanide separations is driven by emerging clean energy, digital technology, and medical isotopes industries, which demand high purity of individual lanthanides (Lns).[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 H_2O and HNO_3 in addition to Lns 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 HNO_3 concentrations. Under these conditions multiple spectroscopic techniques have been utilized (i.e., EXAFS, FT-IR, TRLIFS) in tandem with distribution ratio extractant dependence to determine Ln coordination in non-polar paraffinic organic phases.[4,7–12] These studied demonstrated that Lns are extracted by TODGA in a cationic, trischelate homoleptic complex $[Ln(TODGA)_3]^{3+}$, with outer-sphere NO_3^- located in the clefts between TODGA alkyl tails.[13] Sasaki et al. proposed that the extraction of significant amounts of HNO_3 along with the Lns facilitate 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 HNO_3 with a related NO_3 salt like $LiNO_3$ or $NaNO_3$.[15,16] It is essential to grasp the significance of using HNO_3 versus $LiNO_3$ in these investigations.

In this study, we investigate the impact of varying aqueous phase HNO_3 concentrations on the extracted Ln complex in TODGA with *n*-heptane organic phases. The role of HNO_3 was systematically examined by adjusting its concentration from 0.01 to 1 M, while keeping the NO_3^- concentration constant at 1 M with $LiNO_3$. Distribution ratios were measured at different TODGA concentrations to evaluate the number of TODGA molecules coordinating to Lns under varying HNO_3 levels. UV-Vis, TRLIFS, and FT-IR spectroscopic methods were employed to analyze changes in the Ln coordination sphere and to study the complexation of H_2O and NO_3^- with specific Lns. Combining distribution ratio measurements with spectroscopic analysis offers a comprehensive exploration of how Ln complexes evolve in response to HNO_3 concentrations.

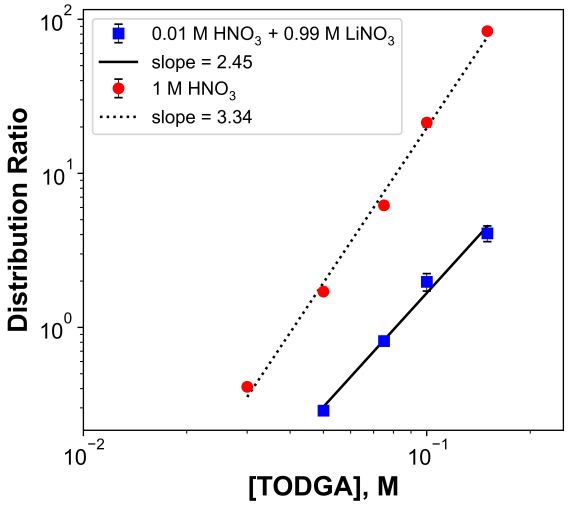

Figure 1. TODGA dependence on D_{Nd} from 0.01 M HNO_3 (blue squares) and 1 M HNO_3 (red circles), with constant $[NO_3^-]$ of 1 M.

To evaluate the role of HNO_3 on complexation of Ln by

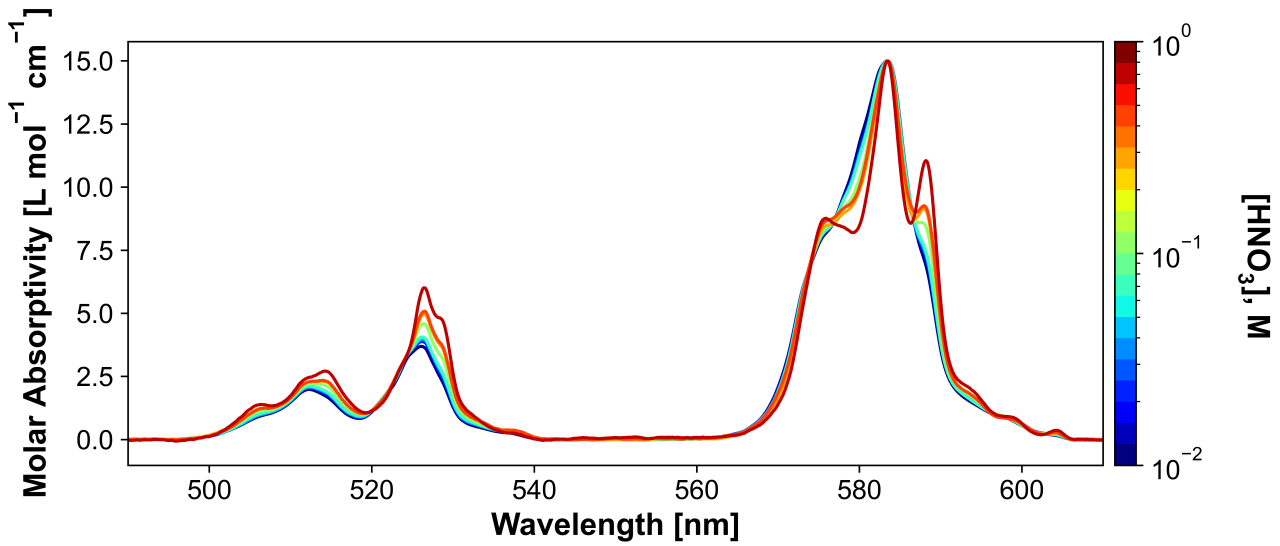

Figure 2. Evolution of Nd absorption spectra as a function of increasing HNO_3 concentration from 0.01-1 M, while maintaining a constant [NO_3^-] of 1 M. Organic phase consisted of 0.2 M TODGA in *n*-heptane.

TODGA, a slope dependence study was conducted where the concentration of TODGA was varied from 0.03-0.2 M in *n*-heptane with a constant aqueous phase of either 0.01 M HNO_3 + 0.99 M $LiNO_3$ or 1 M HNO_3 (Figure 1). The linear relationship between log D_{Ln} and log [TODGA] is dependent on 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 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 has not been previously observed. Changes in the extractant slope dependence is 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 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 extractant dependence. As it is ambiguous from the slope analysis alone if the TODGA stoichiometry varies between the aqueous acidities considered, we now perform a spectroscopic investigation of the Ln complexes.

The combination of extractant slope dependence with spectroscopic investigations, such as UV-Vis enables determining if the change in the slope is a product of changing the Ln inner-sphere complexation. Select Lns that exhibit hypersensitive absorption bands (such as Nd) enable utilizing UV-Vis spectroscopy to determine if 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 HNO_3 concentration (Figure 2). Under dilute concentrations of HNO_3, the Nd spectra exhibits peaks at 515, 525, and 584 nm, with two shoulders observed at 575 and 588 nm. Tracking the peak evolution with increase in HNO_3, involved analyzing changes in the molar absorptivity at 575 and 588 nm (Figure 3b). Increasing the concentration of HNO_3 increased 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 from increasing ligand coordination.[11]

Sengupta et al. performed a spectrophotometic titration of TODGA into a Nd methanol solution with 0.01 M tetramethyl ammonium 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 $LiNO_3$ and 1 M HNO_3 are consistent with the spectra corresponding to 1:2 and 1:3 Nd:TODGA complexes, respectively. Increasing [$LiNO_3$] from 1 to 3 M did not result in a change in the Nd absorption spectrum (Figure S1). Therefore, additional NO_3^- concentration does 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 M 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] 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 spectra 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 the D_{Nd}, until the HNO_3 concentration exceeds 0.5 M, where the D_{Nd} increases by an order of magnitude between 0.5 and 1 M HNO_3. The shape of the dependence of D_{Nd} on [HNO_3], where as crossover is observed between power laws, suggests multiple extracted species. The obtained D(Nd) were compared to refit literature values for HNO_3[18] and H_2O[17] extraction in the absence of metals (Figure 3a). (For the acid concentration depen-

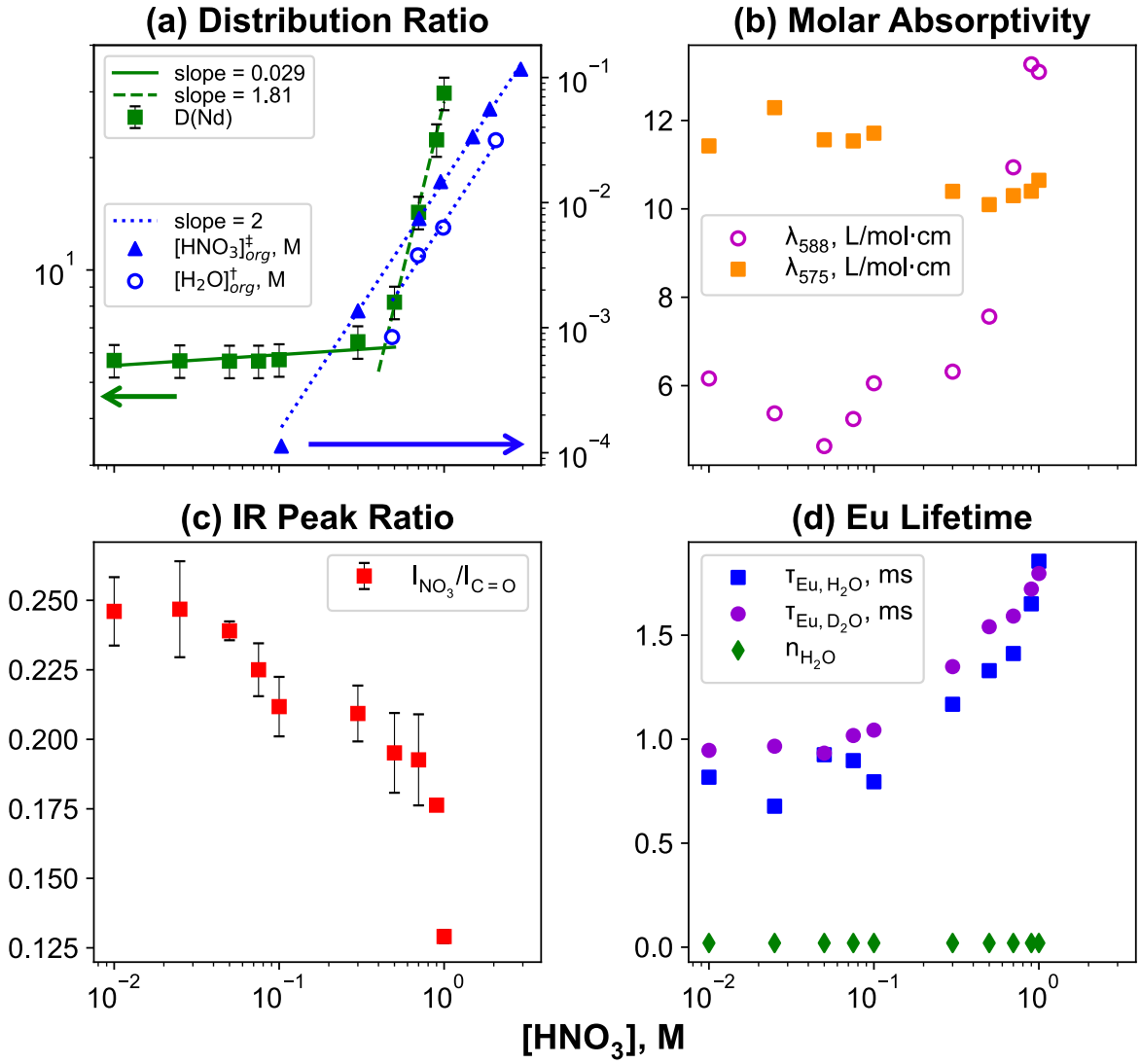

Figure 3. (a) Distribution ratios (this work), $^{\dagger}H_2O$ extraction from Jensen et al. [17] with additional background water content correction (see text), and $^{\ddagger}HNO_3$ extraction from Campbell et al., [18] (b) Nd hypersensitive peak intensities, (c) IR peak ratios, and (d) Eu lifetimes as a function of initial HNO_3 concentration with constant $[NO_3^-]$ of 1 M. Organic phase, 0.2 M TODGA in *n*-heptane.

dence of the 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 $[HNO_3]$ with consistent slopes across all $[HNO_3]$, suggesting that the extraction mechanism does not depend on acid concentration. As 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 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 the inclusion of the additional nitric acid and H_2O in the complex stabilizes—or is stabilized by—the 1:3 complex over the 1:2.

As the maximum coordination number of TODGA is three, through each oxygen atom, the formation of 1:2 complexes at most would result in a Ln coordination number of six 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 extraction 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 Lns. [16,23,24] Comparison of the results obtained after Ln extraction to those after HNO_3 extraction (Figure S2) demonstrate several changes. The first occurs at 1650 cm^{-1}, associated with the TODGA C=O vibration stretch, which after Ln extraction red-shifts to 1608 cm^{-1}. This red-shift by approximately 50 cm^{-1} suggests coordination of C=O moiety to Lns.

While the coordination of TODGA C=O moieties is expected, the appearance of multiple peaks from 700-1400 cm^{-1} suggest 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 Lns. Monodentate nitrate (K^1-NO_3) has signa-

ture peaks at 818, 1325, and 1460 cm^{-1}, whereas bidentate nitrate (K^2-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 comparing 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. Comparison of 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 if H_2O is coordinating to Lns. This involves conducting organic phase TRLIFS lifetime measurements after Eu extraction from both H_2O and D_2O (Figure S3), where observed differences are related to the number of coordination H_2O molecules through Eqn. S1. The obtained Eu lifetimes [ms] from H_2O and D_2O with 0.01-1 M HNO_3 and the number of coordinating H_2O molecules are reported in Figure 3 and Table S1. Lifetime analysis demonstrated that from 0.01-1 M HNO_3, zero H_2O molecules coordinate to Eu. It should be pointed out that while the number of coordinating H_2O molecules is not changing, the Eu lifetimes increase from 0.82 to 1.86 ms with increasing HNO_3 (Figure 3d. An increase in lifetime when the number of H_2O is not changing has previously been attributed to increasing the number of coordinating ligands.[25]

This study has demonstrated the sensitivity of organic phase Ln complexes to HNO_3 concentration at fixed [NO_3] in TODGA/*n*-heptane systems. Extraction of Lns with low acid (0.01-0.1 M HNO_3) results in a decreased number of coordinating TODGA molecules along with coordinating NO_3^-. Increasing the concentration of HNO_3 above 0.5 M increases the number of coordinating TODGA and decreases the number of coordinating NO_3^-. The conditions studied herein resulted in zero coordinating H_2O molecules to Lns. 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 NO_3^- source when conducting solvent extraction experiments, as it can change the Ln inner-sphere coordination. Particularly for systems like diglycolamides with propensity for outer-sphere interactions, the NO_3^- source impacts separation efficacy.

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Supporting Information Available

Experimental procedures and additional characterization of organic phases by TRLIFS and FT-IR spectroscopy.

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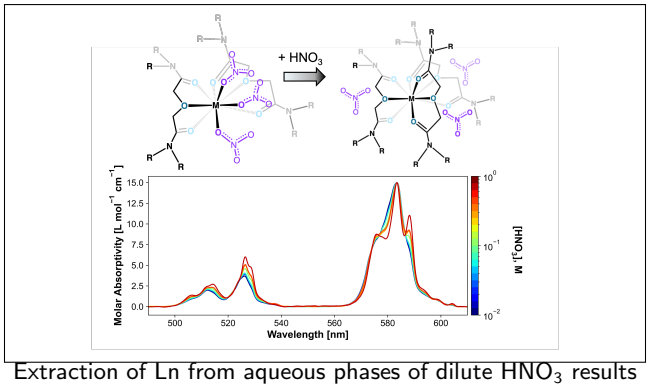
TOC Graphic



Extraction of Ln from aqueous phases of dilute HNO_3 results in 1:2 $[Ln(TODGA)_2(NO_3)_3]$ complexes. Increasing the HNO_3 concentration above 0.5 M, results in a 1:3 $[Ln(TODGA)_3](NO_3)_3$ complex, where the NO_3 are no longer coordinating to Ln but instead found in the outer-sphere.