

Surveying Phase Modifier Functional Groups for Applications to Ln(III) Separations

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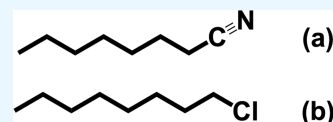


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ABSTRACT: The application of *N,N,N',N'*-tetraoctyl diglycolamide (TODGA) in solvent extraction systems for lanthanide (Ln) separations is well understood. In these systems, the formation of a third phase has motivated the use of phase modifiers to enable higher concentrations of H⁺ and Ln common to industrial processes. Several different phase modifiers with applications to diglycolamide (DGA) systems have previously been reported, with a focus on tri-*n*-butyl phosphate (TBP), *N,N'*-dihexylactanamide (DHOA), *N,N*-dioctyl-2-hydroxyacetamide (DOHyA), *N,N'*-dimethyl-*N,N'*-dioctylhexylethoxy malonamide (DMDOHEMA), and octanol. While the primary utility of phase modifiers is the increased metal loading, they can have significant effects on the metal distribution ratios, which are well described by the energetics of the extraction process itself. However, the mechanisms by which phase modifiers impact distribution ratios are not generally understood. This work considers the ability of phase modifiers to affect Ln distribution ratios by using phase modifiers with two different functional groups (–Cl and –C≡N) and an octyl alkyl chain in a TODGA and *n*-dodecane system. Determining the effect of chlorooctane and octane nitrile is important for understanding how phase modifier functional groups and their hydrogen bonding interactions affect Ln extraction. Through combining distribution ratio measurements with organic phase spectroscopic investigations, the impact of chlorooctane and octane nitrile on Ln extraction and their inner-sphere complexes is reported. The addition of either chlorooctane or octane nitrile to TODGA in *n*-dodecane decreases Ln extraction while maintaining the same inner-sphere Ln complex. The lack of change in inner-sphere Ln-TODGA coordination upon incorporation of phase modifiers and the significant impact of these phase modifiers on distribution ratios suggest the importance of a supramolecular structure. Understanding the role of chlorooctane and octane nitrile on the organic phase structure at longer length scales has been identified as an avenue for future investigations.



INTRODUCTION

Lanthanides (Ln) are used in a vast array of applications (such as digital technology, energy, fluorescent probes, and medical imaging) as a result of their unique magnetic and electronic properties.^{1,2} This requires high purity of individual Ln—motivating the need for highly selective intra-Ln separations. Challenges in separating Ln arise from their similar physicochemical properties, but the difference in ionic radii across the series due to the Ln contraction can be exploited for size-selective-based separations.³ Separation of Ln occurs via solvent extraction—which is advantageous due to its high scalability and throughput.^{3–5} Extraction and selectivity of a particular solvent extraction system is dependent upon extractant selection—an amphiphilic molecule with polar functional groups for metal coordination and a nonpolar aliphatic component for dispersion in organic diluent (generally *n*-dodecane or kerosene).^{6,52} Over the past two decades, the diglycolamide family of extractants, in particular *N,N,N',N'*-tetraoctyldiglycolamide (TODGA), has received particular attention for Ln separations.^{7–9}

High concentrations of H⁺—common in industrial hydro-metallurgical processes—oftentimes result in an unwanted phase behavior: third-phase formation.¹⁰ Third-phase formation involves splitting of an organic phase into a light (diluent rich) organic and a heavy (extractant rich) phase.^{11–13} The latter is termed the third phase. This behavior is always

deleterious because it robs the system of Ln capacity as industrial mixer-settlers are designed for biphasic systems.¹⁴ Third-phase formation occurs when the interactions between extractant molecules and their complexes become so strong that they no longer remain soluble in the nonpolar diluent. In addition to modulating polarity of the extractant and diluent,^{15,16} one route to inhibiting third-phase formation is addition of a cosolvent, often called a phase modifier.¹⁷

Increasing the polarity of the solvent through addition of phase modifiers to *n*-alkane diluents has been demonstrated to prevent third-phase formation.^{18,19} However, in addition to influencing the phase behavior, phase modifiers can also alter the separation behavior of the system. Specifically for metal separations, phase modifiers can improve distribution ratios and separation factors. Previously, tri-*n*-butyl phosphate (TBP), *N,N'*-dihexyloctanamide (DHOA), *N,N*-dioctyl-2-hydroxyacetamide (DOHyA), and alcohols (shown in Figure 1) have been evaluated as potential phase modifiers in organic

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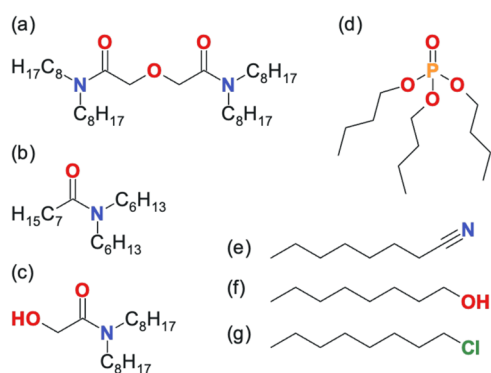


Figure 1. Extractant and phase modifier molecules discussed in text: (a) TODGA, (b) DHOA, (c) DOHyA, (d) TBP, (e) octane nitrile, (f) octanol, (g) chlorooctane.

phases containing a diglycolamide extractant in *n*-alkanes.^{17–25} These studies suggest that incorporating phase modifiers increases the complexity of the organic phase, which could induce changes at molecular and supramolecular length scales.^{24,26,27} One such possibility for the role of phase modifiers in Ln systems is to form a secondary solvation shell around the extracted metal complex, increasing the number of alkyl groups around the complex which enhances the solubility of the complex in the diluent preventing a third phase.²⁸

The current literature has highlighted the importance of considering phase modifier functional groups on their role in solvent extraction for phosphates, monoamides, and alcohols. Although the importance of the selected functional group has been recognized, the expansion of phase modifiers with additional functional groups has not yet been reported. In the absence of metals, phase modifiers can interact with extractants and extracted water and acid molecules impacting phase behavior, i.e., the point at which third-phase formation occurs. Additionally, Lns are extracted by diglycolamides (DGAs) in a trischelate complex with exposed counteranions that hydrogen bond with coextracted water, acid, and, potentially, phase modifiers.^{29,30} This is known to impact separations performance, including in the case of phase modifiers such as linear alcohols.³¹ In order to understand the influence of phase modifiers on Ln extraction, it is vital to distinguish their impact due to hydrogen bonding from other weaker interactions by which they solubilize the Ln–DGA complexes such as dipole–dipole interactions. By investigating phase modifiers that feature only weak hydrogen bonding acceptors, such as chlorooctane and octane nitrile, we can determine the importance of hydrogen bonding interactions on Ln separations. The primary aim for this work is to survey TODGA and *n*-dodecane extraction systems with phase modifiers having two different functional groups (–Cl and –C≡N) for the same alkyl chain length with applications to Ln separations. Organic phase spectroscopic techniques are used to survey the Ln selectivity with phase modifiers to evaluate Ln complexation changes.

EXPERIMENTAL METHODS

Materials. Hydrated lanthanide nitrates [Ln(NO₃)₃·*x*H₂O], (Ln = La, Nd, Eu, Ho, Lu) (99.99%, Sigma-Aldrich), nitric acid (70 vol % Optima grade, Fisher Scientific), tetraoctyl diglycolamide (99%, Technocomm Ltd.), *n*-dodecane (99%, Sigma-Aldrich), chlorooctane (99%, Fisher

Scientific), and octane nitrile (99%, Fisher Scientific) were all used as received.

Solvent Extraction. Equal volumes of organic phases containing 0.1 M TODGA with 0, 5, 10, or 30 vol % of either chlorooctane or octane nitrile in *n*-dodecane and 3 M HNO₃ were contacted for 30 min with a Heidolph Multi reax Vortex Mixer at 2000 rpm and centrifuged for 5 min with a Fisher Druker 614B Fixed Angle Single-Speed Centrifuge at 3250 rpm. The pre-equilibrated organic phase was removed and contacted with 1 or 10 mM Ln(NO₃)₃ in 3 M HNO₃ for distribution ratio measurements or spectroscopic investigations, respectively. Ln contacts were performed under the same conditions as the pre-equilibration step and were sufficient to reach equilibrium. Triplicate distribution ratio measurements were performed for error analysis.

ICP-MS. An Agilent Inductively Coupled Plasma Mass Spectrometer (ICP-MS) was used to quantify the Ln concentration before and after extraction. Organic phases were measured through a two-step dilution, the first dissolving an aliquot of organic phase after Ln extraction into excess ethanol, followed by a 1:100 dilution into 2 wt % HNO₃. The initial aqueous phase and aqueous phase after Ln extraction samples were prepared with a single-step dilution into 2 wt % HNO₃. This approach to quantifying Ln concentration in the aqueous and organic phases after extraction was validated through performing a mass balance, which was within 5 wt % of the initial concentration present in the aqueous phase. Calibration of the ICP-MS was performed with a series of 14 concentrations of Ln standards (from Inorganic Ventures) from 0 to 1000 ppb. Results from the organic and aqueous phases after Ln extraction were used to calculate the equilibrium distribution ratio (*D*)—the ratio of Ln concentration in the organic phase to Ln concentration in the aqueous phase at equilibrium, eq 1, where the overbar represents organic phase species. The error reported on the distribution ratios is from two standard deviations from triplicate measurements.

$$D_{\text{Ln}} = \frac{[\overline{\text{Ln}}]}{[\text{Ln}]_{\text{aq}}} \quad (1)$$

The separation factor (SF) represents the ability of a system to separate two different metals—taken to be a ratio of the distribution ratio of one metal to the distribution ratio of a second metal, shown in eq 2

$$\text{SF}_{M_1/M_2} = \frac{D_{M_1}}{D_{M_2}} \quad (2)$$

Spectroscopy. *UV–vis.* UV–visible spectra were collected on Nd-containing organic phases with an Agilent Cary Series UV–vis–NIR Spectrophotometer. Samples were measured in a glass cuvette with a 1 cm path length, and *n*-dodecane was used for background correction. After data collection, each of the spectra was baseline corrected. As it is of interest to compare the spectra resulting from various extraction conditions, after the absorbance was baseline corrected, the molar absorptivity was calculated from Beer's Law (eq 3),

$$A = \epsilon lc \quad (3)$$

where *A* is absorbance, ϵ is molar absorptivity, *l* is path length of the cuvette, and *c* is concentration of Nd. The concentration of Nd in the samples (i.e., organic phase) was calculated by

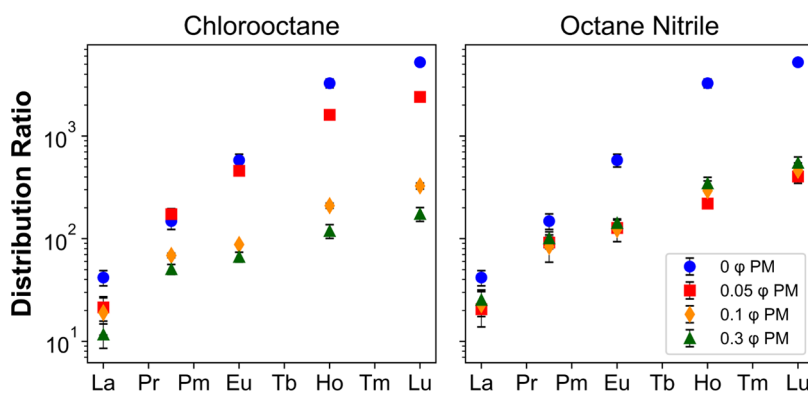


Figure 2. Distribution ratios of select Ln from 0.1 M TODGA with 0–30 vol % of phase modifier in *n*-dodecane from 3 M HNO₃. (left) Chlorooctane and (right) octane nitrile. The volume fraction of the phase modifier is represented by ϕ . The error bars represent 2σ and the 95% confidence interval.

using the distribution ratios for Nd obtained from ICP-MS under each condition.

TRLIFS. Time-Resolved Laser-Induced Fluorescence Spectroscopy (TRLIFS) was used on the organic phases after Eu extraction to collect both emission spectra and lifetime measurements. Both measurements were collected in a 1 cm pathlength quartz fluorescence cuvette with 3 mL of the organic phase, with the sample stirring at 1200 rpm and held at a constant temperature of 20 °C. Emission spectra were collected with a xenon lamp at an excitation of 394 nm, excitation bandwidth of 8 nm, and an emission bandwidth of 0.2 nm. Lifetime measurements were performed with an OPOTEK tunable pulse laser with an excitation of 394 nm at an emission of 617 nm and an emission bandwidth of 0.2 nm. After data collection, the emission spectra were baseline corrected. To quantify the number of H₂O molecules coordinating to Eu, the lifetime measurements were fit with a single exponential function, resulting in the Eu lifetime (τ), which was used in eq 4.³²

$$n_{\text{H}_2\text{O}} = \frac{1.06}{\tau} - 0.19 \quad (4)$$

FT-IR. ATR FT-IR spectra were collected on organic phases before and after Ln extraction using a Thermo Electron Nicolet 4700. The instrument spectral resolution was set to 6 (corresponding to 2 cm⁻¹), and the data was collected from 500 to 1800 cm⁻¹.

RESULTS

Solvent Extraction. First, we survey the trends in the distribution ratio across the Ln series for increasing quantities of phase modifiers. Distribution measurements for both chlorooctane and octane nitrile are shown in Figure 2. Both chlorooctane and octane nitrile have the same trend in distribution ratios with increasing phase modifier, $0 > 5 > 10 > 30$ vol %. However, differences arise when considering the individual distribution ratios at each phase modifier concentration. In the case of chlorooctane, increasing to 5 vol % only slightly decreases D , whereas a drop in distribution ratio by 1–2 orders of magnitude is observed with higher chlorooctane concentrations. In contrast, in the case of octane nitrile, the addition of just 5 vol % drastically decreases the distribution ratio by 1–2 orders of magnitude, and increasing the octane nitrile concentration does not change the distribution ratio from the values obtained at 5 vol %. The trend in decreasing

distribution ratios with an increase in phase modifier concentration has also been reported for TBP, DHOA, and DOHyA.^{17,18,20} In these systems, the decrease in distribution ratio was attributed to the increase in HNO₃ extracted, creating competition for the Ln.

The lower distribution ratios observed with higher concentrations of phase modifier, for both chlorooctane and octane nitrile, have the largest effects on the middle and heavy Ln. Selectivity of each organic phase was quantified by calculating separation factors from eq 2, Table 1. This results

Table 1. Ln Separation Factors for 0.1 M TODGA with Varying Volume Fractions (ϕ) of Chlorooctane (Cl) or Octane Nitrile (CN) in *n*-Dodecane from 3 M HNO₃^a

ϕ_{PM}	PM	SF _{Nd/La}	SF _{Eu/Nd}	SF _{Ho/Eu}	SF _{Lu/Ho}	SF _{Lu/La}
0	-	3.6(8)	3.9(8)	5.6(9)	1.6(1)	120(20)
0.05	Cl	8(2)	2.6(3)	3.5(1)	1.5(1)	110(30)
0.1	Cl	3.6(9)	1.3(1)	2.4(1)	1.6(1)	17(6)
0.3	Cl	4(1)	1.3(2)	1.8(3)	1.5(3)	15(4)
0.05	CN	4.5(9)	1.4(2)	1.7(1)	1.8(2)	19(4)
0.1	CN	3(1)	1.5(5)	2.4(8)	1.6(4)	20(8)
0.3	CN	4(1)	1.4(2)	2.4(4)	1.6(3)	21(5)

^aUncertainties in the last digit of the separation factors are provided in parentheses.

in a drop in the SF(Lu/La) from 125 in the absence of phase modifiers to 15 and 21, for chlorooctane and octane nitrile, respectively. This drop by an order of magnitude in SF(Lu/La) for the end points of the Ln series demonstrates the addition of higher concentrations of chlorooctane or octane nitrile significantly decreases the selectivity between Ln. While the addition of chlorooctane and octane nitrile decreases the separation factors for most of the conditions relevant in this study, it is important to point out the SF(Nd/La) for 5 vol % chlorooctane, which is increased by 2-fold in comparison to the no modifier system. Next, we spectroscopically interrogate the organic phase in the presence of chlorooctane and octane nitrile to determine if the impact on Ln distribution ratios results from changing inner-sphere metal-extractant interactions.

Organic Phase Spectroscopy. Comparing FT-IR spectroscopy of organic phases after pre-equilibration and Ln extraction can be used to determine which functional groups are coordinating to Ln. In organic phases containing neutral extractants with amide functional groups, such as diglycola-

mides and malonamides, the FT-IR spectra are sensitive to changes regarding the extractant C=O stretch (at approximately 1650 cm^{-1}) and the NOO^- stretch (around 1325 cm^{-1}).^{6,33,34} The FT-IR spectra for each of the phase modifiers and their concentrations considered in this study are provided in the Supporting Information. Each organic phase composition considered in this study exhibits similar FT-IR spectra. After HNO_3 extraction, a red-shifted shoulder on the C=O peak appears around 1610 cm^{-1} as a result of the formation of $(\text{HNO}_3)_x(\text{TODGA})_y$ adducts. Further evidence for HNO_3 extraction is demonstrated by the appearance of a NO_3^- peak at around 1325 cm^{-1} . These results are consistent with the literature for extraction of HNO_3 by diglycolamides.^{6,35,36} Following Ln extraction, both chlorooctane and octane nitrile, resulted in an increase in the red-shifted shoulder of the C=O stretch. This additional weakening of the main C=O stretch and increasing in intensity of the red-shifted shoulder is associated with the formation of Ln-TODGA complexes. However, with regard to the NOO^- stretch, no changes are observed between the HNO_3 contact and Ln extraction, suggesting that NO_3^- are not coordinating with the Ln. These results are consistent with previous literature for FT-IR investigations, which found no evidence for Ln- NO_3 coordination and a shift in the C=O stretch indicating Ln-TODGA coordination through the carbonyl moiety.^{6,37,38} Evaluating changes to the vibrational stretches corresponding to the chloro and nitrile groups can be used to evaluate hydrogen bonding interactions with chlorooctane and octane nitrile, respectively. However, both after HNO_3 contact and Eu extraction, there were no changes observed in the IR spectrum with the exception of C=O and NO_3 vibrational stretches, demonstrating that FT-IR spectroscopy provides no evidence of hydrogen bonding interactions with these select phase modifiers.

Additional spectroscopic techniques (i.e., UV-vis and TRLIFS) can be used to monitor changes in the inner sphere of Ln complexes. Select Ln (Pr, Nd, Sm, Eu, Tb, Ho) have transitions observed in the UV-vis-NIR region that are hypersensitive—highly sensitive to the ligand environment around the Ln.^{39–41} Monitoring changes to the hypersensitive transitions in absorption and emission spectra as a function of phase modifier volume fraction is used to determine changes to the inner-sphere Ln complex. In this work, UV-vis absorption spectroscopy was used to monitor changes to the Nd inner-sphere through the $^4\text{G}_{5/2}, ^4\text{G}_{7/2} \leftarrow ^4\text{I}_{9/2}$ (575 nm), $^4\text{S}_{3/2}, ^4\text{F}_{7/2} \leftarrow ^4\text{I}_{9/2}$ (741 nm), and $^4\text{F}_{5/2}, ^2\text{H}_{9/2} \leftarrow ^4\text{I}_{9/2}$ (794 nm) transitions. Emission spectroscopy monitored changes to Eu inner-sphere through the $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions ($j = 0, 1, 2, 3, 4$) (580–720 nm).

Nd absorption spectra were collected for 0–30 vol % chlorooctane and octane nitrile, Figure 3. For each phase modifier, an increase in concentration did not result in a change in the spectra. In addition, there appears to be no change between chlorooctane and octane nitrile systems, and no isosbestic points were observed. These results suggest that the addition of either chlorooctane or octane nitrile does not change the Nd inner-sphere coordination. Comparison of the Nd spectra in Figure 3 to the literature indicates that the result of three peaks for the $^4\text{G}_{5/2}, ^4\text{G}_{7/2} \leftarrow ^4\text{I}_{9/2}$ transition at 575, 580, and 585 nm is consistent with the formation of 1:3 Ln/TODGA complexes.⁴² The inability for chlorooctane or octane nitrile to change the Nd inner sphere is consistent with results

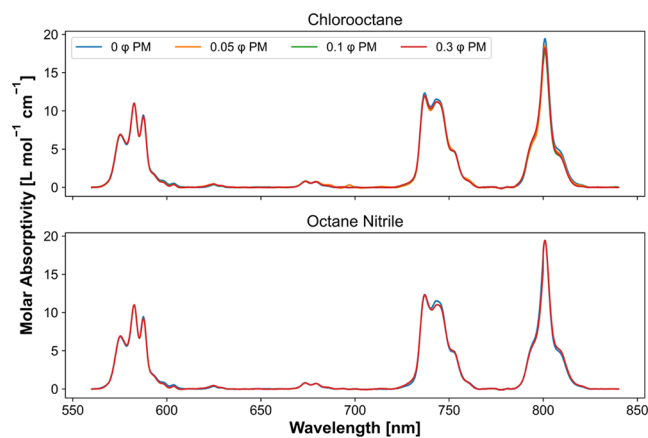


Figure 3. Nd absorption spectra following extraction from 0.1 M TODGA with either chlorooctane or octane nitrile in *n*-dodecane from 3 M HNO_3 . The phase modifiers are represented in volume fractions, represented by ϕ .

in TODGA systems with either octanol or DMDOHEMA phase modifiers.²⁶

Additionally, Eu emission spectroscopy was collected for 0–30 vol % of either chlorooctane or octane nitrile organic phases, Figure 4. Similar to the Nd absorption measurements,

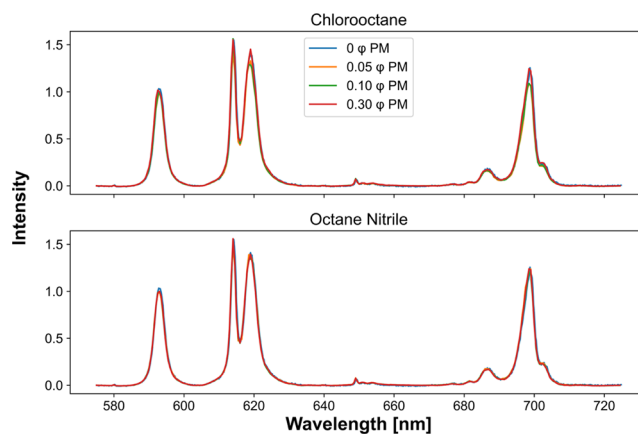


Figure 4. Eu emission spectra following extraction from 0.1 M TODGA with either chlorooctane or octane nitrile in *n*-dodecane from 3 M HNO_3 .

the addition of either chlorooctane or octane nitrile does not result in a change in peak splitting or intensity of each transition. The observed peak splitting pattern, i.e., the number of peaks observed for each $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transition ($j = 0, 1, 2, 3, 4$) has previously been reported for 1:3 Eu/DGA complexes.^{32,43,44} The results from emission spectroscopy are consistent with the results from UV-vis and FT-IR spectroscopy, which indicate that the addition of either chlorooctane or octane nitrile as phase modifiers does not change the inner-sphere metal-extractant interactions.

This work has thus far demonstrated that the dramatic changes in distribution measurements across the 4f-period (Figure 2) with varying ϕ_{PM} are not a product of changing the inner-sphere metal-extractant interactions. Lifetime measurements were also performed to determine the number of coordinating H_2O molecules to Eu. In the absence of phase modifiers, it has previously been reported that there are zero H_2O molecules coordinating to Eu, with Eu lifetimes exceeding

1.5 ms.^{32,44} In Table 2, Eu lifetimes are reported for 0–30 vol % of either chlorooctane or octane nitrile. Note that each

Table 2. Eu Lifetimes, τ (ms), from Solvent Extraction Experiments with 0.1 M TODGA and 0–0.3 ϕ of Either Chlorooctane (Cl) or Octane Nitrile (CN) in *n*-Dodecane in 3 M HNO₃^a

ϕ_{PM}	τ_{Cl}	τ_{CN}
0	2.27	2.27
0.05	2.63	2.44
0.10	2.56	2.29
0.30	2.57	2.21

^aThe phase modifiers are represented in volume fractions, represented by ϕ_{PM} .

lifetime is longer than 1.5 ms. For H₂O molecules to coordinate to Eu, given the relationship between τ and coordinating H₂O (eq 4), shorter Eu lifetimes generally less than 1 ms are consistent with H₂O coordination.⁴⁵

Therefore, the longer Eu lifetimes observed with chlorooctane and octane nitrile, exceeding 2.2 ms, correspond to zero inner-sphere H₂O molecules on Eu. Investigations with TBP added as a phase modifier to T2EHDGA organic phases reported a similar finding.²⁷ Combining FT-IR, UV–vis, and TRLIFS results demonstrated the addition of 5–30 vol % of either chlorooctane or octane nitrile does not change the Ln inner-sphere complex, resulting in a homoleptic trischelate 1:3 Ln/TODGA complex with zero coordinating H₂O or NO₃[−] molecules.

DISCUSSION

The observed decrease in distribution ratios with increasing volume fraction of either chlorooctane or octane nitrile mirrors data reported for TBP, DHOA, and DOHyA phase modifiers.^{17,18,20} In contrast, the addition of alcohol phase modifiers from 5 to 10 vol % increases the D, but at 30 vol %, a decrease in distribution ratio is observed, generally having a lower distribution ratio than the system without phase modifiers.³¹ It is interesting to note that the distribution ratios obtained in chlorooctane systems do not decrease as readily as those obtained in octane nitrile systems. These differences could result from a change in Ln inner-sphere complex, outer-sphere complex, and/or changes in solvent architecture.

This work demonstrated that the addition of either chlorooctane or octane nitrile does not change the inner-sphere Ln complex. This is consistent with investigations with octanol as a phase modifier.^{26,46} Conversely, a change in Ln inner-sphere complexes was observed when either TBP or DOHyA was added to a diglycolamide and *n*-alkane system.^{24,27} This suggests that the impact of phase modifiers on Ln separations results in changes to inner-sphere Ln coordination with TBP and DOHyA. However, with chlorooctane, octane nitrile, and octanol, the lack of change in the Ln inner sphere with significant changes to the distribution ratios suggests extraction is driven by interactions at distances beyond the Ln inner sphere such as outer-sphere complexation, structuring at longer length scales, organization of solutes, and solvent molecules.

Solvents with low dielectric constants (i.e., *n*-alkanes) have enhanced electrostatic interactions, promoting the formation of hydrogen bonding networks.^{47,48} The importance of hydrogen bonding interactions in TODGA systems for

promoting extraction has been demonstrated, where the driving force for Ln separations has been attributed to outer-sphere interactions with coextracted HNO₃ and H₂O molecules.²⁹ As chlorooctane and octane nitrile also have a lower propensity for hydrogen bonding interactions, they are relatively noninteracting with the hydrogen bonding network.⁴⁹ In organic phases, where outer sphere and hydrogen bonding interactions are driving separations, phase modifiers (such as chlorooctane and octane nitrile) that are slightly more polar than *n*-alkanes and have low affinity for hydrogen bonding interactions hinder Ln separations while not impacting the extracted Ln complex. Addition of chlorooctane or octane nitrile could inhibit Ln separations by affecting the extraction of H₂O and HNO₃ that are important for establishing the outer-sphere hydrogen bonding network for Ln extraction.^{29,50} The ability for alcohol phase modifiers to effectively interact with the Ln complex outer-sphere hydrogen bonding interactions, has previously been identified.^{28,51} Alcohols enable a synergistic effect on Ln extraction through participation in the hydrogen bonding network, whereas modifiers with a poor affinity for hydrogen bonding interactions (i.e., chlorooctane and octane nitrile) have a negative impact on separations. These results suggest that the ability for phase modifiers to be both a hydrogen bonding acceptor and a hydrogen bonding donor is vital for improving separation in TODGA systems. As the hydrogen bonding interactions with outer sphere nitrates are presumably very important, this could explain why donating hydrogen bonds in phase modifiers is important.

CONCLUSIONS

This study is the first to report –Cl and –C≡N functional groups as phase modifiers on linear alkanes with applications to Ln separations by TODGA. Increasing the volume fraction of chlorooctane and octane nitrile from 5 to 30 vol % decreases Ln extraction and selectivity, with the largest impacts on the heavier Ln. Spectroscopic characterization of organic phases utilized the combination of FT-IR, UV–vis, and TRLIFS to provide insight into changes regarding the Ln coordination environment in the presence of chlorooctane or octane nitrile. These spectroscopic techniques demonstrated that neither chlorooctane nor octane nitrile change the Ln-TODGA interactions, and there is no evidence for NO₃[−] or H₂O coordination. The large decrease in distribution ratios with an increase in chlorooctane or octane nitrile is not a result of changing the metal-extractant complex. This work demonstrated that solvent extraction is more than metal-extractant coordination chemistry, where influences on distribution ratios go beyond the metal-extractant bond distance. Future investigations are recommended to evaluate how these phase modifiers are influencing phase behavior (i.e., how much the phase modifier is needed to prevent the formation of a third phase) and distribution ratios, as this could be the result of changing organic phase activity, solvent architecture, outer-sphere interactions, long-range electrostatic effects, etc.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.4c06084>.

FT-IR spectra and Eu lifetime measurements (PDF)

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Notes

The authors declare no competing financial interest.

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