Selective Extraction of Light Lanthanides(III) by \(N,N\)-Di(2-ethylhexyl)-diglycolamic Acid: A Comparative Study with \(N,N\)-Dimethyl-diglycolamic Acid as a Chelator in Aqueous Solutions

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Supporting Information

ABSTRACT: The complexation and selectivity of \(N,N\)-di(2-ethylhexyl)-diglycolamic acid (HDEHDGA/kerosene, HA) toward the light lanthanides, La(III), Ce(III), Pr(III), and Nd(III), are presented for the extraction from chloride media. In the low pH region (pH 1.8–2.8), the obtained data reveal that the extraction of Ln(III) is governed by cation-exchange mechanism and is driven by the negative change in enthalpy. The results from the slope analysis method suggest the formation of LnA3(HA)1 or 2 in the extraction process. As major extracted species with a core of LnA3 in the first coordination sphere, LnA3 might connect with one or two additional HA molecules in the second coordination sphere by hydrogen bonding. The LnA3 core might share similar coordination geometry to those of 1:3 Ln(III) complexes (LnA3) with water-soluble \(N,N\)-dimethyl-diglycolamic acid (HDMGDA, HA′) formed in aqueous solutions or in solid-state compounds. The correlation between the extraction with HDEHDGA (HA) as an extractant and the complexation with HDMGDA (HA′) as a chelator has been explored by interpreting the separation factors for HA with the difference in the stability constants for HA′. Consequently, the ratios of the stability constants of the corresponding 1:3 complexes (LnA3) with HDMGDA could be reasonably translated to the separation factors (SFs) with HDEHDGA, providing a valuable approach for understanding the origin of the extraction/separation mechanism. By comparing the extraction selectivity of HDEHDGA with that of the currently deployed extractants in the industry such as P204, P507, and Cyanex 272, HDEHDGA offers outstanding selectivity with considerable SFs (SF\textsubscript{Ce/La} = 6.68, SF\textsubscript{Pr/Ce} = 2.79, and SF\textsubscript{Nd/Pr} = 2.65) for light Ln(III) pairs under conditions of low acid concentrations.

INTRODUCTION

Rare earth elements, including 15 lanthanides (Ln\textsubscript{s}) as well as scandium and yttrium, are of great economic importance because of their extensive applications in various industries such as catalysis, metallurgy, ceramics, medicine, display screens, laser technology, and electronics.\textsuperscript{1–3} In last few decades, the extraction/separation of rare earths (REs) has attracted great attention due to their potential industrial and economical significance in addition to the increased demands of REs of high purity. Liquid—liquid extraction is a well-accepted supreme technique for the separation and purification of REs for commercial production.\textsuperscript{4–6} Besides, extraction processes for the separation of lanthanides from high-level waste in the nuclear industry have also been developed because the light lanthanides are considered one of the major constituents in the fission products in spent nuclear fuel. The functional groups of a given extractant play a critical role in the extraction/purification processes of REs. Based on the functional groups, extractants are mainly sorted as acidic, neutral, and basic that could be employed for the extraction of REs in the research and industrial fields with several proposed mechanisms as discussed earlier.\textsuperscript{7–15} Among these extractants, hydrophobic organophosphorus acidic extractants have been studied with more efforts. One of the most important properties of those acidic extractants is their tunable extraction ability to the desired metal ions, which could be achieved by simply adjusting the pH of the aqueous phase solutions. Although organophosphorus extractants are considered effective ligands for RE extraction, they do have some certain drawbacks such as leaving behind phosphorus residues as byproducts and exhibiting low selectivity in the case of intragroup separation of REs.\textsuperscript{16–18} Moreover, P507 and naphthenic acid have been found ineffective to separate REs from sulfate media due to emulsion formation.\textsuperscript{19} Also, the low
selectivity of Cyanex 921 and the multistage stripping operations required for Cyanex 923 are considered as common drawbacks that may limit their uses in the industry. To overcome these drawbacks, a lot of efforts have been made to develop extractants that are structurally different from the bidentate organophosphorus acids and the neutral organophosphorus extractants. Among those ligands, tetraalkyldiglycolamides (TRDGAs) have been studied due to their high affinity for trivalent lanthanides. Table 1 summarizes the extraction of Ln(III) from different systems using carboxylic acids and amide-based extractants. The TRDGAs exhibit very good extraction ability for the trivalent lanthanides Ln(III) and actinides An(III) from high-level liquid waste as compared to other ligands such as n-octyl phenyl-N,N-disobutyl carbamoylmethyl phosphine oxide, trialkylphosphine oxides, di-isodecyl methyl phosphine oxide, trialkylphosphine oxides, di-isodecyl phosphoric acid, and malonamide-based ligands. The potential extractability of TRDGAs is ascribed to their tridentate functional group. In addition, it has been observed that the structure of the alkyl chain of the TRDGAs plays a key role in their extraction performance, i.e., less steric hindrance in the alkyl chain attached to the amide groups of the TRDGA extractants provides a better extraction ability than higher alkyl chain counterparts.

Table 1. Extraction of Ln(III) Using Some Carboxylic Acids and Amide-Based Extractants

| extractant | metal ions | remarks | ref |
|------------|------------|---------|-----|
| Versatic 10 | Eu, Y, Zr | quantitative extraction at high pH values (pH > 6) | 32 |
| 8Oct[4] | Eu, Y, Zr | high sodium ion concentrations required to enhance the extraction | 32 |
| CH3C00H | Lu | high separation factors (SFs) for light Ln(III) and low SFs for heavy Ln(III) | 33 |
| DODGA | Lu-Lu | confirmation of the extracted complexes | 28 |
| DMDODGA | Lu, Dy, Ho, Er | confirmed as the extracted complexes | 28 |
| TEHDGA | Lu, Sm, Y, Er | Y separated from heavy Ln(III) in the presence of NH4SCN, with low SF between Y and Sm | 29 |
| TBDGA | Gd, Dy, Er, Y | extractability in order of Er < Gd < Dy < Y | 23 |

Calixarene carboxylic derivative. "N,N-Di(2-ethylhexyl)diglycolamic acid. "N, N′-Dimethyl-N,N′-dioxalyl-3-oxadiglycolamide. "N,N,N′,N′-Tetra(2-ethylhexyl)diglycolamide. "N,N,N′,N′-Tetra(2-ethylhexyl)diglycolamide.

By exploiting the advantage of strong affinity for Ln(III) due to the tridentate functional group of TRDGAs, we reported the extraction behavior of europium, uranium, and plutonium from high nitric acid solutions using N,N-di(2-ethylhexyl)-diglycolamic acid (HDEHDGA, HA). HDEHDGA possesses a similar tridentate coordination functional group to the TRDGAs, but it is a carboxylic acid ligand with one of the two amide groups of TRDGAs replaced by a carboxy group, as shown in Scheme 1. The observed results depicted that HDEHDGA might act as normal carboxylic acids in the system of low HNO3 concentration and the extraction process might be governed by the cation-exchange mechanism. In contrast, at a high concentration of nitric acid, the ligand formed a cationic complex with lanthanide and actinide ions and the extraction was performed through the ion-pair mechanism. Usually, the extractants behave quite differently in systems of various anions (such as NO3-, Cl-, and SO42-) for the separation of Ln(III) ions.

To our best knowledge, the extraction of Ln(III) ions from diluted HCl solutions has not been reported so far. Therefore, the current work presents the first study to examine the extraction of four light Ln(III) ions, La(III), Ce(III), Pr(III), and Nd(III) from diluted HCl media using HDEHDGA/ kerosene as an organic phase. Furthermore, the complexation in the aqueous solution and the properties of the solid-state complexes of Ln(III) ions with the water-soluble N,N-dimethyl-diglycolamnic acid (HDMGDA, HA), also shown in Scheme 1 ligand were also investigated to help understanding the extraction/separation mechanism of HDEHDGA. The complexation of Ln(III) with HDMGDA in aqueous solutions and in solid-state compounds parallels the chemistry of Ln(III) being complexed with HDEHDGA in solvent extraction. The difference in the stability constants of the 1:3 Ln(III) complexes (LnA3) in aqueous solutions could be well correlated with the corresponding separation factors obtained from the extraction with HDEHDGA. Therefore, the investigation of the Ln(III) complexation with the N,N-dialkyl-diglycolamic acids not only provides structural and thermodynamic information for the complexes but also develops a preliminary evaluation and research methodology for predicting extraction behaviors of ligands bearing the same functional group but different alkyl chains.

### RESULTS AND DISCUSSION

#### Effect of Acid Concentration on the Extraction.

For acidic extractants, the pH value of the aqueous solution plays a significant role in the extraction process. The dependency of the extraction of Ln(III) as individual metal ions (La(III), Ce(III), Pr(III), and Nd(III)) on the acid concentrations was studied at 25 °C with a constant ligand concentration in the organic phase. As shown in Figure 1, the extraction of Ln(III) ions increases with the increasing pH values of the equilibrated aqueous phase.

The linear plots of log D versus pH suggest that only one major complex species of each Ln(III) was formed in the organic phase. The slope values of 2.7–2.9 for the four linear lines are found in consistence with the common slope value of 3 for the monobasic carboxylic acid extractants. These results indicate that under the conditions of low HCl concentration, HDEHDGA acts as normal acidic extractants and the extraction of light Ln(III) is governed by the ion-exchange mechanism. During the extraction, as one Ln(III) ion is extracted into the organic phase, three H+ are released into the corresponding aqueous phase to balance the charge spontaneously. At pH about 2.8, most of Ln(III) ions were extracted.
The plots of log $D$–$3pH$ against log[$HA$] are in good linear relationships for the four Ln(III) ions ([HA] is the free HDEHDGA concentration in the equilibrated organic phase). As shown in Figure 2, the slopes of the four linear lines depict that the molar ratio of the ligand, [HA + A$^-$], to Ln(III) in the extracted complexes is not 3:1 as that of the number of the exchanged protons for each Ln(III) extraction. Based on these results, we can speculate that one or two neutral HDEHDGA molecules exist in the second coordination sphere of Ln(III) complexes through hydrogen bonding between their –COOH and the –COO$^-$ of A$^-$ in the first coordination sphere. However, it is difficult to predict the exact modes of these extra HA molecules connecting to the LnA$_3$ core without further structural information. For common acidic extractants, it is observed that the neutral protonated extractant molecules may bond to the core of the extracted complexes via hydrogen bonding. Due to the complexity caused by the protonated extractant molecules (HAs) attaching to the core of the extracted complexes, the powerful slope analysis method could not provide useful information about the structures and compositions of the extracted complexes, as discussed in the reference 38. Baba et al. reported a similar observation on the complexation between N-$[N,N$-di(2-ethylhexyl)-aminoacarbonylmethyl] glycine (D2EHAG) and Sc(III). A complex of 1:4 metal/ligand (Sc$_4$H$_4$HR) was determined and verified by the loading tests and Job’s continuous variation technique.

The values of log $K_{ex}$ were directly obtained from the intercepts of the straight lines in Figure 2 using eq 3b. The values of log $K_{ex}$ are 2.89, 3.51, 3.71, and 4.05 with the respective nonintegral $n$ values of 4.45, 4.40, 4.30, and 4.25 for La(III), Ce(III), Pr(III), and Nd(III), respectively. The apparent difference among these values illustrates considerably increasing stability of the extracted complexes of HDEHDGA with Ln(III) as the atomic number increases, possibly hinting good selectivity for the adjacent light Ln(III) ions.

**Effect of Temperature on the Extraction.** The temperature variation method is often used in solvent extraction studies to evaluate the influence of temperature on the extraction and to abstract the thermodynamic information about the extracted complexes. The standard free energy of a complexation/extraction reaction is defined as

\[ \Delta G^o = -2.303RT \log K_{ex} \]  

Figure 1. Effect of pH of the equilibrated aqueous phase on the Ln(III) extraction. Organic phase, 0.01 M HDEHDGA; initial concentrations of Ln(III) in aqueous phase: [La$^{3+}$] = 0.013 mM, [Ce$^{3+}$] = 0.018 mM, [Pr$^{3+}$] = 0.014 mM, [Nd$^{3+}$] = 0.016 mM, in 1 M NaCl.

Figure 2. Effect of HDEHDGA concentration on Ln(III) extraction. Initial aqueous solution: [HCl] = 0.01 M, [La$^{3+}$] = 0.013 mM, [Ce$^{3+}$] = 0.015 mM, [Pr$^{3+}$] = 0.014 mM, [Nd$^{3+}$] = 0.016 mM, in 1 M NaCl.
\[ \Delta G = \Delta H - T \Delta S \]  

(5)

The enthalpy, \( \Delta H \), of the extraction can be indirectly measured by determining the distribution ratios (\( D \) values) at different temperatures as described by eq 6.

\[ \frac{\Delta \log D}{\Delta \frac{1}{T}} = -\frac{\Delta H}{2.303R} \]  

(6)

The distribution ratios of La(III), Ce(III), Pr(III), and Nd(III) between 0.01 M HDEHDGA in kerosene and 0.015 mM of each Ln(III) in 1 M NaCl at pH 2.2 over the range of 25–60 °C were determined. As shown in Figure 3, the \( D \) values for the four studied Ln(III) ions decrease with the increasing temperature. The plots of \( \log D \) against \( 1000/T \) present good linear relationship, indicating that across the tested temperature range, the enthalpies of the extraction might remain constant or do not undergo obvious change. The enthalpies for the extractions of the four Ln(III) ions can be calculated from the slopes of the straight lines in Figure 3, and the data are listed in Table 2. The results might be ascribed to the difference in hydration energy and hydration number among the Ln(III) ions. The hydration energy of Ln(III) becomes more negative from La(III) to Nd(III). Therefore, more energy is required to dehydrate La(III) to form extracted complexes with deprotonated HDEHDGA, resulting in less exothermic enthalpy. The less negative trend in the change of entropy might be explained with the decreasing \( n \) values from La(III) to Nd(III) as described in Figure 2. Smaller \( n \) values suggest that less HA molecules connect to the LnA3 core, resulting in more free HA molecules, less negative entropy, and more favorable extraction from La(III) to Nd(III).

Crystal Structure of La/NdA′3 Complexes. The solid compounds LaA′3 and NdA′3 obtained from 95% ethanol solutions by slow evaporation are isostructural complexes, where A′ stands for the deprotonated HDMDGA. Colorless blocks of LaA′3 and pale blue blocks of NdA′3 were crystallized in \( \beta \)I space group. In the neutral LaA′3 complex, La(III) ion is surrounded by nine oxygen atoms from three tridentate A′ anions, forming a distorted tricapped trigonal prism geometry with six carboxyl oxygen atoms at the corners and three ether oxygen atoms capped on the three faces. For NdA′3, the coordination core is almost identical to the previously reported compound, NdA′3(H2O)7.5, that is obtained from the aqueous solution. The only difference between the two compounds (NdA′3 and NdA′3(H2O)7.5) is the content of the water of crystallization. NdA′3 does not contain any water of crystallization unlike NdA′3(H2O)7.5 that contains some water molecules of crystallization (see the SI).

The structure of LaA′3 is illustrated in Figure 4, and the selected bond lengths of LaA′3 and NdA′3 are listed in Table 3. Furthermore, the corresponding bond lengths of NdA′3, 7.5H2O are also mentioned for comparison.

![Figure 4. Crystal structure of LaA′3 with 30% probability ellipsoids. Lanthanum, light blue; oxygen, red; nitrogen, blue; and carbons, gray. Hydrogen atoms have been omitted for the sake of clarity.](image-url)

The difference in average bond lengths for the three categories of Ln–O in both complexes (LaA′3 and NdA′3) are 0.053, 0.063, and 0.061 Å for Ln–O\textsubscript{carboxylate}, Ln–O\textsubscript{amide} and Ln–O\textsubscript{ether} respectively. These values are very close to 0.056 Å that represents the difference between the radii of La\textsuperscript{3+} and Nd\textsuperscript{3+}. The structural information indicate that there is no/ negligible steric hindrance during the formation of the two 1:3 LnA′3 complexes. As a result, the bonding between the ligand and the central Ln\textsuperscript{3+} is mainly governed by the electrostatic interaction.
ligand complexes of NdA. Obtained spectrum was compared with those of 1:3 metal/spectrum of the extracted Nd(III) complex was collected. The to confirm complexes.

Figure 5. Absorption spectra of NdA′(·(HA)1or2(org.) and NdA′(·(org.) (A′ = N,N-dimethyl-diglycolamide) and the reflectance spectrum of solid compound NdA′3. The organic phase for NdA′(·(HA)1or2 was prepared from extraction with 0.5 M HDEHDGA and 0.05 M Nd(III) in 1 M NaCl at pH 2.

very comparable, suggesting that the extracted complex of Nd(III) with the HDEHDGA in the organic phase possess a very similar coordination geometry to those of NdA′3 in the aqueous solution and in the solid state. Obviously, there are more detailed features in the spectrum of the extracted complex than that of NdA′3 in the aqueous solution, revealing that the extracted complex represents more defined structure. This might be caused by two facts; one is that the ligand-exchange rate for the extracted complex is slower than that for the NdA′3 in aqueous solutions; the other fact is that the additional neutral HA molecules in the second coordination sphere (connected through hydrogen bonding) provide extra stability for the inner core NdA′3 in the organic phase. However, these speculations need to be further confirmed by other techniques in the future such as metal loading tests and electrospray ionization mass spectrometry (ESI-MS) investigations.

Group Extraction/Separation of Light Ln(III) Ions. In the liquid—liquid extraction, the SF is defined as the ratio of the D values for the two interested components. If the SF value is close to one, the separation of two adjacent Ln(III) ions will be very complicated and difficult. Thus, the higher the values of SF, the better the separation of the two elements.

The data in Table 4 illustrate that HDEHDGA might have good selectivity for adjacent light Ln(III) ions. The selectivity of HDEHDGA toward light Ln(III) ions was investigated using more concentrated solutions. The aqueous phase containing 0.003 M each of the four light Ln(III) and 0.01 M HCl in 1 M NaCl was equilibrated with 0.2 M HDEHDGA in kerosene. As listed in Table 4, HDEHDGA presents very good separation ability toward the light Ln(III) including La(III), Ce(III), Pr(III), and Nd(III). It is well known that some organophosphorus ligands such as P204, P507, and Cyanex 272 have been broadly applied for lanthanides extraction/separation in the industry. In comparison to these ligands, HDEHDGA presents much better separation factors for light adjacent Ln(III) ions. Thus, this property can offer more effective processes for the extraction/separation of light Ln(III) ions in the industry.

Table 3. Selected Bond Lengths for La/NdA′3 Complexes

| bond                      | bond length/Å |
|---------------------------|---------------|
| LaA′3                    |               |
| NdA′3                    |               |
| NdA′7·5H2O30             |               |
| Ln−O(carboxylate)         | 2.471         |
|                          | 2.475         |
|                          | 2.482         |
| average                   | 2.476         |
| Ln−O(carboxylate)         | 2.497         |
| average                   | 2.521         |
| Ln−O(carboxylate)         | 2.527         |
| average                   | 2.515         |
| Ln−O(carboxylate)         | 2.601         |
| average                   | 2.630         |

Absorption/Reflectance Spectra of Nd(III) Complexes. To confirm the extraction mechanism via the slope analysis method described by eq 1, the UV–vis absorption spectrum of the extracted Nd(III) complex was collected. The obtained spectrum was compared with those of 1:3 metal/ligand complexes of NdA′3 in the aqueous solution and in the solid compound. As shown in Figure 5, the three spectra are very similar, suggesting that the extracted complex of Nd(III) with the HDEHDGA in the organic phase possesses a very similar coordination geometry to those of NdA′3 in the aqueous solution and in the solid state. Obviously, there are more detailed features in the spectrum of the extracted complex than that of NdA′3 in the aqueous solution, revealing that the extracted complex represents more defined structure. This might be caused by two facts; one is that the ligand-exchange rate for the extracted complex is slower than that for the NdA′3 in aqueous solutions; the other fact is that the additional neutral HA molecules in the second coordination sphere (connected through hydrogen bonding) provide extra stability for the inner core NdA′3 in the organic phase. However, these speculations need to be further confirmed by other techniques in the future such as metal loading tests and electrospray ionization mass spectrometry (ESI-MS) investigations.

Figure 5. Absorption spectra of NdA′(·(HA)1or2(org.) and NdA′(·(org.) (A′ = N,N-dimethyl-diglycolamide) and the reflectance spectrum of solid compound NdA′3. The organic phase for NdA′(·(HA)1or2 was prepared from extraction with 0.5 M HDEHDGA and 0.05 M Nd(III) in 1 M NaCl at pH 2.

Table 4. Separation Factor of Light Ln(III) for HDEHDGA and Some Deployed Extractants

| extractant               | Ce/La  | Pr/Ce  | Nd/Pr  | reference   |
|--------------------------|--------|--------|--------|-------------|
| cyanex 301               | 1.04   | 1.06   | 1.7    | 41          |
| CA12 + Cyanex 301        | 0.19   | 1.62   | 0.43   | 41          |
| Cyanex 572               | 3.53   | 1.77   | 2.49   | 1           |
| R,N′EHEHP′               | 12.9   | 2.4    | 1.7    | 42          |
| EHEHPA + Cyanex 272      | 2.1    | 1.59   | 11     |             |
| PS07                     | 3.76   | 1.52   | 1.25   | 7           |
| P204                     | 4.09   | 1.96   | 1.53   | 7           |
| D2EHPA                   | 4.7    |        |        | 43          |
| Cyanex 272               |        |        |        | 1           |
| CA12                     | 1.53   | 1.13   | 0.94   | 45          |
| PC88A                    | 7.3    |        |        | 46          |
| HDEHDGA                  | 6.68   | 2.79   | 2.65   | this study  |

Table 5. Stripping Nd(III) as a Function of Acid Concentration

| acid concentration, M | St.% | HCl | HNO3 | H2SO4 |
|-----------------------|------|-----|------|-------|
| 0.01                  |      | 16.3| 10.3 | 85.4  |
| 0.05                  |      | 89  | 93   | 87.5  |
| 0.1                   | >99  | 96.2| >99  | 86    |
| 0.2                   | >99  | >99 | >99  | 90.5  |
| 0.5                   | >99  | >99 | >99  | 92.2  |
| 0.7                   | >99  | >99 | >99  | 91.2  |
| 1                     | >99  | >99 | >99  | 89.8  |
The results also indicate that the concentration of 0.1 M of HCl is high enough to quantitatively recover Nd(III) under the investigated conditions. Moreover, at the same acid concentrations, the two monobasic acids (HCl and HNO₃) are found to be better stripping reagents than the dibasic acid H₂SO₄ that provides two times H⁺ at the same concentration. These observations hint that the mechanism for the extraction in the sulfate system could be different and the sulfate anion might be involved in the extraction process.

To examine the reusability of HDEHDGA, six cycles of extraction/stripping were carried out at the same conditions. After each extraction cycle, the loaded organic phase was contacted with 1 M HCl as a stripping agent that was chosen to ensure the quantitative recovery of Nd(III) in one stripping stage. As shown in Figure S2, Section B, SI, the extraction efficiency is practically stable even after six extraction/stripping cycles, indicating that HDEHDGA presents good extraction performance.

**Complexation of Ln(III) Ions with HDMDGA.** To help understanding the extraction/separation of Ln(III) with HDEHDGA, the complexation of the four light Ln(III) ions with HDMDGA was investigated in aqueous solutions and solid-state compounds. The stability constants for Ln(III) ions with HDMDGA were determined by potentiometry in 1 M NaCl at 25 °C. Figure 6 shows representative potentiometric titrations of the complexation of Ln(III) ions with A⁻. The best model to fit the potentiometric data includes the formation of three successive Ln(III)/A⁻ complexes for each Ln(III)

$$\text{Ln}^{3+} + n\text{A}^- = [\text{Ln}(\text{A}')_n]^{(3-n)+}, \quad (n = 1-3)$$

The calculated stability constants for [LnA'ₚ]ⁿ⁻ are listed in Table 6. In this study, the stability constants of the Nd(III)/A⁻ complexes are in a good agreement with those measured in 1 M NaClO₄ in the literature. Under the experimental conditions, only completely deprotonated A⁻ is found in all of the Ln(III) complexes. The Ln(III) ions bear the same charge of +3 in aqueous solutions, but the ionic radii decrease with increasing the atomic number because of the lanthanide contraction effect. Therefore, the overall charge density on the adjacent Ln(III) ions increases slightly from the light to the heavy Ln(III) ions. As a result, stronger complexation along the whole Ln(III) series occurs when the interactions with the ligands are dominantly electrostatic in nature. The data in

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**Figure 6.** Potentiometric titrations of Ln(III) complexation with A⁻ in 1 M NaCl. Cell solution: V₀ = 20 mL, C_{H⁺₀} = 0.6 mM, C_{Nd(III)₀} = 5.45 mM in 1 M NaCl; titrant solution: C_{H⁺} = 0.15 M, C_{A⁻} = 0.35 M in 1 M NaCl.

**Table 6. Stability Constants of the Ln(III) Complexes with HA' in 1 M NaCl**

| complex     | La(III) | Ce(III) | Pr(III) | Nd(III) |
|-------------|---------|---------|---------|---------|
| LnA'₂⁺      | 4.40 ± 0.04 | 4.70 ± 0.05 | 5.03 ± 0.08 | 5.20 ± 0.05 |
| LnA'₃⁺      | 7.23 ± 0.03 | 7.79 ± 0.04 | 8.26 ± 0.07 | 8.56 ± 0.06 |
| LnA'₄⁺      | 9.15 ± 0.04 | 10.00 ± 0.05 | 10.47 ± 0.06 | 10.91 ± 0.07 |
Table 6 verify that the trends in complex stability are consistent with those predicted by the overall charge density.

**Comparison between Extraction and Complexation in Aqueous Solutions.** The comparison between the corresponding extracted complexes with HDEHDGA in the organic phase and the complexes formed with HDMDGA in the aqueous solution is further evaluated. Since there is no/negligible significant steric effect from the alkyl groups of HDEHDGA, it is reasonable to assume that the extracted complexes for all four light Ln(III) ions share a similar composition and coordination geometry. The separation factors are mainly originated from varying electrostatic interaction due to the increasing charge density from La(III) to Nd(III). According to the similarity in the spectra shown in Figure 5, we can infer that LnA' complexes in the extracted complexes and the LnA'3 complexes in aqueous solutions also share a similar coordination geometry to that LnA' complexes in solid compounds. Therefore, by assuming that all other trivial parallel factors can be canceled for a pair of adjacent Ln(III) ions. Thus, the difference in the interaction of Ln(III) with HDEHDGA in the extraction system can be translated to the difference in the stability constants of the corresponding complexes with HDMDGA in the aqueous solution. As recorded in Table 7, the ratios of the stability constants of the 1:3 complexes of HDMDGA for the three adjacent Ln(III) pairs are fairly comparable to those for the corresponding extracted complexes of HDEHDGA. Theoretically, the $K_{ex(M2)/ex(M1)}$ ratio should be equal to the SF ($D_{M2}/D_{M1}$). However, a considerable deviation is shown in Table 7, which may be attributed to the different experimental conditions in conjunction with the experimental errors. For the slope analysis method, a trace amount of Ln(III) was used to obtain the extraction constants (as clear in eq 2), whereas, in Table 7, the SFs are calculated from the $D$ values that originated from the extraction under the conditions of much higher concentrations of Ln(III) ions (0.012 M as total Ln(III) concentration). On the other hand, the ratios of the stability constants of MA3 complexes $\beta_{M3}/\beta_{M1}$ are in a good consistency to the corresponding SFs. It should be noted that the experimental conditions for the SFs and stability constants measurements are very similar particularly for the Ln(III) and ligand concentrations. The consistency in the ratios ($\beta_{M3}/\beta_{M1}$) and SFs furnishes a striking piece of evidence about the assumption that the cores (LnA3) of the extracted complexes share similar coordination geometry and possess common composition with the LnA3 complexes in the aqueous solution.

**CONCLUSIONS**

The extraction behavior of the light Ln(III) ions from the HCl–NaCl system has been investigated in the low pH region using Na,N-di(2-ethylhexyl)-diglycolic acid as an extractant. The results reveal that the extraction is mainly governed by the cation-exchange reaction mechanism and is driven by the negative change in enthalpy. Based on the results from the slope analysis method and absorption spectroscopy, the first coordination core of the major extracted species might be the 1:3 complex, $\text{LnA}_3$ ($A = \text{deprotonated HDEHDGA}$). Furthermore, in the second coordination sphere, there is/are one or two HA molecules attached to the core through hydrogen bonding. By correlating the extraction with HDEHDGA and the complexation with HDMDGA thermodynamically and structurally, the origin of the separation factor (selectivity) for the extraction system is well interpreted with the difference in the stability constants of the corresponding complexes in aqueous solutions. Also, this exploration provides an invigorating approach in revealing the related extraction mechanism and the structural information about the extracted complexes. In comparison to those currently deployed extractants in industry, HDEHDGA exhibits considerably better separation factors for the light adjacent Ln(III) pairs, presenting a practical approach for developing new processes of light Ln(III) extraction/separation in the industry.

**EXPERIMENTAL SECTION**

**Materials and Instrumentation.** HDEHDGA and HDMDGA of purity $>97\%$ were prepared by adopting the previously published procedure at China Institute of Atomic Energy (CIAE).\(^4^7\) Lanthanide chloride salts of high purity ($>99.9\%$) were supplied by Aladdin Industrial Corporation, Shanghai, China. Kerosene of AR grade from Tianjin Hengxing Chemical Preparation Co., Ltd. was used as received. Other chemicals were analytical-grade (AR) or higher. All aqueous solutions were prepared using deionized water. The pH values of the working solutions were adjusted with standardized NaOH or HCl solutions and were monitored with a pH meter (Mettler Toledo FiveEasy plus FP20, Germany). All extraction experiments were conducted in a thermostatic vortex shaker equipped with a temperature controller. The initial and equilibrated metal ion concentrations in the aqueous phase were determined with inductively coupled plasma mass spectrometry (ICP-MS) (IRIS Intrepid II XSP).

**Preparation of the Stock Solutions.** A stock solution of the organic phase (0.5 M) was prepared by dissolving a desired weight of HDEHDGA in kerosene, washing with an equal volume of 1 M HCl once and with deionized water thrice. Stock solutions of metal ions were prepared by dissolving appropriate amounts of Ln(III) chlorides in deionized water, and the pH values were adjusted using diluted HCl solutions. The final concentrations of Ln(III) ions in the stock solutions were determined with ICP-MS.

**Solvent Extraction.** All extraction experiments were carried out in triplicates under the same conditions, and the calculated relative standard deviations were less than 5%. In general, equal volumes (5 mL) of the aqueous phase and organic phase were equilibrated for 15 min at 25 ºC unless otherwise stated. Preliminary experiments indicated that the extraction equilibrium could be reached in 5 min. After extraction, the phase separation was facilitated by centrifugation. The Ln(III) ions loaded in the organic phase were
stripped using 1 M HCl, and then, the concentration of Ln(III) ions in both the aqueous phase and the stripe solution was directly measured by ICP-MS after appropriate dilution with 5% HNO₃, taking into consideration the minimum detection limit (DL) of lanthanides by an ICP-MS instrument, (DL = 0.1 μg L⁻¹). The effect of temperature on the extraction of Ln(III) ions was examined within the range of 25–60 °C. All of the experiments were conducted at a fixed ionic strength of 1 M NaCl. In the stripping experiments, the loaded organic phase was contacted with different concentrations of HCl, HNO₃, and H₂SO₄ at 25 °C for 15 min.

The distribution ratio (D) is defined as

\[ D = \frac{[M]_{\text{org}}}{[M]_{\text{aq}}} \]  

where \([M]_{\text{org}}\) and \([M]_{\text{aq}}\) stand for metal ion concentrations in the organic and aqueous phases, respectively. The extraction and stripping percentages are calculated as

\[ \text{Ext.} \% = \left( \frac{D}{D + \frac{V_{\text{aq}}}{V_{\text{org}}}} \right) \times 100 \]  

\[ \text{St.} \% = \frac{[M]_{\text{aq}}}{[M]_{\text{org}}} \times 100 \]

where \(V_{\text{aq}}\) and \(V_{\text{org}}\) denote the volumes of aqueous and organic solutions, respectively.

The separation factor (SF) is defined as

\[ SF = \frac{D_{M_1}}{D_{M_2}} \]  

where \(M_1\) and \(M_2\) represent different metal ions.

**UV−Vis Absorption/Reflectance Spectroscopy.** The absorption/reflectance spectra of Nd(III) complexes in solutions or solid compound were recorded by a UV−vis−near-infrared (NIR) spectrophotometer (Lambda 950, Perkin Elmer or Cary 7000 UMS, Agilent) with setting of 0.15 nm near-infrared spectrophotometer (Lambda 950, Perkin Elmer) for baseline correction, and then about 20 mg of NdA was used for each titration, an acid/base titration with standard hydrochloric acid and sodium hydroxide was carried out under experimental conditions. The distribution of each Nd(III) with solutions of different initial concentrations of Nd(III) and H⁺. The stability constants of Ln(III)/A⁻ complexes were calculated using a Hyperquad (2013) program.

**Single-Crystal X-ray Diffraction.** Block crystals of LnA₃ (Ln = La, Nd) were obtained from 2 mL of 95% ethanol solutions containing 0.1 M Ln(III) and 0.4 M NaA by slow evaporation. Single-crystal X-ray diffraction data were collected on a Super Nova, Dual, Cu at home/near, AtlasS2 diffractometer using graphite monochromated MoKα radiation (\(\lambda = 0.71073 \) Å). Using Olex2, the structures were solved with the ShelXL refinement package using direct methods and refined with the ShelXL refinement package using least squares minimization. All of the hydrogen atoms were geometrically fixed using the riding model. Crystal data for CCDC 1910604, LaA₃ (\(\lambda = 94.804(5)\) Å, \(b = 12.3468(10)\) Å, \(c = 13.5959(10)\) Å, \(α = 79.729(6)\) °, \(β = 80.339(5)\) °, \(γ = 87.876(5)\) °, \(V = 1543.68(19)\) Å³, \(Z = 2, T = 150.01(10)\) K, \(μ (MoKα) = 1.433 mm⁻¹, D_{calc} = 1.332 g cm⁻³, 13654 reflections measured (6.90° ≤ 2θ ≤ 59.556°), 7271 unique \((R_{int} = 0.0536, R_w = 0.0975)\), which were used in all calculations. The final \(R_w = 0.0446 (I > 2σ(I))\) and \(R_{int} = 0.0858\) (all data). Crystal data for CCDC 1910605, NdA₃ (\(\lambda = 94.804(5)\) Å, \(b = 12.2283 (6)\) Å, \(c = 13.4495(6)\) Å, \(α = 79.596(4)\) °, \(β = 80.582(4)\) °, \(γ = 88.007(4)\) °, \(V = 1519.79(12)\) Å³, \(Z = 2, T = 100.00(10) K, μ (MoKα) = 1.760 mm⁻¹, D_{calc} = 1.365 g cm⁻³, 13903 reflections measured (6.92° ≤ 2θ ≤ 59.266°), 7173 unique \((R_{int} = 0.0358, R_w = 0.0678)\), which were used in all calculations. The final \(R_w = 0.0321 (I > 2σ(I))\), and \(R_{int} = 0.0358\) (all data). More information about the structure refinement is provided in the SI.

![Equation 12](image-url) where \(E^0\) is called the standard electrode potential, \(R\) is the gas constant, \(T\) is the temperature (K), \(F\) is the Faraday constant, and \(\{H^+\}\) is the activity of H⁺. The Nernst equation shows the electrode response to be linear in hydrogen ion activity as indicated by \(\{H^+\}\). Under conditions of relatively high ionic strength, 1 M NaCl, taking account of the activity coefficient quotient of a constant that is considerably different from 1, the standard Nernst equation for the glass electrode was modified as the empirical equation, eq 13:

\[ E = E^0 + \frac{s \log[H^+]}{R T} = E^0 - spH \]  

where \([H^+]\) stands for the concentration of H⁺. To obtain the electrode parameters of \(E^0\) and \(s\), before each titration, an acid/base titration with standard hydrochloric acid and sodium hydroxide was carried out under experimental conditions. These parameters allowed calculating the concentrations of H⁺ from the values of the potential measured in immediately following titration. In a typical titration, a solution (about 20 mL) containing appropriate amounts of H⁺ and one of the four lightest lanthanides was titrated with a solution of partially neutralized HA' in 1 M NaCl. The potential values were recorded with the data collection criterion, i.e., the drift of potential (ΔE) less than 0.1 mV in 180 s after each addition of titrant solution. Sixty to one hundred data points were collected in each titration. Multiple titrations were performed for each Ln(III) with solutions of different initial concentrations of Ln(III) and H⁺. The stability constants of Ln(III)/A⁻ complexes were calculated using the Hyperquad (2013) program.
Determination of the dimerization constants of HEDHDGGA in kerosene; stripping of Nd(III) from the loaded organic phase using different mineral acids (Figure S1); reusability of the extractant (Figure S2); and structure refinement of Ln(III) complexes (PDF)

LaA_{3} (CIF)
NdA_{3} (CIF)

Accession Codes
CCDC 1910604 and 1910605 contain the supplementary crystallographic data for this paper.

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Notes
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