

Highly Efficient Extraction Separation of Lanthanides Using a Diglycolamic Acid Extractant

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Liquid-liquid extraction of lanthanide ions (Ln³⁺) using *N,N*-dioctyldiglycolamic acid (DODGAA) was comprehensively investigated, together with fluorescence spectroscopic characterization of the resulting extracted complexes in the organic phase. DODGAA enables the quantitative partitioning of all Ln³⁺ ions from moderately acidic solutions, while showing selectivity for heavier lanthanides, and provides remarkably high extraction separation performance for Ln³⁺ compared with typical carboxylic acid extractants. Furthermore, the mutual separation abilities of DODGAA for light lanthanides are higher than those of organophosphorus extractants. Slope analysis, loading tests, and electrospray ionization mass spectrometry measurements demonstrated that the transfer of Ln³⁺ with DODGAA proceeded through a proton-exchange reaction, forming a 1:3 complex, Ln(DODGAA)₃. The stripping of Ln³⁺ from the extracting phase was successfully achieved under acidic conditions. Time-resolved laser-induced fluorescence spectroscopy revealed that the extracted Eu³⁺ ions were completely dehydrated by complexation with DODGAA.

Keywords Solvent extraction, separation, lanthanides, diglycolamic acid

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Introduction

Lanthanide (Ln) elements have a wide range of applications in a variety of fields, including advanced materials and high-technology industries, because of their unique electronic, optical, and magnetic properties.¹⁻³ With the increasing demand for Ln elements, the development of efficient separation and purification methods for Ln elements is needed. However, since Ln elements have very similar physicochemical properties, the mutual separation of individual Ln elements from each other is very difficult. This is a major reason for the high cost of Ln elements.

Liquid-liquid extraction is one of the most effective analytical methods for the separation and purification of various metal ions. This technique is a highly versatile method, which is used in laboratories and processing industries to selectively recover target metal ions from aqueous solutions containing various metal ions. The extractant plays a key role in the extraction efficiency and the separation operation. In the extraction separation of Ln cations, commercial organophosphorus compounds such as di(2-ethylhexyl)phosphoric acid (D2EHPA)

and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC-88A) are most frequently used as extractants.⁴⁻⁶ However, these extractants cannot be completely decomposed by incineration, leaving phosphorus residues as secondary wastes. In contrast, extractants consisting only of C, H, O, and N atoms can be completely incinerated to gaseous products, and thus reducing the amounts of harmful solid wastes (CHON-principle).⁷ Much effort has been devoted to the development of CHON-based extractants as green extractants for establishing new residual-waste-free extraction processes. For example, CHON-based extractants such as diglycolamide,⁸⁻¹¹ malonamide,^{12,13} and *N*-heterocyclic ligands¹⁴⁻¹⁸ have been used for the extraction of Ln and actinide cations. These extractants provide high-performance extraction separation of Ln and actinide cations. However, since they are neutral Lewis-base-type extractants, they show quite different extraction behavior to those of ionizable Brønsted-acid-type organophosphorus compounds. The extraction efficiency of Ln cations using neutral Lewis-base-type extractants increases with increasing anion concentration, whereas Ln transfer using ionizable Brønsted-acid-type extractants can be simply controlled by the pH of the aqueous phase, and involves no anionic species. Although CHON-based extractants incorporating Brønsted acids such as carboxylic acids¹⁹⁻²³ or β-diketones^{24,25} have also been developed for the extraction of Ln cations, almost all of these

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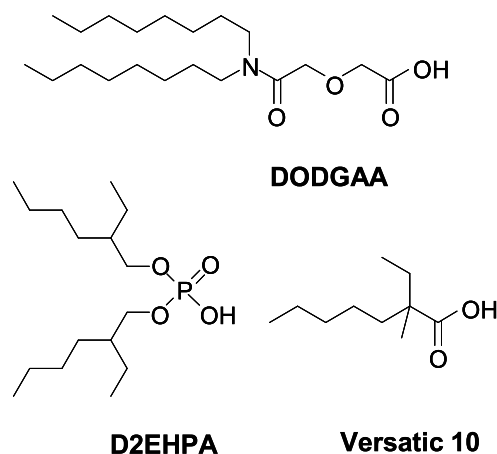


Fig. 1 Molecular structures and abbreviations of extractants.

extractants have very low extraction and separation performances for Ln cations because of their poor coordinating ability and selectivity for Ln cations. The development of Brønsted-acid-type extractants based on the CHON-principle, with superior extraction separation abilities relative to organophosphorus compounds, represents a challenging task.

In recent papers, we reported on the synthesis of a novel CHON-based extractant, *N,N*-dioctyldiglycolamic acid (DODGAA, Fig. 1),^{7,26,27} which is an acidic tridentate ligand with a carbamoyl group and a carboxy group connected by an ether chain. Since the extractant can be synthesized simply in a single step, this helps to reduce the production costs of the extractant. The liquid-liquid extraction and liquid-membrane transfer of rare-earth metal ions from aqueous solutions containing base metal ions were performed using DODGAA, which indicated that DODGAA has higher selectivity for rare-earth metal ions than for base metal ions.²⁸⁻³¹

In the present study, we comprehensively investigated the extraction behavior of all Ln³⁺ ions, except Pm³⁺, with DODGAA, and investigated the extraction mechanism using slope analysis, loading tests, and electrospray ionization mass spectrometry (ESI-MS) measurements. The mutual separation of individual Ln³⁺ ions using DODGAA was compared with mutual separation using D2EHPA (Fig. 1) and the commercial carboxylic-acid-type compound 2-ethyl-2-methylheptanoic acid (Versatic 10, Fig. 1). In addition, the coordination environments of the extracted Eu complexes in the organic phase were characterized using time-resolved laser-induced fluorescence spectroscopy (TRLFS).

Experimental

Reagents

The commercial organophosphorus extractant D2EHPA was obtained from Tokyo Kasei Kogyo Co., Inc. (Tokyo, Japan). The commercial carboxylic-acid-type extractant Versatic 10 was kindly supplied by Shell Japan, Ltd. (Tokyo, Japan). These commercial extractants were used without further purification. Diglycolic anhydride (Tokyo Kasei Kogyo Co., Inc.) and dioctylamine (Aldrich Chemical Co., Inc.) were used for synthesizing of the extractant DODGAA. Ln(III) nitrates (all lanthanides except Pm(III), which is a radioactive element) were purchased from Kishida Chemical Co., Ltd. (Osaka, Japan). All other reagents were commercially available, of analytical grade,

and used as received. Ultrapure water (18.2 MΩ·cm), produced using a Direct-Q system (Millipore), was used throughout this study.

Synthesis of DODGAA

The extractant DODGAA was synthesized according to a published procedure.^{7,26} Diglycolic anhydride (4.17 g, 35.9 mmol) was dispersed in CH₂Cl₂ (40 mL). Dioctylamine (7.0 g, 28.4 mmol) dissolved in CH₂Cl₂ (10 mL) was slowly added dropwise to the solution, in an ice-bath. The mixture was stirred at room temperature overnight. The resulting clear solution was washed four times with ultrapure water and dried with anhydrous sodium sulfate. The solvent was removed *in vacuo* to give the crude product, which was recrystallized from *n*-hexane to obtain DODGAA as a white powder (9.57 g, 94.2% yield). ¹H NMR (400 MHz, CDCl₃, TMS, 25°C): δ 0.89 (t, 6H, N-(CH₂)₇-CH₃), 1.29 (s, 20H, N-CH₂-CH₂-(CH₂)₅-CH₃), 1.55 (s, 4H, N-CH₂-CH₂-C₆H₁₃), 3.10, 3.35 (t, 4H, N-CH₂-C₇H₁₅), 4.22 (s, 2H, N-CO-CH₂-O), 4.40 ppm (s, 2H, CH₂-COOH). Elemental analysis (%) calcd. for C₂₀H₃₉O₄N₁: C, 67.19; H, 10.99; N, 3.92. Found: C, 66.99; H, 11.00; N, 3.94.

Measurement of acid dissociation constants

Potentiometric titrations were performed using a glass electrode (Metrohm, 6.0150.100) and a double-junction Ag/AgCl reference electrode (Metrohm, 6.0726.100, 0.1 M LiCl in H₂O-C₂H₅OH (1:1, v/v) as the inner-filling solution). The titration curves obtained were analyzed using the Bjerrum plot, which provides an excellent means for obtaining the acid dissociation constants (*K*_a) from titration data. The ordinate, *n*_H, was the average number of H⁺ ions bound to a weak acid, defined as (moles of bound H⁺)/(total moles of weak acid). The abscissa was -log [H⁺], where [H⁺] denotes the H⁺ concentration calculated from the EMF value of the electrode, using a blank titration without the weak acid in the same medium. The best-fit curves were obtained by a non-linear least-squares fitting procedure with p*K*_a used as an adjustable parameter.

Extraction procedure

An organic phase was prepared by dissolving DODGAA in isoctane containing 5 vol% 1-octanol as a solubilizer. Aqueous phases were prepared by dissolving Ln(III) nitrate in HNO₃ at concentrations of 0.01 mM (1 M = 1 mol L⁻¹). Equal volumes of the organic and aqueous solutions were mixed and shaken mechanically at 25°C for 30 min to attain equilibrium. After separation of the two phases by centrifugation, the metal ions in the organic phase were back-extracted into 1 M HNO₃. The concentrations of Ln³⁺ in the aqueous phase and the receiving phase were determined using an inductively coupled plasma mass spectrometer (Hewlett Packard HP 4500) to obtain the distribution ratio ($D = [\text{Ln}^{3+}]_{\text{org}}/[\text{Ln}^{3+}]_{\text{aq}}$) and the degree of back-extraction ($= [\text{Ln}^{3+}]_{\text{rec}}/[\text{Ln}^{3+}]_{\text{org}}$). The subscripts org, aq, and rec denote the organic phase, the aqueous phase, and the receiving phase, respectively. The equilibrium pH values of the aqueous phases were also measured.

Electrospray ionization mass spectrometry (ESI-MS)

A Eu³⁺-DODGAA complex solution was prepared according to the following procedure. An isoctane solution (5 vol% 1-octanol) of DODGAA (30 mM) was shaken with an equal volume of aqueous solution containing Eu(NO₃)₃ (10 mM) at 25°C for 30 min. After phase separation, the prepared organic solution was diluted with isoctane containing 5 vol% 1-octanol to the desired concentration of the extracted complex. The mass spectra were recorded in the positive ionization mode using a

JEOL-T100CS AccuTOF spectrometer. The mass range from 250 to 3000 m/z was scanned in 1 min. The desolvation temperature was 250°C and the sample injection flow rate was 20 $\mu\text{L}/\text{min}$.

Fluorescence measurements

Aqueous phases were prepared by dissolving $\text{Eu}(\text{NO}_3)_3$ in H_2O (pH 5.0) or D_2O (pD 5.0) at concentrations of 0.1 mM. The aqueous solutions were shaken with an equal volume of an iso-octane solution (5 vol% 1-octanol) of DODGAA (10 mM) at 25°C for 30 min. After phase separation, the fluorescence lifetimes of the Eu^{3+} -DODGAA complexes in the prepared organic solutions were measured using a pulsed-laser detection system. All samples were put into non-luminescent quartz micro cells (150 μL). The excitation pulse used in this study was the fourth-harmonic generation of an Nd:YAG laser (Quantel) coupled with an optical parametric oscillator unit (Opotek, Inc.) to convert the wavelength of the laser light to 394 nm. The fluorescence of the sample was collected at a right angle to the excitation beam, and directed via two lenses into the entrance slit of a spectrograph (Shamrock RS 303i, 300 lines/mm, Andor Technology). The optically triggered signals from the PIN photodiode to the controller in the PC software were adjusted using a delay generator (DG535, Stanford Research, Inc.). The resulting fluorescence spectra were measured using a time-gated ICCD camera (iStar, Andor Technology). The gate width was 400 μs and the delay time after the excitation laser pulse was 10 μs . The fluorescence emission of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ at 616 nm was measured to obtain the fluorescence lifetimes of $\text{Eu}(\text{III})$ complexes, which represented the average of the three measurements. Fluorescence spectra of the same samples were measured using a spectrofluorometer (JASCO FP-6500). The excitation wavelength was 394 nm (5 nm band-pass), and emission spectra were recorded from 500 to 750 nm (5 nm band-pass).

Results and Discussion

Acid dissociation constant of DODGAA

The value of the acid dissociation constant (K_a) of DODGAA was determined by potentiometric titration. DODGAA is insoluble in water, but is soluble in various alcohols. The measurements were therefore performed in H_2O - $\text{C}_2\text{H}_5\text{OH}$ (1:1, v/v) with a constant ionic strength of 0.1 M LiCl at 25°C (Fig. S1, Supporting Information).³² The $\text{p}K_a$ value of DODGAA was estimated to be 4.11 ± 0.01 in H_2O - $\text{C}_2\text{H}_5\text{OH}$ (1:1, v/v). For comparison, it was confirmed that the $\text{p}K_a$ value of acetic acid was 5.51 ± 0.02 under the same conditions. The results indicate that DODGAA is more acidic than acetic acid, although both ligands incorporate a carboxylic acid. Furthermore, it should be noted that the acidity of DODGAA is stronger in water than in H_2O - $\text{C}_2\text{H}_5\text{OH}$ (1:1, v/v) because of the high permittivity of water. The strong acidity of DODGAA may be advantageous for coordinative and electrostatic interactions with metal ions.

Extraction behavior of Ln(III) with DODGAA

The extraction behavior of 14 Ln cations with DODGAA as a function of the pH in the aqueous phase is shown in Fig. 2. The extractability of Ln cations increased with increasing pH. Quantitative extraction was achieved in moderately acidic solutions ($\text{pH} \geq 2$ for middle and heavy Ln^{3+}). In contrast, typical carboxylic-acid-type extractants based on the CHON-principle (e.g., Versatic 10) generally have low extraction

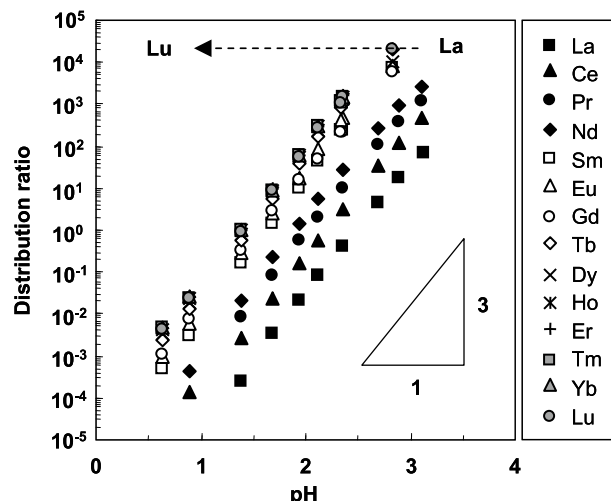
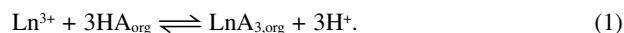


Fig. 2 Dependence of lanthanide extraction using DODGAA on the aqueous phase pH. $[\text{Ln}^{3+}] = 0.01 \text{ mM}$, $[\text{DODGAA}] = 10 \text{ mM}$.

performances for Ln^{3+} , and transfer Ln^{3+} under neutral aqueous conditions ($6 \leq \text{pH} \leq 7$).^{19,28} Although DODGAA is a CHON-based extractant with a carboxy group, this ligand provided remarkably high extraction performance for Ln^{3+} compared with typical carboxylic-acid-type extractants. In fact, the extraction performance of DODGAA was comparable to that of organophosphorus extractants (e.g., D2EHPA and PC-88A). Furthermore, it was found that DODGAA exhibits high selectivity for heavier lanthanides. The slopes of the logarithmic distribution ratio *versus* pH were 3 for all 14 Ln cations, suggesting that three protons from the DODGAA molecules are released into the aqueous phase to form neutral complexes with trivalent Ln^{3+} ions through a proton-exchange reaction. It was confirmed that the pH values in the aqueous phases were lower after extraction.

In addition, the extraction of Ln cations was investigated as a function of the DODGAA concentration to determine the stoichiometry of the Ln^{3+} -DODGAA complexes in the organic phases. La^{3+} , Eu^{3+} , and Lu^{3+} were used as representative light, middle, and heavy Ln cations, respectively. As shown in Fig. 3, logarithmic plots of the distribution ratio *versus* the DODGAA concentration gave straight lines with a slope of 3 for La^{3+} , Eu^{3+} , and Lu^{3+} extractions. These results indicate that three DODGAA molecules were required to extract one Ln^{3+} , and a 1:3 complex, $\text{Ln}(\text{DODGAA})_3$, was formed. On the basis of the slope analysis results, the extraction equilibrium equation of Ln transfer using DODGAA (HA) is represented as follows:



In the cases of D2EHPA and Versatic 10, the extractants are known to exist as dimers in non-polar organic solvents.^{33,34} When the dimers are involved in Ln^{3+} transfer, 1:6 discrete complexes are formed. To confirm the stoichiometry of the Ln^{3+} -DODGAA complexes in Eq. (1), loading tests were conducted by varying the Eu^{3+} concentration in the aqueous phase. Figure 4 shows that the molar ratio of the initial DODGAA concentration to the extracted Eu^{3+} concentration plateaued at a value of 3 with increasing loaded Eu^{3+} concentration. This result is consistent with the formation of a 1:3 complex with DODGAA monomers.

We also used ESI-MS to obtain direct evidence for the

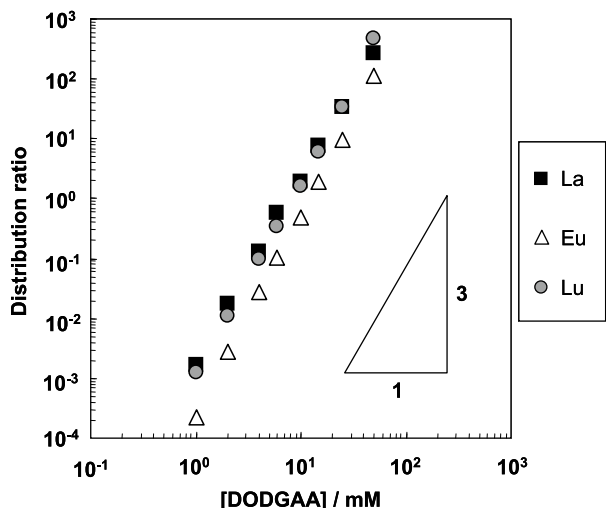


Fig. 3 Dependence of lanthanide extraction using DODGAA on the DODGAA concentration. $[La^{3+}] = [Eu^{3+}] = [Lu^{3+}] = 0.01$ mM, pH 2.5 for La^{3+} , pH 1.5 for Eu^{3+} and Lu^{3+} .

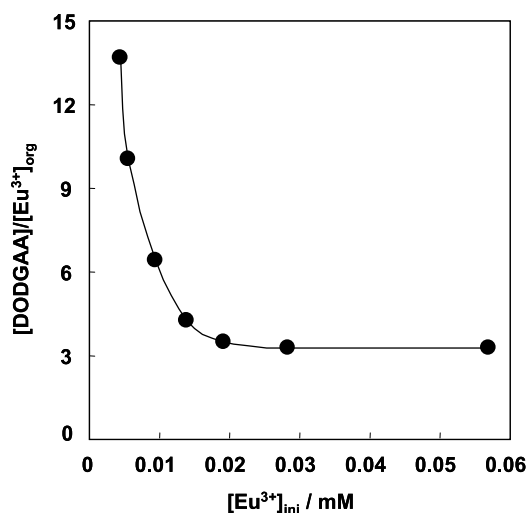


Fig. 4 Loading test for Eu^{3+} extraction using DODGAA. $[DODGAA] = 0.06$ mM; aqueous solutions were adjusted to pH 5.2 using HEPES buffer.

formation of a 1:3 complex. ESI-MS is a soft ionization technique that allows the generation of charged ions without appreciably disrupting any metal-ligand bonds.³⁵ ESI-MS can give complementary information about the formation, stoichiometry, and speciation of complexes involving metal ions and organic ligands. The extracted Eu^{3+} complex in the organic phase with DODGAA was subjected to ESI-MS. As shown in Fig. 5, a new peak was clearly observed at 1223.27 (m/z), which corresponds to $[3DODGAA + Eu^{3+} - 2H^+]^+$. This result is in good agreement with the stoichiometry determined using the methods described above.

The extraction equilibrium constant (K_{ex}) in Eq. (1) is defined as follows:

$$K_{ex} = [LnA_3]_{org}[H^+]^3/[Ln^{3+}][HA]_{org}^3 = D[H^+]^3/[HA]_{org}^3. \quad (2)$$

Equation (2) can be converted to the following equation by taking the logarithms:

$$\log D = 3\log[HA] - 3\log[H^+] + \log K_{ex} \\ = 3\log([HA]/[H^+]) + \log K_{ex}. \quad (3)$$

As shown in Fig. S2 (Supporting Information), plots of $\log D$ versus $\log([HA]/[H^+])$ gave straight lines with a slope of 3 for all 14 Ln cations. The values of $\log K_{ex}$ determined from the extraction data in Fig. S2 are listed in Table 1. The competitive extraction of the 14 Ln cations using DODGAA was also carried out to assess its selectivity. The separation performance of DODGAA for Ln cations was compared with those of the commercial extractants Versatic 10 and D2EHPA (Fig. 6). The distribution ratio of Ln cations with the three extractants was normalized using the distribution ratio of La^{3+} . All three extractants exhibited selectivity for the heavier lanthanides, in the order $D2EHPA > DODGAA > Versatic\ 10$. The higher charge densities of the heavier lanthanides probably facilitated electrostatic interactions with anionic extractants. DODGAA provided remarkably high extraction and separation performances for Ln cations compared with Versatic 10, as the result of a cation-oxygen-donor interaction and a chelate effect created by the tridentate diglycolamic acid frame and an electrostatic interaction. In fact, the separation factor between La^{3+} and Lu^{3+} , which is defined as $K_{ex,Lu}/K_{ex,La}$, is approximately $10^{3.43}$. This value is unprecedentedly high among CHON-based extractants incorporating a carboxylic acid. In contrast, the separation ability of DODGAA is higher for lighter lanthanides from La^{3+} to Gd^{3+} , and is lower for heavier lanthanides from Tb^{3+} to Lu^{3+} than that of D2EHPA. DODGAA is expected to be

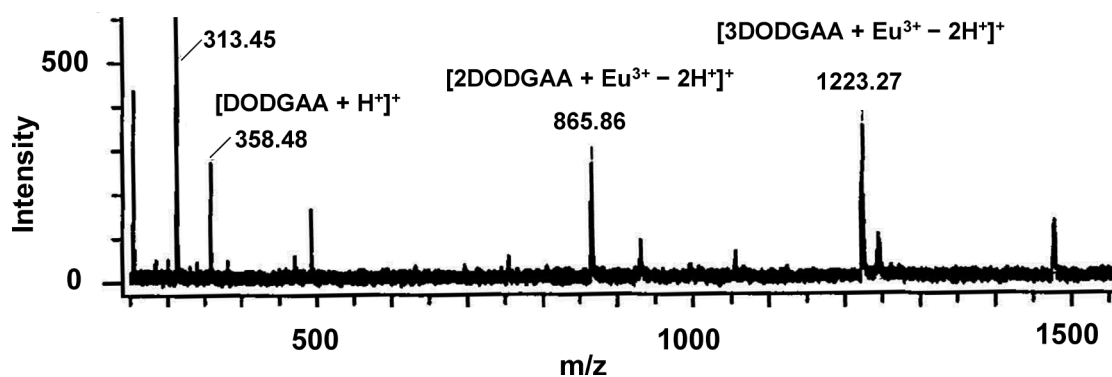


Fig. 5 ESI-MS spectrum of Eu^{3+} -DODGAA complexes in the organic phase. The extracted complexes were prepared by shaking a 30 mM DODGAA solution with 10 mM Eu^{3+} solution, and were diluted to the desired concentration.

Table 1 Extraction equilibrium constants of lanthanides with DODGAA (25°C)

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
$\log K_{\text{ex}}$	-1.50	-0.61	-0.12	0.27	1.19	1.42	1.30	1.76	1.86	1.95	1.98	1.96	1.96	1.93

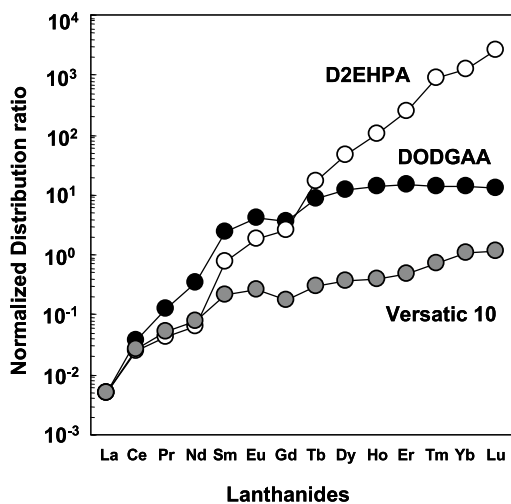


Fig. 6 Selectivity of DODGAA, Versatic 10, and D2EHPA for lanthanides. $[\text{Ln}^{3+}] = 0.01 \text{ mM}$, $[\text{DODGAA}] = 10 \text{ mM}$, pH 2.0 for DODGAA, pH 6.3 for Versatic 10, pH 1.4 for D2EHPA. The distribution ratio of lanthanides with the three extractants was normalized using the distribution ratio of La^{3+} .

useful for the mutual separation of light lanthanides.

Recovery of Ln(III) from organic phase

The recovery of the extracted metal ions is important for separation and purification. Stripping tests of 14 Ln cations from the organic phase into HNO_3 solution were carried out. As shown in Fig. 7, the degree of back-extraction of all 14 Ln cations was enhanced with increasing acidity of the receiving phase. As a result, quantitative recovery was achieved under acidic conditions, where DODGAA loses its ability to coordinate to Ln^{3+} . However, lowering of the degree of back-extraction was observed when using 5 M HNO_3 . DODGAA probably acted as a neutral tridentate extractant under highly acidic conditions, and extracted Ln^{3+} accompanied by NO_3^- as a counter-anion to form ion pairs, like N,N,N',N' -tetra(*n*-octyl)diglycolamide.^{8,9}

Fluorescence spectroscopic characterization of extracted complexes

The coordination environments of the Ln^{3+} -DODGAA complexes in the organic phase were probed using fluorescence spectroscopic methods. Eu^{3+} was used as a representative fluorescent Ln cation. The fluorescence spectra of Eu^{3+} have characteristic peaks corresponding to transitions from the $^5\text{D}_0$ to $^7\text{F}_1$ states (Fig. 8). The $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition at 593 nm is a magnetic-dipole-allowed transition, which is independent of the coordination environment around Eu^{3+} . The spectra were normalized using the peak intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition. The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition at 616 nm is an electric-dipole-allowed hyper-sensitive transition. The intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is highly dependent on the coordination environment around Eu^{3+} , and increases with decreasing symmetry around

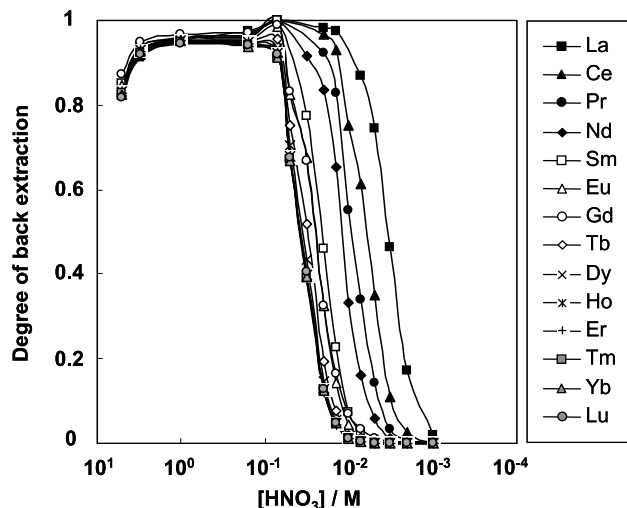


Fig. 7 Back-extraction behavior of lanthanides from the extracting phase. $[\text{Ln}^{3+}] = 0.01 \text{ mM}$, $[\text{DODGAA}] = 10 \text{ mM}$.

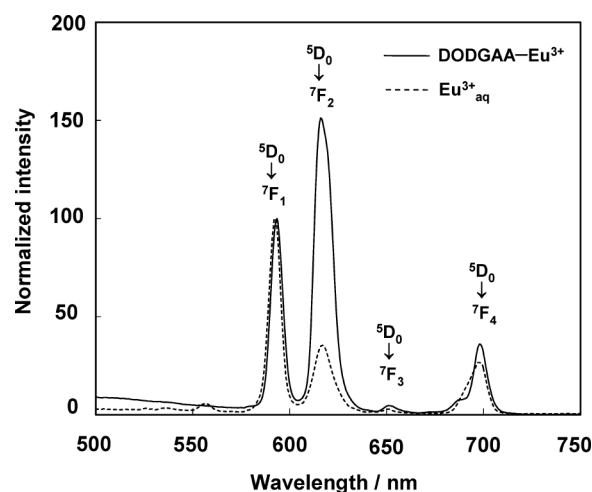


Fig. 8 Fluorescence spectra of Eu^{3+} -DODGAA complexes (solid line) in the organic phase and Eu^{3+} (broken line) in an aqueous solution. Eu^{3+} complex: $[\text{Eu}^{3+}] = 0.1 \text{ mM}$, $[\text{DODGAA}] = 10 \text{ mM}$. Aqua Eu^{3+} : $[\text{Eu}^{3+}] = 1 \text{ mM}$, pH 4.2. Excitation wavelength = 394 nm, band pass = 5 nm.

Eu^{3+} . The intensity ratio of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition was enhanced by transfer into the organic phase. This result indicates that the symmetry of the Eu^{3+} -DODGAA complex in the organic phase is very low relative to Eu^{3+} in water.

TRLFS is an analytical technique capable of discriminating different chemical species of fluorescent metal ions.³⁶⁻³⁸ The fluorescence decays of the Eu^{3+} complexes in the organic phase were measured by TRLFS (Fig. S3, Supporting Information). The decays were normalized using the intensities of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition (616 nm) at the first point. The fluorescence

lifetime (τ) of Eu^{3+} is affected by the hydration state of the Eu^{3+} inner coordination sphere. The hydrating H_2O molecules serve as effective quenchers for the Eu^{3+} fluorescence as a result of vibrational energy transfer to the coordinated H_2O molecules from the Eu^{3+} excited state. In contrast, the hydrating D_2O molecules are ineffective in quenching. The number of water molecules directly coordinated to Eu^{3+} , $N_{\text{H}_2\text{O}}$, can be calculated using the following equation:³⁹

$$N_{\text{H}_2\text{O}} = 1.05(k_{\text{H}_2\text{O}} - k_{\text{D}_2\text{O}}) \quad (4)$$

where $k_{\text{H}_2\text{O}}$ and $k_{\text{D}_2\text{O}}$ ($k = 1/\tau$) are the fluorescence decay constants of the Eu^{3+} complexes containing H_2O and D_2O . The absolute uncertainty of $N_{\text{H}_2\text{O}}$ was estimated to be ± 0.5 . The $k_{\text{H}_2\text{O}}$, $k_{\text{D}_2\text{O}}$, and $N_{\text{H}_2\text{O}}$ of the Eu^{3+} complexes were found to be as follows: $k_{\text{H}_2\text{O}} = 0.45 \pm 0.04$ (ms^{-1}), $k_{\text{D}_2\text{O}} = 0.41 \pm 0.02$ (ms^{-1}), and $N_{\text{H}_2\text{O}} = 0.04$. The results demonstrate that DODGAA molecules displace all of the hydrating water molecules from the primary coordination sphere. Assuming that the total coordination number in the Eu^{3+} primary coordination sphere is nine, it is reasonable to suppose that three DODGAA molecules coordinate to the Eu^{3+} center in a tridentate fashion.

Conclusions

In the present study, the extraction behavior of 14 lanthanides with DODGAA was comprehensively investigated, and the results were compared with those obtained using the commercial extractants Versatic 10 and D2EHPA. All of the lanthanides were quantitatively transferred from acidic solutions with DODGAA, showing selectivity for heavier lanthanides. The metal extraction was confirmed to proceed through a proton-exchange reaction, forming a 1:3 complex, $\text{Ln}(\text{DODGAA})_3$. DODGAA showed unprecedentedly high extraction and separation performances for Ln^{3+} compared with other CHON-based extractants incorporating a carboxylic acid, such as Versatic 10. Furthermore, the mutual separation abilities of DODGAA for light lanthanides are higher than that of organophosphorus extractants such as D2EHPA. The metal ions extracted into the extracting phase were readily recovered under acidic conditions. TRLFS demonstrated that DODGAA completely dehydrated the extracted complexes in the organic phase. DODGAA has a simple molecular structure, but can provide excellent extraction performance and separation ability for lanthanides. We envision the practical use of DODGAA in the industrial extraction and separation of lanthanides as an alternative to commercially available extractants.

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Supporting Information

Figures S1 – S3 showing potentiometric titration curves, logarithmic plots of the distribution ratios of lanthanides as a

function of the logarithm of $[\text{DODGAA}]/[\text{H}^+]$, and fluorescence decays of the Eu^{3+} -DODGAA complexes. This material is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

References

1. V. S. Sastri, J.-C. Bünzli, V. R. Rao, G. V. S. Rayudu, and J. R. Perumareddi, "Modern Aspects of Rare Earths and Their Complexes", **2003**, Elsevier, Amsterdam.
2. J.-C. Bünzli, *Acc. Chem. Res.*, **2006**, *39*, 53.
3. K. Binnemans, *Chem. Rev.*, **2009**, *109*, 4283.
4. F. Kubota, M. Goto, and F. Nakashio, *Solvent Extr. Ion Exch.*, **1993**, *11*, 437.
5. A. Ohashi, T. Hashimoto, H. Imura, and K. Ohashi, *Talanta*, **2007**, *73*, 893.
6. S. Radhikaa, B. N. Kumara, M. L. Kantama, and B. R. Reddy, *Sep. Purif. Technol.*, **2010**, *75*, 295.
7. H. Naganawa, K. Shimojo, H. Mitamura, Y. Sugo, J. Noro, and M. Goto, *Solvent Extr. Res. Dev., Jpn.*, **2007**, *14*, 151.
8. K. Shimojo, K. Kurahashi, and H. Naganawa, *Dalton Trans.*, **2008**, 5083.
9. Y. Sasaki, Y. Kitatsuji, Y. Tsubata, Y. Sugo, and Y. Morita, *Solvent Extr. Res. Dev., Jpn.*, **2011**, *18*, 93.
10. D. Jańczewski, D. N. Reinhoudt, W. Verboom, C. Hill, C. Allignol, and M.-T. Duchesne, *New J. Chem.*, **2008**, *32*, 490.
11. P. K. Mohapatra, M. Iqbal, D. R. Raut, W. Verboom, J. Huskens, and S. V. Godbole, *Dalton Trans.*, **2012**, *41*, 360.
12. G. Y. S. Chan, M. G. B. Drew, M. J. Hudson, P. B. Iveson, J.-O. Liljenzin, M. Skålberg, L. Spjuth, and C. Madic, *J. Chem. Soc., Dalton Trans.*, **1997**, 649.
13. H. B. Yang, E. H. Lee, J. K. Lim, D. Y. Chung, and K. W. Kim, *J. Radioanal. Nucl. Chem.*, **2009**, *280*, 495.
14. Z. Kolarik, *Chem. Rev.*, **2008**, *108*, 4208.
15. M. G. B. Drew, M. R. S. J. Foreman, C. Hill, M. J. Hudson, and C. Madic, *Inorg. Chem. Commun.*, **2005**, *8*, 239.
16. G. Benay, R. Schurhammer, J. Desaphy, and G. Wipff, *New J. Chem.*, **2011**, *35*, 184.
17. F. W. Lewis, L. M. Harwood, M. J. Hudson, M. G. B. Drew, J. F. Desreux, G. Vidick, N. Bouslimani, G. Modolo, A. Wilden, M. Sypula, T.-H. Vu, and J.-P. Simonin, *J. Am. Chem. Soc.*, **2011**, *133*, 13093.
18. T. Kida, Y. Inaba, W. Watanabe, Y. Nakajuma, S. Fukuoka, K. Takeshita, and A. Mori, *Chem. Lett.*, **2010**, *39*, 774.
19. F. Kubota, K. Shinohara, K. Shimojo, T. Oshima, M. Goto, S. Furusaki, and T. Hano, *Sep. Purif. Technol.*, **2001**, *24*, 93.
20. M. Goto, K. Shinohara, K. Shimojo, T. Oshima, and F. Kubota, *J. Chem. Eng. Jpn.*, **2002**, *35*, 1012.
21. T. Nakamura, K. Ohto, T. Oshima, and K. Inoue, *Solvent Extr. Res. Dev., Jpn.*, **2006**, *13*, 89.
22. Y. G. Wang, Y. Xiong, S. L. Meng, and D. Q. Li, *Talanta*, **2004**, *63*, 239.
23. S. Fan, X. Zhao, N. Song, Y. Shi, Q. Jia, and W. Liao, *Sep. Purif. Technol.*, **2010**, *71*, 241.
24. E. Bou-Maroun, H. Chebib, M. J. F. Leroy, A. Boos, and G. J. Goetz-Grandmont, *Sep. Purif. Technol.*, **2006**, *50*, 220.
25. E. Bou-Maroun, A. Boos, and G. J. Goetz-Grandmont, *Sep. Purif. Technol.*, **2007**, *53*, 250.
26. K. Shimojo, H. Naganawa, J. Noro, F. Kubota, and M. Goto, *Anal. Sci.*, **2007**, *23*, 1427.
27. K. Shimojo, A. Nakai, H. Okamura, A. Ohashi, and H. Naganawa, *Anal. Sci.*, **2013**, *29*, 147.

28. F. Kubota, Y. Shimobori, Y. Baba, Y. Koyanagi, K. Shimojo, N. Kamiya, and M. Goto, *J. Chem. Eng. Jpn.*, **2011**, *44*, 307.
 29. F. Yang, Y. Baba, F. Kubota, N. Kamiya, and M. Goto, *Solvent Extr. Res. Dev., Jpn.*, **2012**, *19*, 69.
 30. F. Kubota, Y. Shimobori, Y. Koyanagi, K. Shimojo, N. Kamiya, and M. Goto, *Anal. Sci.*, **2010**, *26*, 289.
 31. Y. Baba, F. Kubota, N. Kamiya, and M. Goto, *Solvent Extr. Res. Dev., Jpn.*, **2011**, *18*, 193.
 32. H. Okamura, A. Ikeda-Ohno, T. Saito, N. Aoyagi, H. Naganawa, N. Hirayama, S. Umetani, H. Imura, and K. Shimojo, *Anal. Chem.*, **2012**, *84*, 9332.
 33. C. Marie, B. Hiscox, and K. L. Nash, *Dalton Trans.*, **2012**, *41*, 1054.
 34. A. C. Dupreez and J. S. Preston, *Solvent Extr. Ion Exch.*, **1992**, *10*, 207.
 35. G. S. Groenewold, G. Elias, B. J. Mincher, S. P. Mezyk, and J. A. LaVerne, *Talanta*, **2012**, *99*, 909.
 36. H. Okamura, H. Sakae, K. Kidani, N. Hirayama, N. Aoyagi, T. Saito, K. Shimojo, H. Naganawa, and H. Imura, *Polyhedron*, **2012**, *31*, 748.
 37. T. Saito, H. Sao, K. Ishida, N. Aoyagi, T. Kimura, S. Nagasaki, and S. Tanaka, *Environ. Sci. Technol.*, **2010**, *44*, 5055.
 38. G. Plancque, V. Moulin, P. Toulhoat, and C. Moulin, *Anal. Chim. Acta*, **2003**, *478*, 11.
 39. W. D. Horrocks Jr. and D. R. Sudnick, *J. Am. Chem. Soc.*, **1979**, *101*, 334.
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