

A New “Green” Extractant of the Diglycol Amic Acid Type for Lanthanides

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A compound having a diglycol amic acid frame, DODGAA, has been synthesized as a new “green” extractant for lanthanides. The new extractant is composed of carbon, hydrogen, oxygen, and nitrogen atoms and is therefore fully combustible, producing gases without solid waste and its solubility in water is found to be very low. These properties avoid production of industrial waste from the incineration of degraded extractants and the risk of aquatic environmental pollution. In its extraction ability for lanthanide ions and its ability for their mutual separation, DODGAA is much superior to carboxylic acid type extractants, such as Versatic 10, which is also completely combustible. The extraction and separation performance of DODGAA is comparable to that of the less “green” organophosphorus extractants, such as PC-88A and DEHPA, that are widely used in current industry.

1. Introduction

The demand for the lanthanide series elements having unique electronic and optical characteristics increases steadily with the demand for materials for advanced devices in industry. The lanthanides resemble each other in physical and chemical properties and are therefore difficult to separate, which is a reason why they are expensive rare metals. Solvent extraction is the main technique for the separation and refining of lanthanides in industry. Organophosphorus compounds are often employed for the extraction of

lanthanides from acidic solutions into an aliphatic organic solvent. For instance, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) and bis(2-ethylhexyl)phosphoric acid (DEHPA) are well-known as extractants used commercially for the solvent extraction of lanthanides. These organophosphorus extractants show excellent performance for the metal extraction and separation [1-9]. However, the extractants are not fully combustible, leaving phosphorous residues as solid waste. Further, their solubilities in water are not low. Thus, they can be potential environmental pollutants that increase the risk of aquatic environment pollution and the burden of industrial waste produced by the incineration of degraded extractants. On the other hand, carboxylic acid type compounds, e.g., 2-methyl-2-ethyl-1-heptanoic acid (Versatic 10), which are relatively inexpensive and readily available, are also used in some commercial processes for the extraction and separation of lanthanides [10-19]. Since such compounds are composed of carbon, hydrogen, and oxygen atoms, they are completely combustible and leave no residue. However, such a more earth-friendly (“green”) extractant as Versatic 10 is no match for PC-88A and DEHPA in the extraction and separation efficiency for lanthanides. With Versatic 10, lanthanide ions are poorly extracted even from weakly acidic solutions (e.g., pH 5); while these metal ions are quantitatively extracted with DEHPA from a considerably acidic solution (e.g., pH 2), not to mention from a slightly acidic or neutral solution. In addition, the separation factor for individual lanthanide pairs with Versatic 10 is much inferior to that for PC-88A or DEHPA.

In contrast, a compound having a diglycolamide frame, such as tetraoctyldiglycolamide (TODGA), is a tridentate Lewis-base type extractant for lanthanides [20-22]. TODGA is composed of carbon, hydrogen, oxygen, and nitrogen atoms and is completely combustible. However, the behavior of such a base type extractant with regard to the extraction and back-extraction of metal ions is quite different from that of the acid type extractants, such as PC-88A, DEHPA, and Versatic 10. In the case of these acid type extractants, the extraction of lanthanides into an organic solvent is promoted with increasing pH (e.g., lower concentration of HNO_3) and the metal ions can be efficiently recovered from the organic phase into a receiving phase with decreasing pH (e.g., higher concentration of HNO_3). In contrast, the extraction and back-extraction behaviors of the metal ions with TODGA are the opposite to those of the acid type extractants, i.e., the extractability of the metal ions is higher at higher HNO_3 concentration and their recovery is higher at lower HNO_3 concentration. A compound having a carboxyl group instead of a carbamoyl group in the diglycolamide frame, i.e., a diglycol amic acid frame, is also fully combustible and can be utilized as a new “green” extractant of the acid type. Such a new compound is expected to extract lanthanide ions efficiently from a moderately acidic solution (e.g., $1 \leq \text{pH} \leq 3$) like PC-88A and DEHPA because the compound in the dissociated form has strong coordination properties. In the present study, an alkylated diglycol amic acid, dioctyldiglycol amic acid (DODGAA), was originally synthesized as a new

extractant for lanthanide ions. The extraction and separation performance of DODGAA and its solubility in water are examined and comparing with the results for PC-88A, DEHPA, and Versatic 10.

2. Experimental

2.1 Materials

Diocetylamine was purchased from Aldrich Chemical Co., Inc. (Milwaukee, WI). Diglycolic anhydride and the commercial extractant, DEHPA, were obtained from Tokyo Kasei Kogyo Co., Inc., Tokyo, Japan. Commercial extractants, PC-88A and Versatic 10, were supplied kindly by Daihachi Chemical Industry Co. Ltd., Japan and Shell Japan Ltd., respectively. These commercial extractants were used without further purification. HPLC grade *n*-hexane was employed as the organic solvent. All other reagents were of analytical grade and were used as received.

2.2 Synthesis of DODGAA

The synthetic route of DODGAA is shown in Fig. 1. The procedure to synthesize DODGAA was as follows: To a slurry of diglycolic anhydride (4.17 g, 35.9 mmol) in CH_2Cl_2 (40 mL), dioctylamine (7.0 g, 28.4 mmol) dissolved in CH_2Cl_2 (10 mL) was carefully added, and then the mixture was stirred at room temperature overnight. The resulting clear solution was washed with deionized water 4 times. After the organic layer was dried with anhydrous sodium sulfate, the solvent was removed in vacuo, and the residue was recrystallized from *n*-hexane; white powder 9.57 g (94.2% yield); ^1H NMR (400 MHz, CDCl_3 , TMS, 25 °C) δ 0.89 (t, 6H, N-(CH_2)₇- CH_3), 1.29, 1.55 (s, 24H, N- CH_2 -(CH_2)₆- CH_3), 3.10, 3.35 (t, 4H, N- CH_2 - C_7H_{15}), 4.22 (s, 2H, N-CO- CH_2 -O), 4.40 (s, 2H, CH_2 -COOH); Anal. Calcd for $\text{C}_{20}\text{H}_{39}\text{O}_4\text{N}_1$: C, 67.19; H, 10.99; N, 3.92. Found: C, 66.99; H, 11.00; N, 3.94.

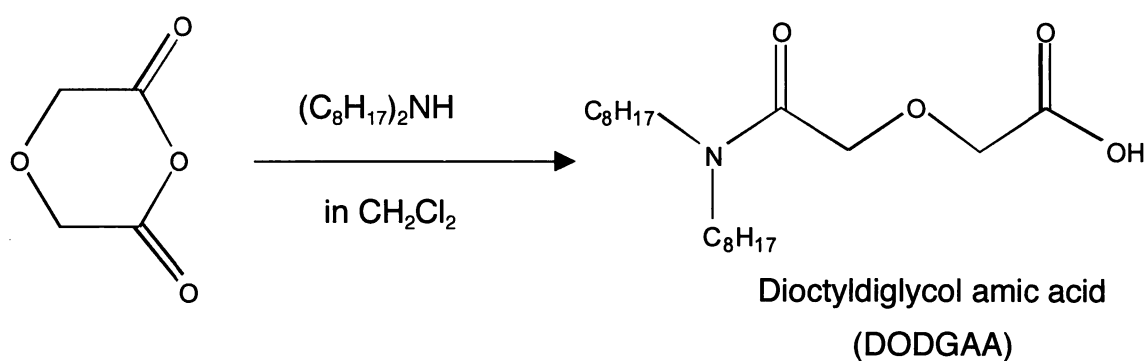


Fig. 1 Synthetic route for diocetyldiglycol amic acid (DODGAA)

2.3 Solvent extraction experiments

All solvent extraction experiments were carried out at 298 K. An aqueous solution containing lanthanide(III) nitrates (Eu(III) or all lanthanides except Pm(III)) and the same volume of *n*-hexane

containing DODGAA, PC-88A, DEHPA, or Versatic 10 were placed in a stoppered tube. In the case of DODGAA, 5 vol% *n*-octanol was added to *n*-hexane to promote the solubility of DODGAA in the organic phase. In the experiments with DODGAA, PC-88A, and DEHPA, HNO₃ was used to adjust pH from 1 to 2.5. HEPES-TRIS buffer solutions were used to adjust the pH between pH 5 and pH 7 for the experiments with Versatic 10. The two phases were vigorously shaken by a vortex mixer for 15 min, and then centrifuged. The organic phase was separated from the aqueous phase and the metal ions in the organic phase were back-extracted into an aqueous solution containing 3 M HNO₃. The concentration of lanthanides(III) in the aqueous phase and that in the organic phase after the back-extraction were measured by inductively coupled plasma mass spectrometry (ICP-MS, Hewlett Packard HP4500). The equilibrium pH in the aqueous phase was also measured.

2.4 Solubility of extractants in water

Each extractant (5 mM) was added to ultrapure water (40 mL) in a stoppered Erlenmeyer flask. The saturated aqueous solutions of extractants were prepared by ultrasonication for 15 min, and were left at 25°C for a week to attain equilibrium. After centrifugation and filtration, the total organic carbon content (TOC) of aqueous solutions was measured by a TOC analyzer (TOC-VCSN, Shimadzu). The solubilities of DODGAA, PC-88A, DEHPA, and Versatic 10 in water as molarities were calculated by dividing the obtained TOC values by the number of carbon atoms in the respective extractants and the atomic weight of carbon.

3. Results and Discussion

3.1 Extraction performance of DODGAA

Figure 2 shows the distribution ratio of Eu(III), $D_{\text{Eu(III)}}$, with 0.03 M DODGAA as a function of the concentration of H⁺ in the aqueous phase at equilibrium ($[\text{H}^+]_{\text{aq}}$), together with the results for PC-88A and DEHPA at the same concentration. The extraction performance of DODGAA for Eu(III) matches that for PC-88A and DEHPA. Specifically, the distribution ratio of Eu(III) with DODGAA is higher than that with PC-88A and is lower than that with DEHPA. The logarithmic plots of the Eu(III) distribution ratio versus the acid concentration show slopes of three in all cases, which indicates a 1 : 3 ion exchange between the trivalent metal ion and H⁺.

DODGAA was compared also with Versatic 10 with regard to its extraction performance for Eu(III). Figure 3 gives the result of the metal extraction on a logarithmic scale. The plot also shows a slope of three. There is a marked difference in the metal extraction ability between DODGAA and Versatic 10. Although Versatic 10 extracts little Eu(III) when the concentration of H⁺ is higher than 10⁻⁵ M, DODGAA extracts Eu(III) quantitatively even when the H⁺ concentration is 0.01 M. The strong complexation ability of the

tridentate DODGAA is considered to be the reason for such powerful metal extraction, as compared to Versatic 10.

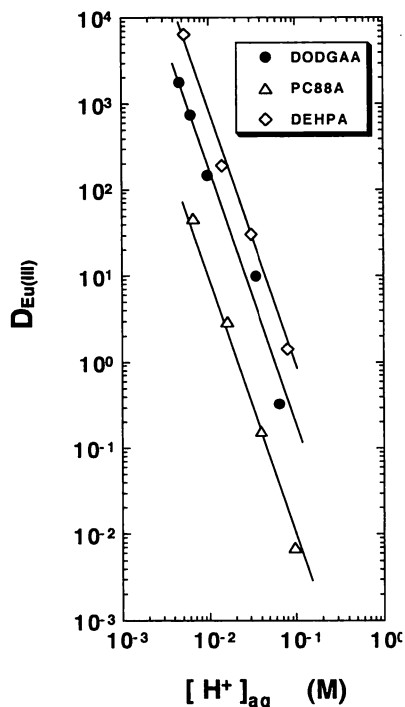


Fig. 2 Comparison between DODGAA and the organophosphorus extractants (PC-88A and DEHPA) in the extraction of Eu(III); the distribution ratio of Eu(III) between aqueous HNO₃ solution and *n*-hexane containing 0.03 M of each extractant as a function of the concentration of H⁺ in the aqueous phase.

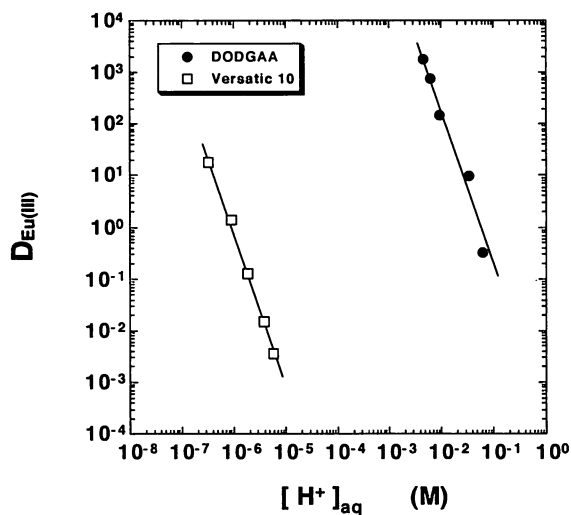


Fig. 3 Comparison between DODGAA and a carboxylic acid type extractant (Versatic 10) in the extraction of Eu(III); the distribution ratio of Eu(III) between aqueous HNO₃ or HEPES-TRIS buffer solution and *n*-hexane containing 0.03 M of each extractant as a function of the concentration of H⁺ in the aqueous phase.

3.2 Selectivity with DODGAA

The selectivities for lanthanide ions with DODGAA, PC-88A, DEHPA, and Versatic 10 are also compared. Figure 4 shows the separation factor of 13 lanthanides from La(III), expressed as the distribution ratio of lanthanides from Ce(III) to Lu(III) except Pm(III) divided by that of La(III), for DODGAA, PC-88A, and DEHPA. The concentration of each extractant in the organic phase is fixed at 0.03 M and the aqueous phase is adjusted to pH 1.5 at equilibrium by using HNO₃. The selectivity for lighter lanthanides from La(III) to Gd(III) with DODGAA is higher than that with PC-88A and DEHPA, although the selectivity for heavier lanthanides from Tb(III) to Lu(III) with DODGAA is lower than that with PC-88A and DEHPA.

Figure 5 shows the comparison between DODGAA and Versatic 10. The concentration of each extractant in the organic phase is 0.03 M. Since Versatic 10 hardly extracts lanthanides at pH 1.5, the distribution ratio of lanthanides with Versatic 10 is determined at pH 6.9 where all lanthanides are measurably extracted with this extractant. For all lanthanides, the selectivity with DODGAA is higher than that with Versatic 10. Especially for the middle and heavier lanthanides from Sm(III) to Lu(III), the separation factor with DODGAA is 10-fold or more compared to that with Versatic 10. The coordinating property of DODGAA as a tridentate ligand also seems to improve not only the extraction ability but also the selectivity for lanthanide ions, compared with Versatic 10.

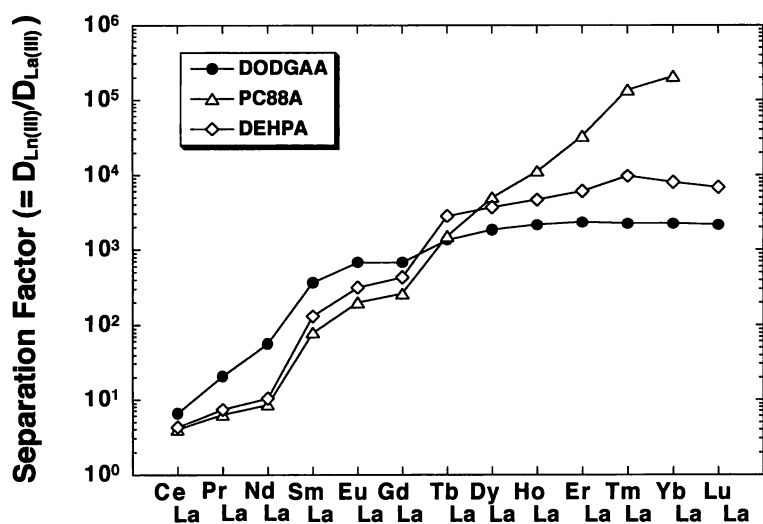


Fig. 4 Comparison of the separation factor for 14 lanthanides (Ln(III)) except Pm(III) between DODGAA and the organophosphorus extractants (PC-88A and DEHPA); aqueous phase: HNO₃ solution of pH 1.5, organic phase: *n*-hexane containing 0.03 M of each extractant.

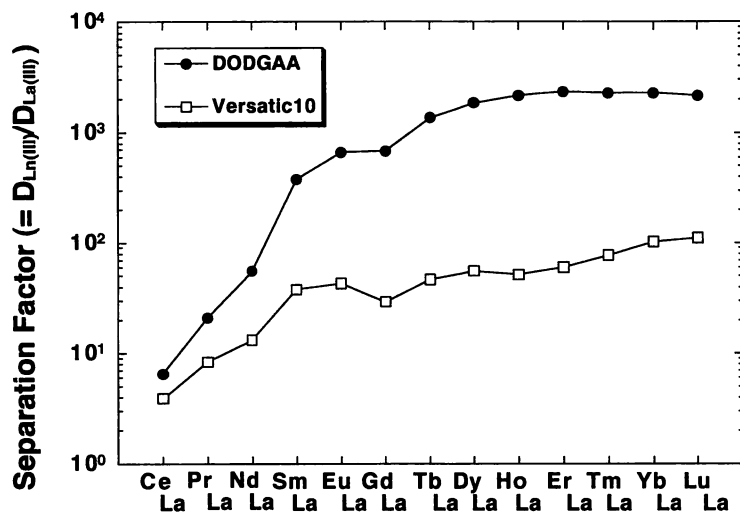


Fig. 5 Comparison of the separation factor for 14 lanthanides (Ln(III)) except Pm(III) between DODGAA and a carboxylic acid type extractant (Versatic 10); aqueous phase: HNO₃ solution of pH 1.5 or HEPES-TRIS buffer solution of pH 6.9, organic phase: *n*-hexane containing 0.03 M of each extractant.

3.3 Solubility of DODGAA in water

Table 1 shows the solubilities of DODGAA, PC-88A, DEHPA, and Versatic 10 in water at 298 K. DODGAA has a very low solubility in water, compared with PC-88A, DEHPA, and Versatic 10. That is, the solubility of DODGAA in water is 38, 13, and 55-fold lower than the solubilities of PC-88A, DEHPA, and Versatic 10 in water, respectively

Table 1 Solubilities of DODGAA, PC-88A, DEHPA, and Versatic 10 in water at 298 K.

Extractant	Solubility (M)
DODGAA	1.5×10^{-5}
PC-88A	5.7×10^{-4}
DEHPA	2.0×10^{-4}
Versatic 10	8.3×10^{-4}

4. Conclusions

We have synthesized a new “green” extractant, DODGAA, for lanthanide ions. DODGAA is composed of carbon, hydrogen, oxygen, and nitrogen atoms and is fully combustible leaving no residue. In addition, the solubility of DODGAA in water is found to be very low, i.e., 1.5×10^{-5} M, which is 1/38, 1/13, and 1/55 compared with the case of PC-88A, DEHPA, and Versatic 10, respectively. Thus, DODGAA is an

environmentally-friendly “green” extractant that greatly decreases the risk of aquatic environmental pollution and is easily incinerated without producing solid waste.

Carboxylic acid type compounds, such as Versatic 10, are also completely combustible. However, they are no match for PC-88A and DEHPA with regard to its extraction and separation performance for lanthanide ions. On the other hand, DODGAA is comparable to the organophosphorus extractants in its ability to extract lanthanide ions and to mutually separate them. Concerning the extraction performance for lanthanides, the extraction of Eu(III) from an aqueous HNO₃ solution into *n*-hexane with DODGAA is between that for PC-88A and that for DEHPA. With regard to its ability to separate lanthanides, the selectivity for the lighter lanthanides with DODGAA is higher than that for PC-88A or DEHPA; while, for the heavier lanthanides, the selectivity with DODGAA is lower than that with the organophosphorus extractants.

Furthermore, from the viewpoint of the cost of the synthesis of DODGAA, it is produced through a simple single reaction step with high yield (see Experimental) and thus has an advantage over many other commercial extractants. The fact that DODGAA has a very low solubility in water is also economically favorable, i.e., an organic phase containing DODGAA can be repeatedly used with almost no loss of the extractant into the aqueous phase.

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