

**A Comprehensive Extraction Study
Using a Mono-alkylated Diglycolamic Acid Extractant:
Comparison Between a Secondary Amide Group and a Tertiary Amide Group**

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(Received December 28, 2016; Accepted March 3, 2017)

The extraction characteristics of *N*-dodecyldiglycolamic acid (C₁₂DGAA), with a secondary amide group, for 56 metal ions have been investigated, and compared with those of *N,N*-dioctyldiglycolamic acid (DODGAA) with a tertiary amide group. C₁₂DGAA is capable of quantitative transfer for a variety of metal ions through a proton-exchange reaction, and the extraction behavior as a function of the aqueous-phase pH is similar for C₁₂DGAA and DODGAA. Compared with DODGAA, C₁₂DGAA has a poor extraction performance and separation ability for rare-earth metal ions, except for Sc(III). However, C₁₂DGAA tended to provide better extraction for relatively small-sized metal ions than DODGAA. In addition, it was found that C₁₂DGAA enables the selective removal of Hg(II) from aqueous solutions containing various divalent metal ions (Hg(II), Pb(II), Cu(II), Cd(II), Zn(II), Mn(II), Co(II), and Ni(II)).

1. Introduction

Liquid–liquid extraction is an effective separation method for the purification of valuable metals [1-3], removal of toxic metals [4,5], and recovery of fission products [6-9]. The efficiency of metal separation with liquid–liquid extraction depends on the extractant. To date, numerous extractants, which have superior extraction performance and separation ability, have been developed [10-14]. Most novel extractants, however, are expensive for large-scale applications because of laborious and elaborate synthetic processes, and are unsuitable for industrial extraction processes. Therefore, traditional organophosphorous extractants such as di(2-ethylhexyl)phosphoric acid (D2EHPA) and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC-88A) have been generally employed in industrial processes.

Recently, we developed *N,N*-dioctyldiglycolamic acid (DODGAA, Figure1), which is a carboxylic acid-type extractant with an amide group and an ether oxygen donor [15-21]. The extractant can be synthesized simply and readily in a single step, which helps to reduce its production cost. Although DODGAA is a carboxylic acid-type extractant and has a simple molecular structure consisting only of C, H, O, and N atoms, the compound provides an excellent extraction performance for a variety of metal ions compared with commercial carboxylic acid-type extractants (*e.g.*, Versatic 10). In fact, the extraction

performance of DODGAA is comparable to that of organophosphorous extractants (e.g., D2EHPA and PC-88A). This is attributed to the chelate effect created by the tridentate diglycolamic acid (DGAA) framework.

We have been interested in the influence of amide groups on the extraction performance of DGAA-type extractants. In a previous study, we synthesized *N*-dodecyldiglycolamic acid (C₁₂DGAA, Figure 1) with a secondary amide group (R–NH–C=O) as an analogous extractant to DODGAA with a tertiary amide group (R–NR–C=O), and compared the extraction performance for rare-earth elements with both extractants [22].

In the present study, we comprehensively investigated the extraction of 56 metal ions using C₁₂DGAA to collect basic data on the extraction performance and selectivity of C₁₂DGAA. The obtained extraction data for C₁₂DGAA were compared with those for DODGAA to evaluate the effect of the amide group on the extraction performance and selectivity of DGAA-type extractants. In addition, selective removal of toxic metal ions from a metal ion mixture was carried out using C₁₂DGAA.

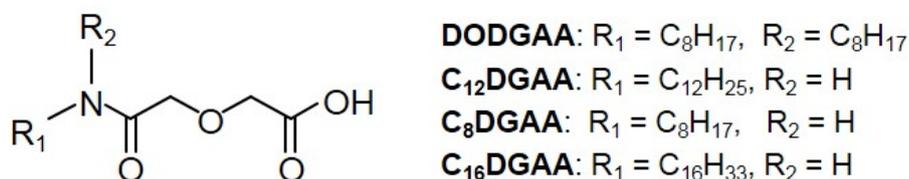


Figure 1. Molecular structures and abbreviations of extractants.

2. Experimental

2.1 Reagents

The metal salts and metal ion standard solutions used in this study were: LiNO₃, NaNO₃, KNO₃, RbNO₃, CsNO₃, Mg(NO₃)₂·6H₂O, Ca(NO₃)₂·4H₂O, Sr(NO₃)₂, Ba(NO₃)₂, Al(NO₃)₃·9H₂O, Cr(NO₃)₃·9H₂O, Mn(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O, Co(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O, Cu(NO₃)₂·3H₂O, Zn(NO₃)₂·6H₂O, Ga(NO₃)₃·*n*H₂O, AgNO₃, Cd(NO₃)₂·4H₂O, In(NO₃)₃·3H₂O, Hg(NO₃)₂·*n*H₂O, TlNO₃, Pb(NO₃)₂, Sc(NO₃)₃·4H₂O, Y(NO₃)₃·6H₂O, La(NO₃)₃·6H₂O, Ce(NO₃)₃·6H₂O, Pr(NO₃)₃·6H₂O, Nd(NO₃)₃·6H₂O, Sm(NO₃)₃·6H₂O, Eu(NO₃)₃·6H₂O, Gd(NO₃)₃·5H₂O, Tb(NO₃)₃·6H₂O, Dy(NO₃)₃·5H₂O, Ho(NO₃)₃·5H₂O, Er(NO₃)₃·5H₂O, Tm(NO₃)₃·4H₂O, Yb(NO₃)₃·3H₂O, Lu(NO₃)₃·3H₂O, HfCl₄, RuCl₃·*n*H₂O, HAuCl₄·4H₂O, Ti(SO₄)₂ in 1 M (1 M = 1 mol L⁻¹) H₂SO₄ (1000 ppm), ZrO(NO₃)₂ in 1 M HNO₃ (1000 ppm), NH₄VO₃ in 2-3% HNO₃ (1000 ppm), NbF₅ in 1 M HF (1000 ppm), TaF₅ in 1 M HF (1000 ppm), Mo in 0.4 M HCl + 0.2 M HNO₃ (1000 ppm), Na₂WO₄ in H₂O (1000 ppm), NH₄ReO₄ in H₂O (1000 ppm), (NH₄)₂OsCl₆ in 7% HCl (1000 ppm), IrCl₃ in 7% HCl (1000 ppm), RhCl₃ in 0.1 M HCl (1000 ppm), PdCl₂ in 1 M HCl (1000 ppm), and H₂PtCl₆ in 1 M HCl (1000 ppm). The oxidation state of the Mo ion is unknown. All other reagents were commercially available, of analytical grade, and used as received. Ultrapure water (18.2 MΩ·cm), produced using a Direct-Q (Millipore), was used throughout this study.

2.2 Synthesis of DGAA-type extractants

C₁₂DGAA and DODGAA were synthesized according to published procedures [15,16,18,22]. The analogous extractant *N*-octyldiglycolamic acid (C₈DGAA, Figure 1) was synthesized as follows: diglycolic

anhydride (6.5 g, 53.2 mmol) was dispersed in dry CH₂Cl₂ (40 mL). Octylamine (7.0 g, 53.1 mmol) dissolved in dry CH₂Cl₂ (10 mL) was slowly added dropwise to the solution in an ice-bath. The mixture was stirred at room temperature for 22 h. The resulting clear solution was washed three times with 1 M HCl (3 × 60 mL) and water (4 × 100 mL). The organic layer was dried with anhydrous Na₂SO₄. After filtration, the solvent was removed *in vacuo* to give the crude product, which was recrystallized from chloroform and *n*-hexane to obtain C₈DGAA as a white powder (12.6 g, 96.8% yield). ¹H NMR (400 MHz, CDCl₃, TMS, 25°C): δ 0.88 (t, 3H, N-(CH₂)₇-CH₃), 1.27 (d, 10H, N-CH₂-CH₂-(CH₂)₅-CH₃), 1.54 (quintet, 2H, N-CH₂-CH₂-C₆H₁₃), 3.31 (quartet, 2H, N-CH₂-C₇H₁₅), 4.14 (s, 2H, N-CO-CH₂-O), 4.21 (s, 2H, CH₂-COOH), 6.92 (s, 1H, NH). MS (MALDI-TOF) *m/z*: 246.1 [M + H]⁺. Anal. Calcd for C₁₂H₂₃NO₄: C, 58.75; H, 9.45; N, 5.71. Found: C, 58.68; H, 9.50; N, 5.66.

The analogous extractant *N*-hexadecyldiglycolamic acid (C₁₆DGAA, Figure 1) was synthesized as follows: hexadecylamine (3.7 g, 15 mmol) was dissolved in dry THF (40 mL) by heating to 45°C. Diglycolic anhydride (2.2 g, 18 mmol) dissolved in dry THF (15 mL) was slowly added dropwise to the solution. The mixture was refluxed at 70°C for 1 day. After evaporation of the solvent *in vacuo*, the resulting crude product was dissolved in ethanol by heating and was re-precipitated by adding water. After filtration, the compound was recrystallized from acetonitrile to obtain C₁₆DGAA as a white powder (4.7 g, 87.6% yield). ¹H NMR (400 MHz, CDCl₃, TMS, 25°C): δ 0.88 (t, 3H, N-(CH₂)₁₅-CH₃), 1.26 (d, 26H, N-CH₂-CH₂-(CH₂)₁₃-CH₃), 1.54 (quintet, 2H, N-CH₂-CH₂-C₁₄H₂₉), 3.31 (quartet, 2H, N-CH₂-C₁₅H₃₁), 4.13 (s, 2H, N-CO-CH₂-O), 4.21 (s, 2H, CH₂-COOH), 6.76 (s, 1H, NH). MS (MALDI-TOF) *m/z*: 358.2 [M + H]⁺. Anal. Calcd for C₂₀H₃₉NO₄: C, 67.19; H, 10.99; N, 3.92. Found: C, 66.72; H, 11.02; N, 3.90.

2.3 Extraction procedure

Aqueous phases containing each metal ion were prepared with different pH values. The pH of the aqueous solutions was adjusted by the addition of either HNO₃ or NaOH to a 10 mM or 100 mM 2-morpholinoethanesulfonic acid (MES) buffer. In the extraction tests with metal chlorides (Ru(III), Rh(III), Pd(II), Hf(IV), Os(IV), Ir(III), Pt(IV), and Au(III)), the pH was adjusted by the addition of HCl to a 50 mM sodium acetate buffer at a constant ionic strength of 0.1 M NaCl because the MES buffer can easily reduce Au(III) to Au(0) [23-25]. In the extraction of K(I), Hg(II), and Ag(I), the contamination of aqueous solutions by potassium ions and chloride ions from the pH electrode was prevented. For all aqueous phases, stock solutions containing each metal salt were added to the aqueous solutions to give metal ion concentrations of 0.01 mM. The organic phase was prepared by dissolving C₁₂DGAA in isooctane containing 5 vol% 1-octanol as a modifier. 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 equal volumes of 1 M HNO₃ or 1 M HCl. The concentrations of the metal ions in the aqueous phase and the receiving phase were determined by inductively coupled plasma mass spectrometry (PerkinElmer NexION 300X) or inductively coupled plasma atomic emission spectrometry (SII Nano Technology SPS 3500) to obtain the extractability ($E = [M^{n+}]_{\text{org}}/[M^{n+}]_{\text{ini}} \times 100$). Mⁿ⁺ denotes metal ions, and the subscripts org and ini denote the organic phase and the initial condition, respectively. The equilibrium pH (pH_{eq}) of the aqueous phases was also measured. When the H⁺ concentration is over 0.1 M, the activity of H⁺ was calculated on the basis of the Debye-Hückel theoretical equation. For comparison, extraction tests with DODGAA were also conducted

according to the same procedure [19].

3. Results and Discussion

3.1 Extraction characteristics of C₁₂DGAA for 56 metal ions

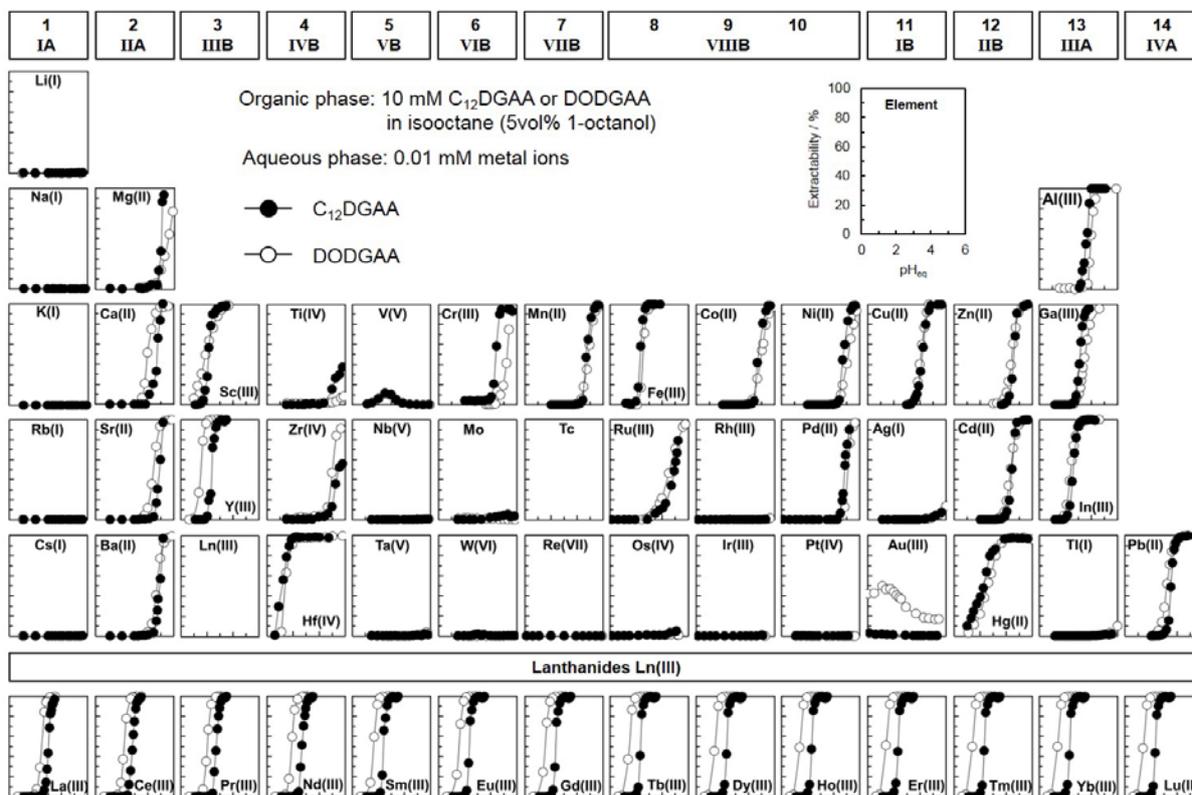


Figure 2. Extraction performance of C₁₂DGAA for 56 metal ions as a function of pH_{eq} in the aqueous phase. Organic phase, 10 mM C₁₂DGAA in isooctane containing 5 vol% 1-octanol; aqueous phase, 0.01 mM metal ions in corresponding buffer solutions. Extraction data on DODGAA were reconstructed on the basis of the previous study [ref.19] and additional new data.

In a preliminary experiment, we examined the distribution of C₁₆DGAA, C₁₂DGAA, and C₈DGAA between the organic and aqueous phases. Although alkane solvents such as isooctane or dodecane are acceptable in industrial extraction processes, the DGAA-type extractants with a linear alkyl chain were poorly soluble in isooctane. In contrast, the extractants were readily soluble in 1-octanol. Thus, isooctane containing a small amount of 1-octanol (5 vol%) was employed as an extracting solvent in this study. As a result, C₁₆DGAA was not dissolved in isooctane containing 5 vol% 1-octanol at all although C₁₆DGAA consists of the same number of carbon atoms as in DODGAA. C₁₂DGAA and C₈DGAA were soluble in the organic solution, but C₈DGAA slightly distributed from the organic phase into the aqueous phase, decreasing the pH values in the aqueous phases. Therefore, C₁₆DGAA and C₈DGAA are unsuitable for extraction of metal ions, and C₁₂DGAA was selected as the extractant.

Figure 2 shows the extraction behavior of 56 metal ions using C₁₂DGAA as a function of pH_{eq} in the

aqueous phase, together with that using DODGAA. For the alkali metal ions (group-1 elements), the extractability of the metal ions was negligible in both the C₁₂DGAA and DODGAA systems. It is likely that monovalent alkali metal cations would form a 1: 1 complex with DGAA-type extractants to neutralize their monovalent cationic charge. Therefore, the hydration waters of the metal ions are not sufficiently removed and less hydrophobic metal complexes are formed.

For the alkaline-earth metal ions (group-2 elements), the extractability of the metal ions increased with increasing pH. The metal ions were quantitatively extracted at around pH_{eq} 5.2. The extraction performance of C₁₂DGAA was higher for Mg(II) and lower for Ca(II), Sr(II), and Ba(II) than that of DODGAA. The selectivity of C₁₂DGAA for the alkaline-earth metal ions was in the following order: Ca(II) > Sr(II) = Ba(II) > Mg(II), and C₁₂DGAA exhibited a low separation ability for the alkaline-earth metal ions compared with DODGAA (Ca(II) > Sr(II) > Ba(II) > Mg(II)). In addition, slope analysis showed that the slopes of the logarithmic distribution ratio *versus* pH_{eq} plots were approximately 2 for the alkaline-earth metal ions, except for Mg(II). The results indicate that two protons from the C₁₂DGAA molecules were released to form neutral complexes with divalent alkaline-earth metal ions through a proton-exchange reaction. The slope for Mg(II) was 0.98, which is not equivalent to the valence of Mg(II). It is likely that hydroxylated Mg(OH)⁺ is involved in the extraction [26].

For rare-earth (RE) metal ions (group-3 elements), C₁₂DGAA enabled quantitative transfer of light RE(III) at pH_{eq} ≥ 3.5 and middle and heavy RE(III) at pH_{eq} ≥ 2.8 [22]. Although C₁₂DGAA performs better than typical carboxylic acid-type extractants, the metal transfer with C₁₂DGAA occurred in higher pH ranges than that with DODGAA. The results indicate that C₁₂DGAA has a lower extraction performance for RE(III) cations than DODGAA. Both DGAA-type extractants exhibited selectivity for the heavier RE(III) because the higher charge densities of the heavier RE(III) probably facilitated electrostatic interactions with the anionic extractants. In particular, C₁₂DGAA showed the highest selectivity for Sc(III) among 16 RE(III) cations, contrary to the low selectivity of DODGAA for Sc(III). However, C₁₂DGAA had a much lower mutual separation ability of individual RE(III) cations from each other than DODGAA. In contrast, the extraction performance of DGAA-type extractants was much higher for RE(III) cations compared with the other metal ions tested in this study, thus the extractants are useful for the separation of RE(III) cations from foreign metal ions. In addition, slope analysis and structural characterization by X-ray diffraction revealed that three C₁₂DGAA molecules coordinated to the RE(III) cation in a tridentate fashion through three oxygen atoms from the amide group, three oxygen atoms from the ether group, and three oxygen atoms from the carboxy group, forming a 1:3 complex, RE(C₁₂DGAA)₃ [22].

For the group-4, 5 elements, Mo, W(VI), and Re(VII), the maximum extractabilities of Ti(IV) and Zr(IV) with C₁₂DGAA were approximately 40 and 55%. Hf(IV) was quantitatively extracted. In contrast, the group-4 elements were not completely back-extracted from the organic phase with a 1 M HNO₃ solution as the receiving phase. This is possibly attributed to aggregation of the unstable metal complexes at the liquid-liquid interface. The extraction behavior of V(V) with C₁₂DGAA was almost identical to that with DODGAA, and around 10% of V(V) was transferred. The stripping of V(V) was also successfully achieved using a 1 M HNO₃ solution. The partitioning of Nb(V), Mo, Ta(V), W(VI), and Re(VII) was negligibly small.

For Cr(III), Mn(II), Fe(III), Co(II), Ni(II), and Cu(II), quantitative extraction was achieved in mildly

acidic solutions and C₁₂DGAA showed the following selectivity for the metal ions: Fe(III) >> Cu(II) > Cr(III) > Mn(II) = Co(II) = Ni(II). The extraction efficiency of Cr(III) was greatly enhanced by using C₁₂DGAA compared with DODGAA. In addition, a slightly greater extraction performance of C₁₂DGAA for Mn(II), Fe(III), Co(II), and Ni(II) was observed. The slopes of the logarithmic distribution ratio *versus* pH_{eq} plots for each metal ion were consistent with the valence of the corresponding metal ions, except for Cr(III). The slope for Cr(III) was 1.6, likely because hydrolysis of Cr(III) partially occurred in the pH range of the extraction [26].

For noble metal ions (platinum group elements, Ag(I), and Au(III)), C₁₂DGAA showed high extraction performance for Ru(III) and Pd(II), as in the case of DODGAA. However, complete back-extraction of Ru(III) and Pd(II) was difficult using a 1 M HNO₃ solution although back-extraction was possible in the DODGAA system [19]. The other platinum group elements (Rh(III), Os(IV), Ir(III), Pt(IV)) were not extracted at all. A similar extraction behavior was observed for Ag(I) when using C₁₂DGAA and DODGAA, and around 10 % of Ag(I) was extracted into the organic phase. In contrast, Au(III) exhibited a different extraction behavior between C₁₂DGAA and DODGAA, and C₁₂DGAA did not show any extractability for Au(III).

For the group-12 elements and Pb(II), C₁₂DGAA quantitatively extracted all of the metal ions with the following selectivity: Hg(II) >> Pb(II) >> Cd(II) > Zn(II). Compared with DODGAA, C₁₂DGAA showed a slightly higher extraction performance for Hg(II) and somewhat lower extraction performance for Pb(II). The extraction behavior of Cd(II) and Zn(II) was similar between C₁₂DGAA and DODGAA. The slopes of the logarithmic distribution ratio *versus* pH_{eq} plots for each metal ion were 0.9 for Hg(II), 2.1 for Pb(II), 2.2 for Cd(II), and 1.9 for Zn(II). The slope values are consistent with the valence of the corresponding metal ions, except for Hg(II). To demonstrate the usefulness of C₁₂DGAA in removing toxic

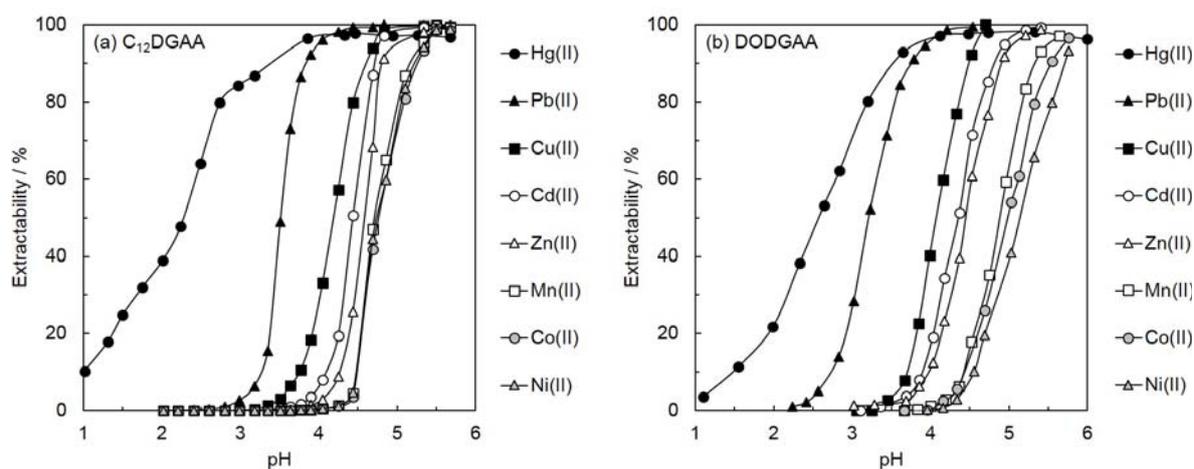


Figure 3. Extraction removal of the toxic metal Hg(II) from various divalent metal ions with (a) C₁₂DGAA and (b) DODGAA. Organic phase, 10 mM C₁₂DGAA or DODGAA in isoctane containing 5 vol% 1-octanol; aqueous phase, 0.01 mM metal ions in MES buffer solutions. Each aqueous phase contained 8 divalent metal ions.

metal ions, we investigated here the selective separation of Hg(II) from aqueous solutions containing various divalent metal ions (Hg(II), Pb(II), Cu(II), Cd(II), Zn(II), Mn(II), Co(II), and Ni(II)). As shown in Figure 3, C₁₂DGAA provided the highest selectivity for Hg(II) among 8 divalent metal ions, which permits the selective removal of Hg(II) from the metal mixture. In contrast, DODGAA can remove Hg(II) and Pb(II) from the other metal ions, but mutual separation between Hg(II) and Pb(II) is less efficient than with C₁₂DGAA.

For the group-13 elements, quantitative partitioning was observed for the metal ions, except for Tl(I), and C₁₂DGAA had the following selectivity for the group-13 elements: In(III) > Ga(III) > Al(III) >> Tl(I). Compared with DODGAA, the extraction performance of C₁₂DGAA was slightly higher for Al(III) and Ga(III), and was a little lower for In(III). Neither C₁₂DGAA nor DODGAA were very effective for Tl(I) extraction. The slopes of the logarithmic distribution ratio *versus* pH_{eq} plots for Al(III), Ga(III), and In(III) were 3.4, 3.2, and 3.0, respectively.

3.2 Classification of metal ions based on extraction efficiency

Based on the extraction data described above, the metal ions are divided into the following two groups, depending on whether C₁₂DGAA provides a higher or lower extraction performance for the metal ions than DODGAA:

- C₁₂DGAA > DODGAA

Mg(II), Al(III), Sc(III), Ti(IV), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Ga(III), Pd(II), Hf(IV), Hg(II)

- C₁₂DGAA < DODGAA

Ca(II), Sr(II), Y(III), Zr(IV), Ru(III), In(III), Ba(II), Au(III), Pb(II), Lanthanides

The DGAA framework with a tertiary amide group (DODGAA) has a relatively rigid molecular geometry because of the partial double-bond character of the C–N bond of the amide group, which leads to a stronger basicity of the amide oxygen atom [27]. In contrast, the DGAA framework with a secondary amide group (C₁₂DGAA) makes the basicity of the amide oxygen atom weaker. Therefore, it is obvious that DODGAA offers high coordination ability for metal ions compared with C₁₂DGAA. In fact, the disadvantage of C₁₂DGAA was clearly observed for lanthanide transfer. However, C₁₂DGAA tended to provide better extraction for relatively small-sized metal ions compared to DODGAA, with a few exceptions. Although the reason for the difference in extraction behavior between C₁₂DGAA and DODGAA is unclear at this stage, we postulate that the steric hinderance of the alkyl chain of the extractants is involved in the extraction of small-sized metal ions. In summary, the 56 metal ions are classified in the following seven groups, according to the degree of extraction performance of C₁₂DGAA for metal ions:

(1) Quantitative extraction at pH_{eq} > 2.8

Hf(IV), Sc(III), Lu(III), Yb(III), Tm(III), Er(III), Ho(III), Dy(III), Tb(III), Fe(III), Gd(III), Eu(III), Y(III), Sm(III)

(2) Quantitative extraction at pH_{eq} > 3.5

Hg(II), In(III), Nd(III), Pr(III), Ce(III), La(III)

(3) Quantitative extraction at pH_{eq} > 4.0

Ga(III), Pb(II), Al(III)

(4) Quantitative extraction at pH_{eq} > 5.0

Cu(II), Cr(III), Cd(II), Zn(II)

- (5) Quantitative extraction at $\text{pH}_{\text{eq}} > 5.5$
Ca(II), Mn(II), Co(II), Ni(II), Pd(II), Sr(II), Ba(II), Mg(II), Ru(III)
- (6) Extractability $< 60\%$
Zr(IV), Ti(IV), V(V), Ag(I)
- (7) Unextractable metal ions
Li(I), Na(I), K(I), Rb(I), Cs(I), Nb(V), Mo, Ta(V), W(VI), Re(VII), Rh(III), Os(IV), Ir(III), Pt(IV), Au(III), Tl(I)

The metal ions in each category are arranged in order of high extractability.

4. Conclusion

In the present study, liquid–liquid extraction of 56 metal ions using C₁₂DGAA with a secondary amide group was comprehensively investigated, and compared with the results obtained using DODGAA with a tertiary amide group. The extraction performance of C₁₂DGAA for RE(III) cations was lower compared to DODGAA. However, C₁₂DGAA provided a slightly higher extraction performance for small-sized metal ions than DODGAA. In addition, C₁₂DGAA showed the highest selectivity for Hg(II) among various divalent metal ions, thereby separating selectively Hg(II) from the metal mixture, whereas DODGAA had difficulty in separating Hg(II) from Pb(II). The present findings suggest that the amide group of DGAA-type extractants has a significant influence on the extraction characteristics of the extractants. We might be able to control the extraction performance and separation ability of DGAA-type extractants by modulating the chemical property of the amide group. Further studies on development of novel extractants by modification of the DGAA framework with appropriate functional groups are currently under way.

Acknowledgement

This work was financially supported by JSPS KAKENHI Grant Number 25410161 (to K.S.). We thank the Center for Instrumental Analysis at Ibaraki University for the elemental analysis, NMR, and MALDI-TOF/MS measurements.

References

- 1) S. Syed, *Hydrometallurgy*, **115-116**, 30-51 (2012).
- 2) A. M. Wilson, P. J. Bailey, P. A. Tasker, J. R. Turkington, R. A. Grant, J. B. Love, *Chem. Soc. Rev.*, **43**, 123-134 (2014).
- 3) M. K. Jha, A. Kumari, R. Panda, J. R. Kumar, K. Yoo, J. Y. Lee, *Hydrometallurgy*, **165**, 2-26 (2016).
- 4) M. K. Jha, V. Kumar, J. Jeong, J. Lee, *Hydrometallurgy*, **111-112**, 1-9 (2012).
- 5) T. Tsend-Ayush, M. Wenzel, K. Gloe, K. Gloe, J. J. Weigand, Y. V. Fedorov, O. A. Fedorova, S. P. Gromov, P. G. Plieger, *Solvent Extr. Res. Dev., Jpn.*, **23**, 31-41 (2016).
- 6) Y. Miyazaki, S. Suzuki, T. Kobayashi, T. Yaita, Y. Inaba, K. Takeshita, A. Mori, *Chem. Lett.*, **44**, 1626-1636 (2015).
- 7) K. Nash, *Solvent Extr. Ion Exch.*, **33**, 1-55 (2015).
- 8) E. Krahn, C. Marie, K. Nash, *Coord. Chem. Rev.*, **316**, 21-35 (2016).

- 9) J. Veliscek-Carolan, *J. Hazard. Mater.*, **318**, 266-281 (2016).
- 10) N. Kanaya, S. Matsuhashi S. Katsuta, *Solvent Extr. Res. Dev., Jpn.*, **22**, 17-24 (2015).
- 11) A. B. Chetry, B. B. Adhikari, S. Morisada, H. Kawakita, K. Ohto, *Solvent Extr. Res. Dev., Jpn.*, **22**, 25-35 (2015).
- 12) Y. Sasaki, M. Uto, T. Oshima, Y. Baba, *Solvent Extr. Res. Dev., Jpn.*, **23**, 1-8 (2016).
- 13) Y. Baba, F. Kubota, N. Kamiya, M. Goto, *Solvent Extr. Res. Dev., Jpn.*, **23**, 9-18 (2016).
- 14) H. Suzuki, Y. Tsubata, T. Kurosawa, M. Shibata, T. Kawasaki, S. Urabe, T. Matsumura, *Anal. Sci.*, **32**, 477-479 (2016).
- 15) H. Naganawa, K. Shimojo, H. Mitamura, Y. Sugo, J. Noro, M. Goto, *Solvent Extr. Res. Dev., Jpn.*, **14**, 151-159 (2007).
- 16) K. Shimojo, H. Naganawa, J. Noro, F. Kubota, M. Goto, *Anal. Sci.*, **23**, 1427-1430 (2007).
- 17) K. Shimojo, A. Nakai, H. Okamura, A. Ohashi, H. Naganawa, *Anal. Sci.*, **29**, 147-150 (2013).
- 18) K. Shimojo, N. Aoyagi, T. Saito, H. Okamura, F. Kubota, M. Goto, H. Naganawa, *Anal. Sci.*, **30**, 263-269 (2014).
- 19) K. Shimojo, A. Nakai, H. Okamura, T. Saito, A. Ohashi, H. Naganawa, *Anal. Sci.*, **30**, 513-517 (2014).
- 20) F. Kubota, Y. Shimobori, Y. Koyanagi, K. Shimojo, N. Kamiya, M. Goto, *Anal. Sci.*, **26**, 289-290 (2010).
- 21) F. Kubota, Y. Shimobori, Y. Baba, Y. Koyanagi, K. Shimojo, N. Kamiya, M. Goto, *J. Chem. Eng. Jpn.*, **44**, 307-312 (2011).
- 22) K. Shimojo, I. Fujiwara, K. Fujisawa, H. Okamura, T. Sugita, T. Oshima, Y. Baba, H. Naganawa, *Solvent Extr. Res. Dev., Jpn.*, **23**, 151-159 (2016).
- 23) A. Habib, M. Tabata, Y. G. Wu, *Bull. Chem. Soc. Jpn.*, **78**, 262-269 (2005).
- 24) J. Xie, J. Y. Lee, D. I. C. Wang, *Chem. Mater.*, **19**, 2823-2830 (2007).
- 25) K. Shimojo, T. Niide, T. Taguchi, H. Naganawa, N. Kamiya, M. Goto, *Analyst*, **137**, 2300-2303 (2012).
- 26) C. F. Baes, Jr, R. E. Measmer, "*The hydrolysis of cations*", Wiley, New York (1976).
- 27) H. Stephan, K. Gloe, J. Beger, P. Mühl, *Solvent Extr. Ion Exch.*, **9**, 435-458 (1991).