Synthesis of a Carboxylic Acid Extractant Containing an Amino Group and its Selective Extraction of In(III) and Ga(III)

Yuji SASAKI, Misaki UTO, Tatsuya OSHIMA and Yoshinari BABA*

Department of Applied Chemistry, Faculty of Engineering, University of Miyazaki, 1-1
Gakuen Kibanadai-nishi, Miyazaki 889-2192, Japan

A new extractant, [di-(2-ethylhexyl)amino]acetic acid (DEHAA), was synthesized for the mutual separation of In(III), Ga(III), and Zn(II). The extraction selectivity for the metal ions in a 1 M aqueous ammonium nitrate solution with DEHAA was In(III)>Ga(III)>Cu(II)>Zn(II), while Co(II), Cd(II), Se(IV), Se(VI), and Ni(II) were not extracted. The extraction behavior of DEHAA for In(III) and Ga(III) is different from the commercial extractant Versatic 10. The results indicate that the amino moieties in DEHAA play an important role in the selective extraction of In(III), Ga(III), and Zn(II). The extraction equilibria of In(III) and Ga(III) with DEHAA were also discussed. It is observed that In(III) and Ga(III) were extracted as 1:4 complexes, with extraction equilibria constants of $K_{In} = 8.03 \times 10^{-2}$ [(mol dm^{-3})$^{-1}$] and $K_{Ga} = 9.52 \times 10^{-4}$ [(mol dm^{-3})$^{-1}$] respectively.

1. Introduction

In recent years, there has been an increasing demand for indium and gallium for use in electronic devices. In particular, indium tin oxide is used in liquid crystal displays such as those in cell phones, tablet computers, and portable electrical devices. Gallium is used in semiconductor materials for light-emitting diodes, e.g., gallium arsenide (GaAs). These metals are also used in solar cells such as copper indium gallium selenide (CIGS) cells. Therefore, a reliable supply of these metals is important for the electronics industry. The resources for indium and gallium are by-products from zinc refinery residues, and waste secondary products such as electrical devices and CIGS solar cells. Mutual separation of indium, gallium and zinc is difficult because indium and gallium have similar chemical properties to the boron group, and gallium and zinc are classified as amphoteric metals. Because of large amounts of zinc in zinc refinery residues and CIGS solar cells, separation of indium and gallium is necessary. Therefore, the development of new separation techniques for In(III) and Ga(III) is important.

The separation of In(III) and Ga(III) with D2EHPA [1, 2] and PC-88A [3], and impregnated resins [4, 5] has been reported. These extractants show high selectivity for In(III) over Ga(III). In addition, new phosphonic acid extractants containing an amino moiety have been reported as having a mutual separation ability for In(III), Ga(III), and Zn(II) [6]. Oxime extractants for the separation of In(III) and Ga(III) have also been studied [7], although they have long extraction equilibrium times and low resistance towards hydrolysis. The recovery of Ni(II), Co(II) [8], rare earths [9], In(III), Ga(III) [10, 11], and Cu(II) [12] has also been studied using extractants containing carboxylic acid groups. However, it is reported that the

mutual separation of In(III) and Ga(III) with carboxylic acid extractants is difficult.

In this study, a new extractant with an amino acid group was synthesized for the mutual separation of In(III), Ga(III), and Zn(II). Because In(III) and Ga(III) are regarded as hard acids according to the Hard and Soft Acids and Bases (HSAB) principle [13], it is expected that selective separation of In(III) and Ga(III) from Zn(II) should be possible. In addition, the amino moiety could bring about an anion exchange under low pH conditions, while the carboxylic acid undergoes cation exchange and chelation with the nitrogen atom. The extraction selectivity of the extractant (di-(2-ethylhexyl)amino]acetic acid; DEHAA) for metal ions was investigated. The extraction equilibria of In(III) and Ga(III) were examined to identify the extracted species and extraction equilibrium constants.

2. Experimental

2.1 Materials and analysis

Metal nitrates of analytical grade (Wako Pure Chemical Industries Ltd.) were used to prepare test solutions of the metal ions. Bromoacetic acid (Wako Pure Chemical Industries Ltd.), di(2-ethylhexyl)amine (Wako Pure Chemical Industries Ltd.), and potassium hydroxide (Wako Pure Chemical Industries Ltd.) were used as raw materials to prepare the new extractant. All other reagents and solvents were of analytical grade and used without further purification. ^{1}H-NMR (400 MHz) spectra of the extractants in CDCl$_3$ were recorded with a nuclear magnetic resonance spectrometer model AV400 M (Bruker Co., Rheinstetten, Germany). The pH of the aqueous solutions was measured using a pH meter (HM-30S, DKK-TOA Co., Tokyo, Japan). A flame atomic absorption spectrophotometer model Z-2310 (Hitachi Co., Tokyo, Japan) was used to determination metal concentrations using an air-acetylene flame.

2.2 Synthesis of [di-(2-ethylhexyl)amino]acetic acid (DEHAA)

A stirred solution of di(2-ethylhexyl)amine (0.1 mol) in methanol (300 cm^3) containing potassium hydroxide (0.4 mol) as a catalyst was treated dropwise with a methanol solution (50 cm^3) containing bromoacetic acid (0.2 mol), and the resulting mixture was reacted at 60°C for 19 h (Scheme 1). The methanol was evaporated *in vacuo* and the crude product was dissolved in chloroform, washed with distilled water to remove unreacted raw materials, and dried over anhydrous sodium sulfate. After filtration, the chloroform was evaporated *in vacuo* and a yellow liquid was obtained. ^{1}H-NMR (400 MHz, CDCl$_3$, 25°C) 0.89–0.92 (12H, m, C-CH$_3$), 1.25–1.52 (16H, m, C-CH$_2$-C), 1.67–1.73 (2H, m, CH-(CH$_2$)$_3$), 3.02–3.03 (4H, d, -CH$_2$-N-(CH$_2$)$_2$), 3.67 (2H, s, CH$_2$-N-(CH$_2$)$_2$)), 9.47 (1H, s, -COOH).
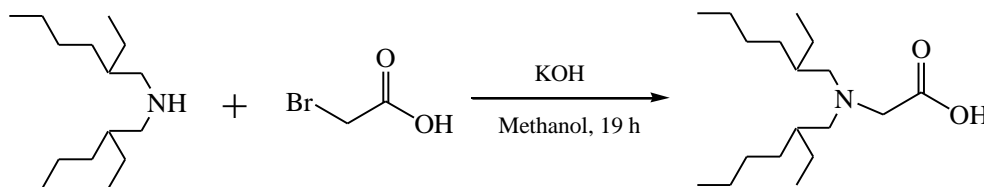
Scheme 1. Synthesis of [di-(2-ethylhexyl)amino]acetic acid (DEHAA).

2.3 Extraction tests for metal ions with DEHAA

All extraction tests for metal ions were performed with aqueous solutions containing a single metal ion. To evaluate the extractability of DEHAA, liquid-liquid extraction was carried out using a 1.0 M

(mol dm^{-3}) aqueous ammonium nitrate solution containing 1 mM metal ions. The pH was adjusted with concentrated HNO$_3$ or NH$_3$. Toluene was used as the organic phase, containing 50 mM DEHAA. Equal volumes (10 cm^3) of the aqueous phase and the organic phase were shaken mechanically in a 50 cm^3 Erlenmeyer flask for 24 h at 303 K. After phase separation, the pH of the aqueous solution was measured with a pH meter. The metal concentration in the aqueous solution was determined using flame atomic absorption spectrophotometry. The metal ion concentration in the organic phase was calculated from the mass balance between the aqueous and organic phases. The extraction percentage (*E%*) and the metal distribution ratio (*D*) were calculated according to equations (1) and (2), respectively.

$$E\% = \frac{[\text{M}]_{org,eq}}{[\text{M}]_{aq,init}} \times 100 = \frac{[\text{M}]_{aq,init} - [\text{M}]_{aq,eq}}{[\text{M}]_{aq,init}} \times 100 \tag{1}$$

$$D = \frac{[\text{M}]_{org,eq}}{[\text{M}]_{aq,eq}} = \frac{[\text{M}]_{aq,init} - [\text{M}]_{aq,eq}}{[\text{M}]_{aq,eq}} \tag{2}$$

where $[\text{M}]_{aq,init}$ represents the initial concentration of metal ion in the aqueous phase, and $[\text{M}]_{aq,eq}$ and $[\text{M}]_{org,eq}$ are the total concentrations of metal ion in the aqueous and organic phases at equilibrium, respectively.

3. Results and Discussion

3.1 Effect of contact time

The extraction percentages of In(III) and Ga(III) with DEHAA were measured at different time intervals at an initial pH of 1.8 and 2.5, respectively (Figure 1). This results show that extraction equilibria for In(III) and Ga(III) were attained within 10 and 5 min, respectively, therefore the equilibration time of the distributing metals was over 10 min in all subsequent experiments.
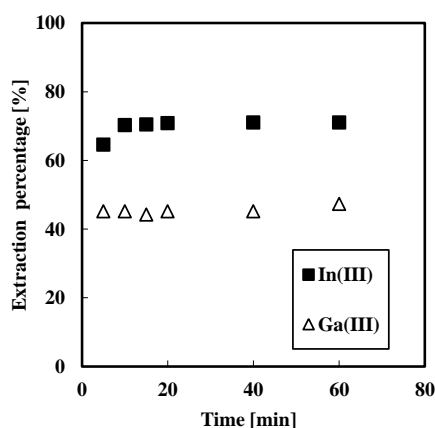

Figure 1. Effect of contact time on the extraction percentage of In(III) and Ga(III) with DEHAA. pH$_{init}$ = 1.8 for In(III) and pH$_{init}$ = 2.5 for Ga(III).

3.2 Extraction selectivity of metals with DEHAA

The extraction selectivity of DEHAA was examined using various metal ions such as In(III), Ga(III), Zn(II), Co(II), Cd(II), Cu(II), Se(IV), Se(VI), and Ni(II). Figure 2 shows the effect of equilibrium pH on

the extraction percentage of metal ions from a 1 M aqueous ammonium nitrate solution with DEHAA. The extraction order for the metals with DEHAA was In(III)>Ga(III)>Cu(II)>Zn(II), while Co(II), Cd(II), Se(IV), Se(VI), and Ni(II) were not extracted in the tested pH range. This indicated that the selective separation of In(III) and Ga(III) in the presence of Zn(II), Se(IV), and Se(VI) was possible, and showed promise for the selective recovery of In(III) and Ga(III) from zinc refinery residues and CIGS solar cells. The extraction behavior of DEHAA for In(III) and Ga(III) is different from the commercial extractant Versatic 10, possibly owing to the presence of the amino group in DEHAA.
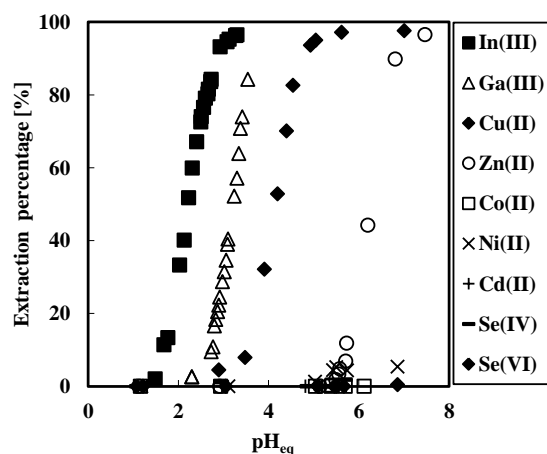

Figure 2. Effect of equilibrium pH on the extraction percentage of metal ions in 1.0 mol dm^{-3} aqueous ammonium nitrate solution with 0.05 mol dm^{-3} DEHAA.

3.3 Selectivity of In(III), Ga(III), and Zn(II) with carboxylic acid extractants

The extraction selectivity for In(III), Ga(III), and Zn(II) with DEHAA was compared with those of 2-[(4-octylphenyl)amino] acetic acid (AN) [11] and Versatic 10 [11]. Table 1 shows the pH values for 50% extraction ($pH_{0.5}$) of the metal ions with the carboxylic acid extractants. The order of $pH_{0.5}$ was In(III)>Ga(III)>Zn(II). The values of $pH_{0.5}$ for In(III) and Ga(III) with DEHAA and AN were shifted to a more acidic pH compared with Versatic 10. The $pH_{0.5}$ for Zn(II) with AN was also shifted to a more acidic pH compared with the other extractants. The $pH_{0.5}$ value is related not only to the pKa of the extractant, but also to the base strength of the amino moiety. According to the HSAB principle, In(III) and Ga(III) are regarded as hard acids, and Zn(II) is a borderline acid. However, aliphatic amines are regarded as hard bases, and aromatic amines are borderline bases. Consequently, amino moieties are considered to play an important role in the selective extraction of In(III), Ga(III), and Zn(II).

Table 1. $pH_{0.5}$ values in the extraction of metal ions with carboxylic acid extractants.

Extractant	$pH_{0.5}$ values for metal extraction		
	In(III)	Ga(III)	Zn(II)
DEHAA	2.2	3.2	6.3
2-[(4-octylphenyl)amino] acetic acid [11]	2.8	2.9	4.5
Versatic 10 [11]	3.7	4.5	6.3

3.4 Extraction equilibria of In(III) and Ga(III) with DEHAA

The distribution equilibrium of DEHAA to the aqueous phase is important to elucidate the extraction equilibria of metal ions. As reported earlier [14], the aqueous solubility of *N*, *N*-dioctylglycine (DOG) having a similar chemical structure to DEHAA was very low ($K_D = 2.2 \times 10^{-5}$ [mol dm^{-3}]). Therefore, the aqueous solubility of DEHAA was assumed to be very low in this study.

3.4.1 Effect of equilibrium pH

Figure 3 shows the effect of the equilibrium pH on the distribution ratio of In(III) and Ga(III) with DEHAA. The slopes of the straight lines indicate the number of protons that have been exchanged with the metals during the extraction. The plots of logD for In(III) and Ga(III) extraction versus pH were linear with a slope of 2.0. Other anions may influence the extraction reaction of In(III) and Ga(III), as charge neutralization is necessary for distribution of the metal-extractant complex to the organic phase. Therefore, the effect of the nitrate anion on the extraction of In(III) and Ga(III) with DEHAA was studied.

3.4.2 Effect of the nitrate ion

Figure 4 shows the effect of the nitrate ion on the distribution ratio of In(III) and Ga(III) with DEHAA. The plots of logD-npH (n:number of hydrogen ion that takes part in the extraction obtained from Figure 3) versus log[NO$_3^-$] were straight lines, both with a slope of 1.0, indicating that one nitrate ion is incorporated in the formation of the In(III) and Ga(III)-extractant complexes.
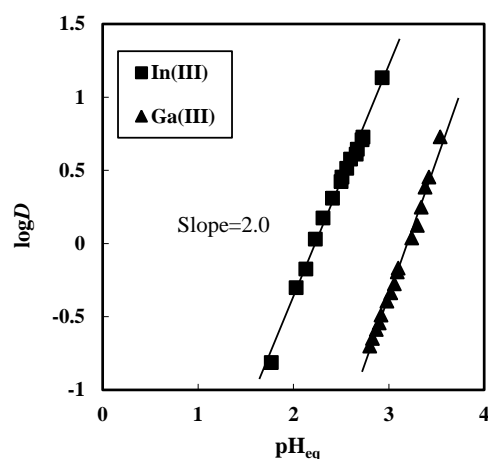

Figure 3. Effect of equilibrium pH on the distribution ratio of In(III) and Ga(III) with DEHAA.
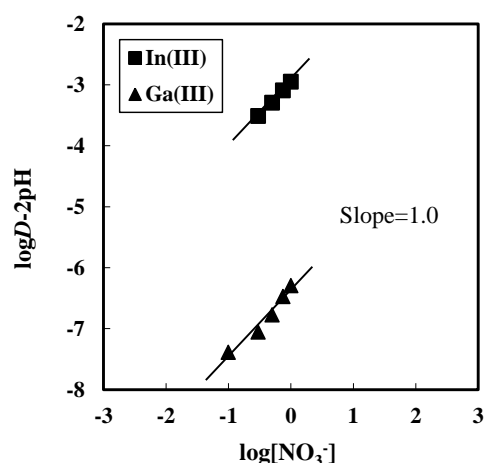$[\overline{(HR)_2}] = 25$ mmol dm^{-3}

Figure 4. Effect of nitrate ion on the distribution ratio of In(III) and Ga(III) with DEHAA.
$[\overline{(HR)_2}] = 25$ mmol dm^{-3}, pH$_{init} = 1.9$ for In(III), and pH$_{init} = 2.7$ for Ga(III).

3.4.3 Effect of extractant concentration

Figure 5 shows the effect of concentration of the extractant on the distribution ratio of In(III) and Ga(III) with DEHAA. The distribution ratios of these metals increase with increasing concentration of the extractant.

It is reported that the DOG, similar to a chemical structure of DEHAA, mostly exisits as a dimer in toluene [14]. Therefore, we assumed that DEHAA is also considered to be in the dimer form in toluene. The plots of logD-npH versus log[$\overline{(HR)_2}$] give lines with a slope of 2.0 in the extraction of In(III) and

Ga(III) with DEHAA, indicating that 4 molecules of the extractant are involved in the complex formation with In(III) and Ga(III), respectively.
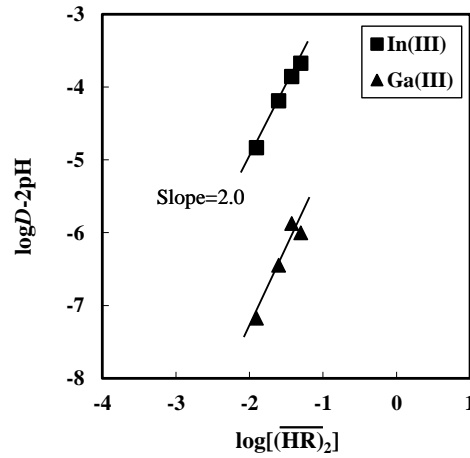

Figure 5. Effect of DEHAA concentration on the distribution ratio of In(III), and Ga(III) in 1.0 mol dm^{-3} aqueous ammonium nitrate solution. pH_{init}=2.0 for In(III) and pH_{init}=2.5 for Ga(III).

3.4.4 Extraction equilibria for In(III) and Ga(III) with DEHAA

Based on the above results, the extraction equilibrium of In(III) and Ga(III) with DEHAA can be expressed as follows:

$$M^{3+} + 2\overline{(HR)_2} + NO_3^- = \overline{MR_2(HR)_2NO_3} + 2H^+, \qquad K_M \qquad (3)$$
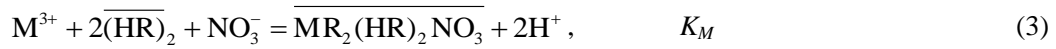
where the bars denote the species in the organic phase.

The extraction equilibrium constant K_M can be expressed as follow:

$$K_M = \frac{\overline{[MR_2(HR)_2NO_3]}[H^+]^2}{[M^{3+}]\overline{[(HR)_2]}^2[NO_3]} \qquad (4)$$

The distribution ratio of M^{3+} between the organic and aqueous phases is defined as:

$$D = \frac{\overline{[MR_2(HR)_2NO_3]}}{[M^{3+}]} \qquad (5)$$

The mass balance equation of the extractant is given by the following equations:

$$\overline{[(HR)_2]}_{init} = \overline{[(HR)_2]} + \overline{[MR_2(HR)_2NO_3]} \approx \overline{[(HR)_2]} \qquad (6)$$

$$[NO_3^-]_{init} = [NO_3^-] + \overline{[InR_2(HR)_2NO_3]} \approx [NO_3^-] \qquad (7)$$

$\overline{[HR]}_{init}$ and $[NO_3^-]_{init}$ indicate the initial analytical concentrations of DEHAA and NO_3^- in the organic and aqueous phases, respectively.

By combining equations (4)–(7), we obtained the following equation in its logarithmic form:

$$\log D = \log\left(\frac{K_M\overline{[(HR)_2]}^2[NO_3]}{[H^+]^2}\right) \qquad (8)$$

To determine K_{In} and K_{Ga}, the experimental results using DEHAA in Figure 5 were correlated with equation (8). The extraction equilibrium constants of In(III) using DEHAA were determined to be $K_{In} = 8.03\times10^{-2}$ [(mol dm^{-3})$^{-1}$] and $K_{Ga} = 9.52\times10^{-4}$ [(mol dm^{-3})$^{-1}$] from the interception with the ordinates in Figure 5.

3.5 Back-extraction of In(III), Ga(III), and Zn(II).

The back-extraction of In(III), Ga(III), and Zn(II) from the loaded organic phase was examined using aqueous solutions of HCl, HNO$_3$, and NaOH and varying their concentrations. The back-extraction percentage (*B.E%*) was calculated according to equation (9).

$$B.E\% = \frac{[M]_{aq}}{[M]_{org,init}}\times100 , \qquad (9)$$

where $[M]_{org,init}$ represents the initial concentration of metal ion in the organic phase.

Table 2 summarizes the back-extraction percentage with each stripping agent. As shown in the table, appropriate concentrations of HNO$_3$ and HCl are suitable for the selective stripping of In(III), Ga(III), and Zn(III), but NaOH is not a suitable stripping agent for these metals. Using 5 N HCl and 1N HCl as the stripping agents, the B.E% of Ga(III) and Zn(II) were low, respectively. These results indicate that these metal ions form anion species with chloride anions, and then the metal anions complexes were extracted as the counter anions of the protonated DEHAA. Further investigation of this supposition is necessary because the B.E% of gallium is very low.

Table 2. Back-extraction of In(III), Ga(III), and Zn(II).

Back-extraction reagents	B.E(%)		
	In(III)	Ga(III)	Zn(II)
1 mol dm^{-3} HCl	94.8	86.1	39.3
5 mol dm^{-3} HCl	83.2	4.5	62.5
1 mol dm^{-3} HNO$_3$	95.6	20.7	98.2
0.1 mol dm^{-3} NaOH	2.6	6.7	2.3

4. Conclusions

DEHAA was efficient for the mutual extraction of In(III), Ga(III), and Zn(II) ions compared with Versatic 10. According to the HSAB principle, it is considered that amino moieties play an important role in the selective extraction of In(III), Ga(III), and Zn(II). In addition, the selective recovery for In(III) and Ga(III) from CIGS solar cells using DEHAA is viable because Se(IV) and Se(VI) were not extracted. The stoichiometries in the extraction reactions of In(III) and Ga(III) with DEHAA were determined based on the results of the slope analysis. Finally, the back extraction of the extracted In(III), Ga(III), and Zn(II) from the organic phase was achieved using appropriate concentrations of HNO$_3$ and HCl.

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