Synthesis of Phosphonic Acid Extractants and Selective Extraction of In(III) and Ga(III) from Acidic Media Containing Zn(II)

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Abstract

Two types of bis-alkylaminophosphonic acid, [bis(2-ethylhexyl)amino]methyl phosphonic acid monobutyl ester (BEAMP) and [bis(2-ethylhexyl)amino]methyl phosphonic acid (BEAAP) as novel extraction reagents were synthesized to develop selective extractants for In(III) and Ga(III) in acidic media containing Zn(II). These newly synthesized extractants were successful in the selective separation of In(III), Ga(III) and Zn(II), a separation that the commercial phosphorus acid extractants such as D2EHPA and PC-88A could not achieve. Their extraction selectivity for the metal ions in aqueous ammonium nitrate solution was in the following order: In(III) > Ga(III) > Zn(II). The extraction equilibria for In(III), Ga(III), and Zn(II) with BEAMP were quantitatively investigated by a batchwise method at 303 K. In(III), Ga(III) and Zn(II) were extracted with BEAMP (HR) according to the following reactions, respectively:

\[
\text{In}^{3+} + 1.5(\text{HR})_2 \rightleftharpoons \text{InR}_3 + 3\text{H}^+, \quad \text{Ga}^{3+} + 2.5(\text{HR})_2 + \text{NO}_3^- \rightleftharpoons \text{GaR}_2(\text{HR})_3(\text{NO}_3) + 2\text{H}^+, \quad \text{Zn}^{2+} + 1.5(\text{HR})_2 + \text{NO}_3^- \rightleftharpoons \text{ZnR}(\text{HR})_2(\text{NO}_3) + \text{H}^+.
\]

The extraction equilibrium constants of In(III), Ga(III) and Zn(II) with BEAMP were determined to be \(K_{ex,M} = 3.16 \times 10^3 \) (mol dm\(^{-3}\))\(^{1.5}\), 44.67 [mol dm\(^{-3}\)]\(^{1.5}\) and 0.14 [mol dm\(^{-3}\)]\(^{-1.5}\), respectively.

1. Introduction

In recent years, the demand for In(III) and Ga(III) has increased because of their use as semiconductor materials such as InP or GaAs. In particular, indium tin oxide (ITO) is used as the electrode in liquid crystal flat-panel displays and plasma TVs because it is a transparent conductive high-performance material. Also Ga(III) is mainly used in the electronic industry for the manufacturing of Ga(III) arsenate laser diodes,
semiconductors, gallium-gadolinium garnets and magnetic bubble memories. Thus, In(III) and Ga(III) have emerged as important strategic metals which are vital for the electronic industry. However, In(III) and Ga(III) are not mined individually since they are very widely dispersed on the earth’s surface, and one significant source of these metals is zinc refinery residues wherein they are contained as minor components. Hence, In(III) and Ga(III) have been generally recovered as by-products from zinc refinery residues. The development of separation techniques to recover these metals is very important since the use of these metals is likely to increase in the near future [1,2]. However, In(III) and Ga(III) show similar chemical properties, and therefore a highly selective recovery process must be developed to effectively recover a small amount of In(III) and Ga(III) from acidic media containing a large amount of Zn(II).

Solvent extraction processes have been employed for the separation and concentration of metal ions in the fields of hydrometallurgy and the treatment of wastewater. The most important factor in the solvent extraction of metals is high selectivity of extractant for the specified metal ion to be recovered. This technique is available for selective recovery of rare metals from wastes containing some base metals. Thus far, a large number of extractants have been developed, and some of these extractants have been commercially available in the field of hydrometallurgy. Therefore, solvent extraction can be expected to be one of the preferred separation techniques for recovery and separation of In(III) and Ga(III) from Zn(II) refinery residues[3-6].

Ga(III) and In(III) can be extracted with various reagents such as octylphenyl phosphoric acid, 3,5-bisbromosalicylaldehyde acylhydrazone, acidic organophosphorus extractants, alkyl carbonyl substituted N-phenyl hydroxyl amines and 4-acyl-3-phenyl-5-isoazolones[7,8]. In addition, neutral organophosphorus compounds, such as triphenylphosphate oxide (TPPO), tributylphosphate (TBPO) and trioctylphosphate oxide (TOPO), have been used for the extraction of In(III) and Ga(III) from hydrochloric acid. Alkylphosphorus compounds like bis(2-ethylhexyl)phosphinic acid [9], bis(2-ethylhexyl)phosphonic acid[10,11], tributylphosphate [12], trioctylphosphine oxide [13-16], bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301) and trialkylphosphine oxide (Cyanex 923) [17] have also been used as extractants for In(III) and Ga(III). Among these, the alkylphosphine derivatives are reported to be better extractants as compared to the other organophosphorus compounds like tributylphosphate (TBP) and bis-(2-ethylhexyl) phosphoric acid) (D2EHPA) because of their low aqueous solubility and resistance to hydrolysis.

In this study, two types of novel bis-alkylaminophosphonic acid were synthesized for the separation of In(III) and Ga(III). Since these extractants have a tertiary amine moiety along with a phosphonic acid group, the extraction selectivities for metal ions are expected to be different from that of commercial phosphorus acid extractants. In particular it is expected that the amino moiety could bring about an anion exchange reaction at low pH while the phosphonic acid will result in a cation exchange and also chelate formation with the nitrogen atom. The extraction selectivities of these extractants for metal ions were compared with those for the commercially available phosphonic acid extractant, 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester (PC-88A). The extraction equilibria of In(III), Ga(III)[18], and Zn(II) were examined to determine the stoichiometry of the extracted species and the extraction equilibrium constants.
2.  Experimental

2.1 Materials and analysis

Bis(2-ethylhexyl)amine, dibutylphosphonic acid and phosphorous acid (Wako Pure Chemical Ind. Ltd.) were used for the synthesis of the new extractants. The commercial extractant, PC-88A was kindly supplied by Daihachi Chemical Industry Co. Ltd Japan and used without further purification. Analytical-grade In(III), Ga(III), and Zn(II) nitrates (Wako Pure Chemical Ind. Ltd.) were used to prepare the test solutions containing each metal. Nuclear magnetic resonance spectra were recorded on a Bruker AV400M for $^1$H NMR (400 MHz) in CDCl$_3$ with TMS as the internal standard for the identification of products.

2.2 Synthesis of [bis(2-ethylhexyl)amino]methylphosphonic acid dibutyl ester (BEADP)

A mixture of bis(2-ethylhexyl)amine (9.66 g, 0.04 mol) and dibutyl phosphonic acid (7.77 g, 0.04 mol) in hydrochloric acid (200 cm$^3$) was prepared followed by the dropwise addition of a formaldehyde solution (6.48 g, 0.08 mol) to the mixture and refluxing for 24 h as shown in Scheme 1. The product was dissolved in chloroform and then washed with 1.0 mol dm$^{-3}$ (= M) HCl for removal of unreacted residues. The organic phase was washed with water several times and then dried over anhydrous MgSO$_4$. After decantation, the chloroform was evaporated in vacuo. The product was obtained with a yield of 86 %. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.00 (quint, 1H, CH), 3.70 (w, 2H), 2.30 (m, 4H), 1.60 (m, H), 1.3 (m, 22H), 0.87 (m, 18H).

Scheme 1. Synthesis of [bis(2-ethylhexyl)amino]methylphosphonic acid dibutyl ester (BEADP).

2.3 Synthesis of [bis(2-ethylhexyl) amino]methylphosphonic acid monobutyl ester (BEAMP)

A mixture of [bis(2-ethylhexyl)amino]methylphosphonic acid dibutyl ester (BEADP) (17.91 g, 0.04 mol) and potassium hydroxide (8.96 g, 0.16 mol) in ethanol (300 cm$^3$) and water (20 cm$^3$) was prepared and the mixture was refluxed for 72 h. The ethanol in the reaction mixture was evaporated in vacuo. The organic phase was washed with water several times and then dried over anhydrous MgSO$_4$. After decantation, chloroform was evaporated in vacuo. The product was obtained with a yield of 71 %. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.80 (br, 1H, OH), 3.92 (quint, 2H), 3.10 (m, 6H), 1.50 (m, 22H), 0.90 (m, 15H, CH, CH$_2$)

Scheme 2. Synthesis of [bis(2-ethylhexyl)amino]methylphosphonic acid monobutyl ester (BEAMP).
2.4 Synthesis of [bis(2-ethylhexyl)amino]methylphosphonic acid (BEAAP)

A mixture of bis(2-ethylhexyl)amine (12.07 g, 0.05 mol) and phosphorous acid (16.77 g, 0.05 mol) in hydrochloric acid (100 cm$^3$) was prepared followed by dropwise addition of a formaldehyde solution (8.1 g, 0.1 mol) to the mixture and refluxing for 24 h as shown in Scheme 3. The compound was dissolved in chloroform and washed with 1.0 mol dm$^{-3}$ (= M) HCl for the removal of unreacted residues. The organic phase was washed with water several times and then dried over anhydrous MgSO$_4$. After decantation, the chloroform was evaporated in vacuo. The product was obtained with a yield of 84 %. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.2 (br, 2H, OH), 3.00 (m, 4H), 2.20 (m, 2H), 1.50 (m, 18H), 0.90 (m, 12H).

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2.5 Liquid-liquid extraction

To evaluate the extraction ability of BEAMP and BEAAP, liquid-liquid extraction was carried out using 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 diluent containing BEAMP or BEAAP. Equal volumes (10 cm$^3$) of the aqueous phase and the organic phase were shaken mechanically in a 50 cm$^3$ conical flask for over 30 minutes at 303 ± 0.1K. After phase separation, the pH of the aqueous solution was measured using a pH meter (HM-30S, DKK-TOA Co., Ltd., Japan) and was determined by the acid-base titration at pH values lower than 0.5. The metal concentration in the aqueous solution was determined by atomic absorption spectrophotometry (AAS, Perkin-Elmer Analyst 100, Japan). 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 metal distribution ratio ($D$) were calculated according to Eqs. (1) and (2), respectively.

\[
E\% = \frac{[M]_{org}}{[M]_{aq,init}} \times 100
\]  \hspace{1cm} (1)

\[
D = \frac{[M]_{org}}{[M]_{aq}}
\]  \hspace{1cm} (2)

where $[M]_{aq,init}$ represents the initial concentration of the metal ions in the aqueous phase. $[M]_{aq}$ and $[M]_{org}$ are the total concentrations of the metal ions in the aqueous and organic phases after equilibrium, respectively.
3. Results and discussion

3.1 Extraction equilibria of In(III), Ga(III) and Zn(II) from 1 M aqueous ammonium nitrate solution

3.1.1 Effect of contact time

The extraction percentages of In(III) and Ga(III) with BEAMP were measured at different time intervals at an initial pH of 1.0 and 2.0, respectively. The experimental results are shown in Fig. 1. The results show that the extraction equilibria of In(III) and Ga(III) were attained within almost 1 minute and 10 minutes, respectively. Therefore, in all subsequent experiments, an equilibration time of at least 30 minutes was maintained to ensure distribution equilibrium.

![Figure 1. Effect of contact time on the extraction percentage of In(III) and Ga(III) with BEAMP. Initial HNO₃ = 2 mol dm⁻³ for In(III) and initial pH=1 for Ga(III). [M]_{aq,\text{init}}=1 \text{ mmol dm}^{-3}.]

3.1.2 Extraction selectivity of metals with BEAMP

The extraction selectivity of BEAMP was examined using various metal ions such as In(III), Ga(III), Zn(II), Co(II), Co(II) and Ni(II). Figure 2 shows the effect of equilibrium pH on the extraction percentage of metal ions from 1 M aqueous ammonium nitrate solution with BEAMP. As seen in Fig. 2, the extraction order for metal ions with BEAMP was In(III) > Ga(III) > Zn(II) > Cu(II) > Co(II) ≈ Ni(II). The extraction behavior of BEAMP for metal ions is different from that of commercial bis(alkyl)phosphorus acids such as PC-88A and D2EHPA, suggesting that a selective separation and recovery of In(III) and Ga(III) from Zn(II) refinery residues is possible.

![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 BEAMP. [M]_{aq,\text{init}}=1 \text{ mmol dm}^{-3}.]

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3.1.3 Selective extraction of In(III), Ga(III) and Zn(II) with BEAMP and BEAAP

The extraction selectivities for In(III), Ga(III), and Zn(II) using BEAMP and BEAAP were investigated and compared with those of PC-88A. As shown in Fig.3, the degree of extraction of these metals increases with increasing aqueous pH. The extraction of In(III) and Ga(III) with BEAMP and BEAAP was shifted to more acidic pH values while Zn(II) was almost the same as for PC-88A. The order of extraction for metal ions with BEAMP and BEAAP was In(III) > Ga(III) > Zn(II), which is the same order as that for PC-88A.

Figure 3. Effect of equilibrium pH on the extraction percentage of In(III), Ga(III), and Zn(II) from 1.0 mol dm$^{-3}$ aqueous ammonium nitrate solution with (a) BEAMP, (b) BEAAP, and (c) PC-88A. $[M]_{aq,\text{init}}$ = 1 mmol dm$^{-3}$.

However, the extraction pH of each metal ion was different and the selectivity order for In(III), Ga(III) and Zn(II) was as follows: BEAMP > BEAAP > PC-88A. The degree of relative separation for these metals gives a first possible approach for the mutual separation of these metal ions. Table 1 summarizes the pH values for 50% extraction of the metal ions using the phosphonic acid extractants. In the extraction of In(III), Ga(III) and Zn(II) with BEAMP, the values of pH$_{0.5}$ for metals were significantly different and their values were found to be -0.35, 1.15, and 3.12, respectively. These results are probably due to the different pK$_a$ values (BEAMP: 3.9, BEAAP: 2.8, and PC-88A: 4.2[19]) of the extractants. Theses results also indicate that the selective separation and recovery of In(III) and Ga(III) from Zn(II) refinery residues would be possible with only pH control. As is seen from Fig. 3, BEAMP is the most suitable extractant for the selective separation of these metal ions.

Table 1. pH$_{0.5}$ values in the extraction of metal ions with phosphonic acid extractants.

<table>
<thead>
<tr>
<th>Extractant</th>
<th>pH$_{0.5}$ values for metal extraction</th>
<th>$\Delta$pH$_{0.5}$ values for metal extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta$pH$_{0.5}$In(III)-Ga(III)</td>
<td>$\Delta$pH$_{0.5}$Ga(III)-Zn(II)</td>
</tr>
<tr>
<td>BEAMP</td>
<td>-0.35 1.15 3.12</td>
<td>1.50 1.97</td>
</tr>
<tr>
<td>BEAAP</td>
<td>— -0.30 1.94</td>
<td>— 2.24</td>
</tr>
<tr>
<td>PC-88A</td>
<td>0.66 1.98 2.69</td>
<td>1.32 0.71</td>
</tr>
</tbody>
</table>
3.2 Extraction equilibria of In(III), Ga(III) and Zn(II) with BEAMP

3.2.1 Effect of equilibrium pH

Figure 4 shows the effect of the equilibrium pH on the distribution coefficient ratio of In(III), Ga(III) and Zn(II) with BEAMP. As is seen in Fig. 4, the slopes of these straight lines indicate the number of protons that have been exchanged for the metals during extraction. The plots of logD for In(III), Ga(III) and Zn(II) extraction versus pH were linear with a slope of 3.0(In(III)), 2.0(Ga(III)) and 1.0(Zn(II)), respectively. It is considered that the aqueous anion is participating in the extraction reaction of Ga(III) and Zn(II) because charge neutralization is necessary for distribution of the metal-extractant complex to the organic phase. Therefore, the effect of nitrate anion participation in the extraction of Ga(III) and Zn(II) with BEAMP was studied.

![Figure 4](image1)

Figure 4. Effect of equilibrium pH on the distribution ratio of In(III), Ga(III) and Zn(II) with BEAMP. [M]_{aq,init}=1 \text{ mmol dm}^{-3}

3.2.2 Effect of the nitrate ion

Figure 5 shows the effect of the nitrate ion on the distribution ratio of Ga(III) and Zn(II) with BEAMP. The plots of logD-npH versus log[NO$_3^-$] were straight lines with a slope of 1.0, respectively, indicating that one nitrate ion is incorporated in the formation of the metal-extractant complexes.

![Figure 5](image2)

Figure 5. Effect of nitrate ion on the distribution ratio of (a) In(III), (b) Ga(III) and (c) Zn(II) with BEAMP. [M]_{aq,init}=1 \text{ mmol dm}^{-3}
3.2.3 Effect of extractant concentration

In this study, the extraction equilibria of metal ions were analyzed by assuming that BEAMP in the organic phase exists mostly as a dimer. Figure 6 shows the effect of the dimer concentration ([\((\text{HR})_2\)]) of the extractant on the distribution coefficient of In(III), Ga(III) and Zn(II) with BEAMP [18]. The distribution coefficients of these metals increase with increasing extractant concentration.

The plots of \(\log D-n\cdot \log pH\) (\(n\) number of hydrogen ion taking part in the extraction obtained from Fig. 4) versus \(\log [\text{HR}_2]\) give lines with the same slope of 1.5 in the extraction of In(III) and Zn(II) with BEAMP, indicating that 3 molecules of the extractant are involved in complex formation with In(III) and Zn(II). On the other hand, the plot of \(\log D-2pH\) versus \(\log [\text{HR}_2]\) for Ga(III) gives a straight line with a slope of 2.5, indicating that 5 molecules of the extractant are involved in the complex formation with In(III).

![Figure 6. Effect of BEAMP concentration on the distribution coefficient of (a) In(III) (b) Ga(III) (c) Zn(II) in 1.0 moldm\(^{-3}\) aqueous ammonium nitrate solution. \([M]_{\text{aq,init}}=1\text{ mmol dm}^{-3}\)](image)

3.2.4 Extraction equilibria of In, Ga(III) and Zn(II) with BEAMP

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

\[
\text{In}^{3+} + 1.5(\text{HR})_2 \rightleftharpoons \text{InR}_3 + 3\text{H}^+ \quad : \quad K_{\text{ex,In}} (3)
\]

where the bars denote the species in the organic phase.

The extraction equilibrium constant \(K_{\text{ex,In}}\) is given by Eq. (4):

\[
K_{\text{ex,In}} = \frac{[\text{InR}_3][\text{H}^+]^3}{[\text{In}^{3+}][(\text{HR})_2]^5} \quad (4)
\]

Also, the distribution coefficient of In(III) between organic and aqueous phases is defined as

\[
D = \frac{[\text{InR}_3]}{[\text{In}^{3+}]} \quad (5)
\]

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

\[
[\text{HR}]_{\text{init}} = 2[(\text{HR})_2] + 3[\text{InR}_3] \approx 2[(\text{HR})_2] \quad (6)
\]
[HR]_{init} indicates the initial analytical concentration of BEAMP in the organic phase. By combining Eqs. (4)-(6), we obtained the following equation in its logarithmic form:

$$\log D = \log\left(\frac{([HR]_2)}{[H^+]}\right)^{1.5} + \log K_{ex,In} \quad (7)$$

Rearrangement of Eq.(7) gives the following equation.

$$\log D - 3pH = 1.5 \log([HR]_2) + \log K_{ex,In} \quad (8)$$

For the extraction equilibrium of Ga(II), the following equations also were obtained in a similar manner as above.

$$\text{Ga}^{3+} + 2.5([HR]_2) + \text{NO}_3^- \rightleftharpoons \text{GaR}_2([HR]_2)(\text{NO}_3^-) + 2\text{H}^+ : K_{ex,Ga} \quad (9)$$

$$\log D - 2pH = 2.5 \log([HR]_2) + \log[\text{NO}_3^-] + \log K_{ex,Ga} \quad (10)$$

In a similar manner as above, the following equations were obtained for the extraction equilibrium of Zn(II).

$$\text{Zn}^{2+} + 1.5([HR]_2) + \text{NO}_3^- \rightleftharpoons \text{ZnR}_2([HR]_2)(\text{NO}_3^-) + \text{H}^+ : K_{ex,Zn} \quad (11)$$

$$\log D - pH = 1.5 \log([HR]_2) + \log[\text{NO}_3^-] + \log K_{ex,Zn} \quad (12)$$

The experimental results for In(III), Ga(III) and Zn(II) shown in Fig. 6 are consistent with Eqs. (8), (10) and (12). The extraction equilibrium constants for In(III), Ga(III) and Zn(II) using BEAMP were determined to be $K_{ex,M} = 3.16 \times 10^3 (\text{mol dm}^{-3})^{1.5}$, 44.67 (mol dm$^{-3}$)$^{-1.5}$, and 0.14(mol dm$^{-3}$)$^{-1.5}$, respectively from their interceptions with the ordinate in Fig. 6.

3.3 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 HCl, HNO$_3$ and EDTA by varying their concentrations. The back extraction percentage ($B. E\%$) was calculated according to Eq. (13).

$$B. E\% = \frac{[M]_{org}}{[M]_{org,init}} \times 100 \quad (13)$$

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

Table 2 summarizes the back extraction percentage for each stripping agent. As seen in Table 2, EDTA was found to be suitable for back extraction while appropriate concentrations of HNO$_3$ and HCl provide opportunities for selective stripping of In(III), Ga(III) and Zn(III), thus offering the possibility that these metals can be separated in the stripping step.


4. Conclusions

[Bis(2-ethylhexyl)amino)methylphosphonic acid (BEAAP) and [bis(2-ethylhexyl)amino)methyl phosphonic acid monobutyl ester (BEAMP) were synthesized as selective extractants for In(III) and Ga(III) in acidic media containing Zn(II). Both BEAAP and BEAMP exhibited higher extractability and selectivity (In > Ga > Zn) at lower pH values than the commercially available extractant, PC-88A. This is probably due to the difference in $pK_a$ and steric hinderance in the extractants caused by the introduction of the tertiary amine moiety and o-butyl moiety, respectively. The stoichiometries of the complexes formed in the extraction reactions for In(III), Ga(III) and Zn(II) with BEAMP were determined based on the results of slope analysis. Moreover, the back extraction of the extracted In(III), Ga(III), and Zn(II) from the organic phase was achieved using EDTA while appropriate concentrations of HNO$_3$ and HCl play an important role for selective stripping.

### References