Selective Extraction of Indium(III) and Gallium(III) with 2-Ethylhexyl Thioglycolate

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Extraction selectivity of In (III) and Ga (III) was investigated using 2-ethylhexyl thioglycolate (EHTG) with a thiol group and an oxygen atom to recover these metals from zinc refinery residue and waste solar panels. The extraction order with EHTG was Cu(II)>In(III)>Ga(III)>Zn(II), while Al (III) was hardly extracted at all. While In(III) and Ga(III) were not extracted at all with 1-dodecanethiol (DDT) with contains only a thiol group although Zn (II) and Cu (II) were extracted. This indicates that the oxygen atom in the EHTG ester plays an important role in the extraction of these metals. The mutual separation of In(III), Ga(III), Zn(II) and Cu(II) is possible in almost one step with EHTG. The extraction equilibria of In(III) and Ga(III) with EHTG are also discussed. Furthermore, the stripping of In(III) and Ga(III) extracted into the organic phase was achieved using appropriate concentrations of NaOH and acids.

1. Introduction

In(III) and Ga(III) are attracting much attention because of their electrochemical characteristics and are classified as critical metals as demand for them is currently growing fast. ITO (indium tin oxide) is used as a transparent electrode in liquid crystal televisions. Ga (III) is used as a compound semiconductor such as GaAs. These metals are also used in CIGS (Copper Indium Gallium Selenide) solar cells and are indispensable for modern society. Thus far, the resources for In(III) and Ga(III) have been obtained as a by-product from zinc refinery residues. However, these metals are likely to experience supply difficulties. Therefore, in this study, we have conducted basic experiments in order to recover selectively these metals from the wastes of solar panels that contain much of these metals.

Solvent extraction processes have been employed for the separation and recovery of metal ions [1]. Toward the development of recovery techniques of In(III) and Ga(III), a variety of extractants such as organic phosphoric acids[2–9], amines[10,11], carboxylic acids[12] and oximes[6,12,13] have been actively studied for the selective extraction of In (III) and Ga (III). Gupta et al. reported that In (III) and Ga (III) were qualitative extracted at hydrochloric acid concentrations of over 0.01 M(= mol dm$^{-3}$) and 1 M hydrochloric acids, respectively when Cyanex 923 in toluene was used[14]. Nusen et al. reported on a synergistic extraction system of LIX 63 and Versatic 10[12]. The extraction of Ga (III) was improved by the synergistic effect of Versatic 10 and LIX 63 compared with Versatic 10 alone. Although various extractants for the recovery of In(III) and Ga(III) have been studied as described above, studies using alkylated thiols have hardly been made.

In this study, the selectivity of In(III) and Ga(III) was investigated using 2-ethylhexyl thioglycolate
(EHTG) having thiol and oxygen atoms as donor atoms. In (III) and Ga (III) are classified as hard acids by the HSAB (Hard and Soft Acids and Bases) principle[15]. EHTG has a thiol group which is a soft base and an oxygen atom which is a hard base. We have clarified the extraction behavior of In (III) and Ga (III) with EHTG. The extraction selectivity of EHTG for metal ions was compared with that of 1-dodecanethiol (DDT). The extraction equilibria of In(III) and Ga(III) using these extractants were examined to determine the extracted species and the extraction equilibrium constants.

2. Experimental

2.1 Materials

Analytical grade In(III), Ga(III), Cu(II) and Zn(II) nitrates (Wako Pure Chemical Ind. Ltd.) were used to prepare test solutions of the metal ions. EHTG and DDT of analytical grade (Tokyo Kasei Co., Japan) were purchased for the extraction tests and used without further purification. All other reagents and solvents were of analytical grade and were used as received.

2.2 Extraction procedures

To evaluate the extraction ability of EHTG and DDT, liquid-liquid extraction was carried out using 1 M aqueous ammonium nitrate solution containing 1 mM metal ions. The extraction experiments were carried out on a single metal system. The pH (HM-30S, DKK-TOA Co., Tokyo, Japan) was adjusted with concentrated HNO₃ and NH₄OH. Toluene was used as the diluent for EHTG and DDT. The extraction equilibria for metal ions were determined using a batchwise method at 303 K for 24 h. Equal volumes (10 cm³) of the aqueous phase and organic phase were mixed in a 50 cm³ stoppered Erlenmeyer flask and mechanically shaken (120 rpm) for 24 h. After phase separation, the hydrogen ion concentration of the aqueous solution was measured with a pH meter and was determined by acid-base titration at pH values lower than 0.5. The initial and equilibrium concentrations of metal ions in the aqueous solution were determined using a flame atomic absorption spectrophotometer model Z-2310 (AAS, Hitachi Co., Tokyo, Japan). The metal concentration in the organic phase was calculated from the mass balance between the aqueous and organic phases. The extraction percentage (E%) of the metal ions and the metal distribution ratio (D) were calculated by Eqs. (1) and (2), respectively.

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

where \([M]_{\text{aq},\text{init}}\) and \([M]_{\text{aq},eq}\) represent the initial and equilibrium concentrations of the metal ions in the aqueous phase and \([M]_{\text{org},eq}\) is the total concentration of the metal ions in the organic phase after equilibrium.

3. Results and Discussion

3.1 Effect of contact time

The extraction percentages of In(III) and Ga(III) with EHTG were measured at different time intervals at initial pH values of 2 and 3.5, respectively. The experimental results are shown in Figure 1. The result shows that the extraction equilibria of In(III) and Ga(III) were attained within 6 and 12 h, respectively. In general, it is said that the ester and thiol groups are not stable to acids and bases, however, we think that EHTG is stable up to 24 h as shown in Figure 1. The equilibration time for the extraction of these metals was performed for 24 h in all subsequent experiments.

![Figure 1. Effect of contact time on the extraction percentage of In(III) and Ga(III) with EHTG.](image)

\([M] = 1 \text{ mM}, [\text{RSH}] = 0.5 \text{ M}, \text{pH}_{\text{init, In(III)}} = 2, \text{pH}_{\text{init, Ga(III)}} = 3.8.\]

3.2 Extraction selectivity of metal ions with EHTG

The extraction selectivity of EHTG was examined using various metal ions such as In(III), Ga(III), Zn(II), Cu(II) and Al(III). In addition, the extraction selectivity of EHTG was compared with that of DDT.

Figure 2 shows the effect of equilibrium pH on the extraction percentage of metal ions from 1 M aqueous ammonium nitrate solution with (a) EHTG (b) DDT, respectively. The extraction of Ga (III) with DDT could not be carried out at pH_{eq} higher than 3 because of the precipitation of Ga(OH)₃. As seen from Figure 2 (a), the extraction order for the metals with EHTG was Cu(II)>In(III)>Ga(III)>Zn(II), while Al (III) was not extracted with EHTG. It is considered that the difference in the extraction behavior of In (III) and Ga (III) is related to the ease in formation of the hydroxide complexes. At low pH, In (III) forms more stable complexes with EHTG than with hydroxide ions. On the contrary, Ga (III) easily forms complexes with hydroxide ions even at low pH. Thus, it is concluded that In (III) was selectively extracted at a lower pH than Ga(II). EHTG extracted In (III) and Ga (III) which were not extracted by DDT. Therefore, In(III) and Ga(III) were selectively extracted from Zn(II) and Al(III) with EHTG. This shows that it is possible to separate In (III) and Ga (III) from zinc refining residues and bauxite, respectively.
Table 1 summarizes the pH values for 50 % extraction (= pH$_{0.5}$) of the metal ions using EHTG. As seen from this table, the selective separation and recovery of In(III) from Ga(III) can be performed in one step because the $\Delta$ pH$_{0.5}$ values for In(III)-Ga(III) extraction were greater than 2 [16].

| pH$_{0.5}$ values for metal extraction | $\Delta$ pH$_{0.5}$ values for In(III)-Ga(III) extraction |
|---------------------------------------|------------------------------------------------------|
| In(III) | Ga(III) | Zn(II) | Cu(II) | $\Delta$ pH$_{0.5}$ In(III)-Ga(III) |
| 1.88 | 4.2 | 4.97 | 0.51 | 2.22 |

### 3.3 Extraction equilibrium of In(III) with EHTG

The extraction equilibrium for In(III) with EHTG was investigated using slope analysis. Figure 3 (a) shows the effect of the equilibrium pH on the distribution ratio of In(III) with EHTG. As is seen in Figure 3 (a) [RSH] = 0.5 M, (b) pH$_{init}$, In(III) = 2.
(a), the plot of \( \log D \) versus pH for In(III) extraction showed a straight line with a slope of 3, indicating the number of protons that have been exchanged for In (III) during the extraction. Figure 3 (b) shows the effect of EHTG concentration ([RSH]) on the distribution ratio of In(III). The plots of \( \log D-npH \) (\( n \): the number of hydrogen ion that takes part in the extraction, which was obtained from Figure 3 (a)) versus \( \log [RSH] \) was a straight line with a slope of 3, indicating that 3 molecules of EHTG participate in the extraction reaction of In(III).

Based on these experimental results, the extraction equilibrium of In(III) with EHTG can be expressed as follows:

\[
\text{In}^{3+} + 3\text{RSH} \rightleftharpoons \text{In(RS)}_3 + 3\text{H}^+, \quad K_{\text{ex,In(III)}}
\]  

where the bars denote the species in the organic phase.

The extraction equilibrium constant \( K_{\text{ex,In(III)}} \) can be expressed as follows:

\[
K_{\text{ex,In(III)}} = \frac{[\text{In(RS)}_3][\text{H}^+]^3}{[\text{In}^{3+}][\text{RSH}]^3}
\]  

The distribution ratio of In(III) between the organic and aqueous phases is defined as

\[
D_{\text{In(III)}} = \frac{[\text{In(RS)}_3]}{[\text{In}^{3+}]} \]  

By combining equations (4) and (5), we obtained the following equation in its logarithmic form:

\[
\log D_{\text{In(III)}} - 3pH = 3\log[RSH] + \log K_{\text{ex,In(III)}}
\]  

The experimental result for In(II) shown in Figure 3 (b) is consistent with equation (6). The extraction equilibrium constant for In(III) using EHTG was determined to be \( K_{\text{ex,In(III)}} = 1.54 \times 10^{-5} \) [-] from the interception with the ordinate in Figure 3 (b).

### 3.4 Extraction equilibrium of Ga(III) with EHTG

The extraction equilibrium of Ga (III) can be assumed as the following reaction:

\[
\text{Ga}^{3+} + 3\text{RSH} \rightleftharpoons \text{Ga(RS)}_3 + 3\text{H}^+, \quad K_{\text{ex,Ga(III)}}
\]  

where, the bars denote the species in the organic phase.

The extraction equilibrium constant \( K_{\text{ex,Ga(III)}} \) can be expressed as follows:

\[
K_{\text{ex,Ga(III)}} = \frac{[\text{Ga(RS)}_3][\text{H}^+]^3}{[\text{Ga}^{3+}][\text{RSH}]^3}
\]  

Ga (III) forms the following hydroxide-complexes with hydroxide ions in the aqueous phase.

\[
\text{Ga}^{3+}+i\text{OH}^- \rightleftharpoons \text{Ga(OH)}_{i-1}^{(3-i)+} \quad (i = 1 - 3), \quad \beta_i
\]
\[
\beta_i = \frac{[\text{Ga(OH)}_{(3-i)^+}]}{[\text{Ga}^{3+}][\text{OH}^-]}
\]  
(10)

\[
(\log \beta_1 = 10.95, \log \beta_2 = 21.40 \text{ and } \log \beta_3 = 30.98) \quad [17]
\]

where \(\beta_i\) denotes \(i\)-th overall stability constant.

In this case, the distribution ratio can be expressed as follows in consideration of hydroxy complex formation.

\[
D_{\text{Ga(III)}\alpha_3} = \frac{K_{ex,\text{Ga(III)}}[\text{RSH}]}{[\text{H}^+]^3}
\]  
(11)

\[
\alpha_3 = (1 + \beta_1[\text{OH}^-] + \beta_2[\text{OH}^-]^2 + \beta_3[\text{OH}^-]^3)
\]

The validity of the assumed extraction equilibrium of Ga (III) (equation (11)) can be confirmed by examining the effect of pH and extractant concentration on \(\log (D \alpha_3)\).

Figure 4 (a) shows the effect of the equilibrium pH on \(\log (D \alpha_3)\) for Ga(III) with EHTG. The plots of \(\log (D \alpha_3)\) versus pH for Ga(III) extraction showed a straight line with a slope of 3, indicating the number of protons that have been exchanged for Ga (III) during the extraction.

The following equation was obtained in logarithmic form of equation (11):

\[
\log D_{\text{Ga(III)}\alpha_3} - 3 \text{pH} = 3 \log [\text{RSH}] + \log K_{ex,\text{Ga(III)}}
\]  
(12)

Based on equation (12), the experimental results were plotted in Figure 4 (b). The plots of \(\log (D \alpha_3) - 3\text{pH}\) versus \(\log ([\text{RSH}]\) gave a straight line with a slope of 3 in the extraction of Ga(III) with EHTG, indicating that 3 molecules of EHTG participate in the Ga(III) extraction reaction.

Figure 4. Effect of (a) pH eq and (b) extractant concentration on \(\log (D \alpha_3)\) for Ga(III).
(a) \([\text{RSH}] = 0.5 \text{ M}\), (b) \(\text{pH}_{\text{init, Ga(III)}} = 3.8\).

The extraction equilibrium constant for Ga(III) using EHTG was determined to be \(K_{ex,\text{Ga(III)}} = 1.28 \times 10^{-9} [-]\) from the interception with the ordinate in Figure 4 (b).
3.5. Back-extraction of In(III) and Ga(III)

Stripping of In(III) and Ga(III) from the loaded organic phase was examined using HCl, HNO₃, H₂SO₄, NaOH and (COOH)₂ by varying their concentrations. The back-extraction percentage (B.E. %) was calculated according to equation (13).

\[
B.E.\% = \frac{[M]_{aq}}{[M]_{org, init}} \tag{13}
\]

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

Table 2 summarizes the percentage of In(III) and Ga(III) stripped from the organic phase with the stripping reagents. As seen in Table 2, a high stripping percentage of In(III) was achieved with all stripping reagents, while 1 M NaOH as the stripping reagent of Ga(III) was effective.

| Back-extraction reagents | B. E (%) |
|--------------------------|----------|
|                          | In(III)  | Ga(III) |
| 0.1 M HCl                | 97.4     | 78.2    |
| 0.1 M HNO₃               | 97.4     | 81.6    |
| 0.05 M H₂SO₄             | 96.0     | 81.2    |
| 1 M HCl                  | 96.5     | 77.5    |
| 1 M HNO₃                 | 96.7     | 75.0    |
| 0.5 M H₂SO₄              | 94.7     | 78.1    |
| 1 M NaOH                 | 100      | 92.5    |
| 0.05 M (COOH)₂           | 100      | 80.2    |
| 0.5 M (COOH)₂            | 100      | 77.1    |

4. Conclusions

The extraction order for the metals with EHTG was Cu(II)>In(III)>Ga(III)>Zn(II), while Al (III) was almost not extracted with EHTG. In contrast, 1-dodecanethiol (DDT) did not extract In(III), Ga(III) and Al(III) although Zn (II) and Cu (II) were extracted with DDT. The extraction selectivity with EHTG is considered to be due to the chelate formation between the thiol moiety and the oxygen atom in the EHTG ester. The mutual separation of In(III) and Ga(III) is possible from zinc refinery residues and solar panel wastes since the extraction pH of In (III), Ga (III), Zn (II), Cu (II) and Al (III) are different with EHTG. The stoichiometries of the complexes formed by the extraction reactions for In(III) and Ga(III) with EHTG were determined in detail based on the slope analysis results. In(III) and Ga(III) were extracted with EHTG as 1:3 complexes with extraction equilibrium constants, \(K_{ex, In(III)} = 1.54 \times 10^{-5} \text{ [-]}\) and \(K_{ex, Ga(III)} = 1.28 \times 10^{-9} \text{ [-]}, \) respectively. Finally, back extraction of the extracted In(III) and Ga(III) from the organic phase was achieved using appropriate concentrations of NaOH and acids.

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