Selective Extraction of In(III) and Ga(III) Using N-Lauroylsarcosine (NLS)

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(Received October 25, 2019; Accepted December 2, 2019)

In(III) and Ga(III) are included in zinc refining, the wastes of solar panel and electronics and so on. In solvent extraction which is a useful method of separation of metals, we used N-lauroylsarcosine (NLS), containing tertiary amine which is alkyl amide derivative with the sarcosine moiety in the molecule structure in order to separate and recover these metal ions. We studied about the extraction equilibria of these metals using NLS. The selective extraction order of NLS is Ga(III) > In(III) >> Zn(II). It was found that NLS was able to separate these metals by pH difference. Versatic acid 10 (VA10) with only carboxylic acid group in the molecule structure extracted In(III) and Ga(III) simultaneously in the same pH region. Therefore, we found that the amide group included in the molecule structure of NLS has an important role to extract these metals. Mutual separation of In(III), Ga(III) and Zn(II) was carried out by a one-step experiment using NLS. Slope analysis was used to investigate the extraction equilibria of In(III) and Ga(III) with NLS. Suitable concentrations of acids were able to strip these metals from the loaded organic phase.

1. Introduction

For these several years, the demand of In(III) and Ga(III) has been growing for use in electronic devices owing to the chemical and physical properties of these metals. These metals are used in light-emitting diodes and liquid crystal displays [1]. In recent years, the application of these metals to Cu-In-Ga-Se(CIGS) cells [2] has become prominent. In general, manufacturing costs of a CIGS solar cell is lower compared to crystalline-based solar panels, and age deterioration of power generation performance is low. For these reasons, demand for In (III) and Ga(III) is predicted to increase in CIGS solar cells in future. However, their metals have been generally recovered as by-products of the zinc refinery residues, and the development of selective separation techniques from the wastes of solar panel and electronics for In(III) and Ga(III) over Zn(II) is desired [3,4].

In this study, the solvent extraction has been studied as the method of separation and purification of these metals. The solvent extraction is widely used in industries and known as one of the most important separation techniques for metal ions. Few studies with respect to development of new extractants with high
selectivity for the metal ions have been performed [5]. For example, VA10, which has carboxylic group in the molecule structure, has been reported as a mixture with other extractants for solvent extraction. This is the study concerning "synergism" owing to VA10. It is especially known that it has selectivity for a base metal group [6-8]. Many extractants were examined as extractants for extraction of In(III) and Ga(III) [1,9]. Here, we decided to use N-lauroylsarcosine (NLS) which is almost not used as an extractant for solvent extraction. This chemical compound is especially known as a medical material and NLS has been studied for its skin penetration enhancer [10,11]. NLS has a carboxylic group in the molecular structure like VA10 and it has an amide group as well. We expected the presence of an amide group would make it easier to attract cations during extraction of metals and then a carboxylic acid group would be expected to chelate with cations. Figure 1 shows the chemical structures of VA10 and NLS.

2. Experimental

2.1 Materials and analysis

Analytical-grade indium(III), gallium(III) and zinc(II) nitrates (Wako Pure Chemical Ind. Ltd.) were used to prepare the metal solutions. VA10 (Shell Chem) and NLS (Tokyo Kasei Co., Japan) diluted with toluene (Wako Pure Chemical Ind. Ltd.) was used as an organic solution.

2.2 Measurement of pKa of NLS by potentiometric titration

All potentiometric measurements were performed in a beaker at a constant temperature of 298 K. The extractant was dissolved in ethanol/water (65:35, 70:30, 80:20 v/v, respectively) containing 0.1 mol/dm³ NaCl. The combined pH electrodes were calibrated by Gran’s method [12], which determined the standard potential, E₀. The pKa was determined using an automatic potentiometric titrator (Kyoto Electronics Mfg. Co., Ltd.).

2.3 Liquid-liquid extraction of In(III), Ga(III) and Zn(II)

To reveal the extractability of NLS, liquid-liquid extraction tests were carried out by a batch method. The aqueous phase of 1.0 M ammonium chloride solutions was used as a buffer solution containing 1.0 mM metal ion. The initial pH was adjusted with HCl and NH₃ aqueous solution. Toluene was used as an organic solvent for dissolving NLS. In a 30 mL sample tube, the volume of each solution was unified at 5 mL. They were shaken by orbital shaker for 24 h, at 120 rpm and 303K. After extraction, the pH of the aqueous solution was measured by a pH meter (HM-30S, DKK-TOA Co., Tokyo, Japan). Metal ion concentrations in the aqueous phase were measured by a flame atomic absorption spectrophotometer model Z-2310 (AAS, Hitachi Co., Tokyo, Japan), and then the metal concentrations in the organic phase were calculated from the mass balance between the initial and equilibrium concentrations in the aqueous phase.
The extraction percentage \( (E\%) \) and the distribution ratio \( (D) \) were calculated according to the following equations (1) and (2).

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

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

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

2.4 Back extraction

In order to study the back extraction ability from NLS, back extraction experiments were carried out by a batch method. The In(III)- or Ga(III)-loaded organic phase was prepared by extracting their metals. We separated the organic phase from the aqueous phase. HCl, H\(_2\)SO\(_4\), HNO\(_3\) and NaOH were used as the stripping reagents. These reagents were put into the metal-loaded organic phase. They were shaken for 24 h, at 120 rpm and 303 K. The back extraction percentage \( (B. \ E. \ (\%)) \) was calculated according to Eq.(3).

\[
B. \ E. \ (\%) = \frac{[M]_{aq}}{[M]_{org, init}} \times 100 \tag{3}
\]

where \([M]_{org, init}\) represents the initial concentration of the metal ion in the organic phase and \([M]_{aq}\) is the total concentration of the metal ion in the aqueous phases after equilibrium.

3. Results and Discussion

3.1 Determination of pKa for NLS

Figure 2 shows the pKa value versus the volume ratio of ethanol/water mixtures containing NLS. The apparent values of pKa were defined as pKa\(_1\). The apparent pKa\(_1\) values in the aqueous phase were calculated from the intercepts of these approximate lines. The apparent pKa\(_1\) value of NLS was 2.14. This value is almost the same as that of sarcosine.
3.2 Extraction equilibrium time of In(III) and Ga(III)

The extraction percentages of In(III) and Ga(III) with NLS were measured at different time intervals at initial pH values of 2.7 and 1.9, respectively. The result of effect of contact time on the metals concentration in the aqueous phase is shown in Figure 3. This shows that the both extraction equilibria of In(III) and Ga(III) were attained within 1 h.

![Graph showing metal concentrations over time](image)

Figure 3. Effect of the contact time on the metal concentrations in the aqueous phase.

3.3 Effect of equilibrium pH on the extraction of In(III), Ga(III) and Zn(II)

Three kinds of 1.0 M aqueous ammonium chloride solutions containing individually 1.0 mM In(III), Ga(III) and Zn(II) were prepared and adjusted to the initial pH 0.0 – 7.0 using 1.0 M hydrochloric acid and 0.1 M ammonia. In the organic phase, 0.5 M VA10 and NLS were diluted with toluene. Figures 4 and 5 show the effect of equilibrium pH on the extraction percentage of each metal. Figure 4 shows that VA10 extracted In(III) and Ga(III) at same pH, while NLS could not only extract In(III) and Ga(III) but also separate their metals as shown in Figure 5. Moreover NLS was able to extract them at lower pH than VA10. This difference is due to the difference of the acid dissociation constants between NLS and VA10. It was reported that the acid dissociation constant of VA10 is $1.1 \times 10^{-6}$ mol/dm$^3$ [13]. While, Zn(II) has not been extracted with both extractants in the examined pH region.

The relationship between the equilibrium pH and the distribution ratio of Ga(III) or In(III) was shown in Figure 6. The slopes of the straight lines indicated the number of protons ion-exchanged with a metal ion and both slopes gave the value of 3.0. Therefore, it can be considered that three protons are released during extracting metal ions.
Figure 4. Effect of the equilibrium pH on the extraction percentages of metal ions from 1.0 M aqueous ammonium chloride solution with 0.5 M VA10.

Figure 5. Effect of the equilibrium pH on the extraction percentages of metal ions from 1.0 M aqueous ammonium chloride solution with 0.5 M NLS.

Figure 6. Effect of the equilibrium pH on the distribution ratio of metal ions from 1.0 M aqueous ammonium chloride solution with 0.5 M NLS.
3.4 Effect of the extractant concentration on extraction of In(III) and Ga(III)

The effect of the concentration of NLS in the organic phase was investigated by varying the concentration of NLS from 0.2 to 0.8 M for In(III) and from 0.4 – 1.0 M for Ga(III), respectively. It has been reported that alkylated carboxylic acid forms a dimer in the organic diluent [14]. Since sarcosine contains carboxylic acid in its molecular structure, it can be considered that sarcosine also forms a dimer like carboxylic acid in toluene. Figure 7 shows the relationship between extractant concentration and log$D$ – 3pH according to Eq. (7). Two slopes shown in Figure 7 gave the value of 2.0. Therefore, it can be considered that two sarcosine dimers were involved in forming the complex between 4 molecules of sarcosine and each metal ion.

![Figure 7. Effect of the extractant concentration on log$D$ – 3pH from 1.0 M aqueous ammonium chloride solution.](image)

3.5 Extraction equilibria of In(III) and Ga(III) with NLS.

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

$$M^{3+} + 2(\text{HR})_2 \rightleftharpoons M R_3 RH^- + 3H^+$$  (4)

where the bars donate the species in the organic phase and “$M$” refers to metal ions of In(III) and Ga(III).

The extraction equilibrium constant $K_{ex,M}$ can be expressed as follows:

$$K_{ex,M} = \frac{[MR_3RH][H^+]^3}{[M^{3+}][(HR)_2]^2}$$  (5)

The distribution ratio of metal “$M$” between the organic phase and aqueous phases is defined as

$$D = \frac{[MR_3RH]}{[M^{3+}]}$$  (6)
The logarithm of the equation obtained by combining Eq.(5) with Eq.(6) gives the following Eq.(7).

$$\log D - 3pH = \log K_{ex, M} + 2\log [(HR)_2]$$

The extraction equilibrium constants for In(III) and Ga(III) using NLS were determined to be $K_{ex,In(III)} = 1.21 \times 10^{-8} \text{ mol/dm}^3$ and $K_{ex,Ga(III)} = 1.94 \times 10^{-6} \text{ mol/dm}^3$, respectively.

### 3.6 Back extraction of In(III) and Ga(III).

Back extraction of In(III) and Ga(III) from the metal-loaded organic phase was examined using HCl, H$_2$SO$_4$, HNO$_3$ and NaOH. The reason for using the base was because Ga(III) is an amphoteric metal. Table 1 shows the back extraction percentage of In(III) and Ga(III) back-extracted from NLS with each stripping reagent. Every acid could act as stripping reagent but NaOH could not act like that. When NaOH touched an organic phase loaded metal ion, the solution became cloudy.

| Stripping reagents | B.E. [%] |
|--------------------|----------|
| In(III)           | Ga(III)  |
| 1.0 M HCl         | 100      | 84.1 |
| 2.0 M HCl         | 98.2     | 88.4 |
| 1.0 M H$_2$SO$_4$ | 100      | 82.9 |
| 1.0 M HNO$_3$     | 85.3     | 86.3 |
| 0.1 M NaOH        | -        | -    |
| 1.0 M NaOH        | -        | -    |

### 4. Conclusion

The new kind of extractant, N-lauroylsarcosine (NLS) has the molecular structure with an alkyl amide group with chelating ability of amino carboxylic acid, and it was used for separation of In(III) and Ga(III) over Zn(II). The extraction order was Ga(III) > In(III) >> Zn(II) ≈ 0. As the results of the experiments, we found NLS could selectively separate In(III) and Ga(III) over Zn(II) from 1 M NH$_4$Cl aqueous solution containing 1.0 mM metal ions around the pH$_{eq} = 2.5$. VA10 with only carboxylic acid group in the molecule structure was able to extract In(III) and Ga(III) in the same pH region but was not able to separate of In(III) from Ga(III). This result let us know that the amide groups in the extractant molecular plays an important role in the selectivity for In(III) and Ga(III). The equilibrium extraction constants of In(III) and Ga(III) are $K_{ex,In(III)} = 1.21 \times 10^{-8} \text{ mol/dm}^3$ and $K_{ex,Ga(III)} = 1.94 \times 10^{-6} \text{ mol/dm}^3$, respectively. In addition, we found HCl, H$_2$SO$_4$ and HNO$_3$ act as stripping reagents for In(III) and Ga(III) from an metal-loaded organic phase.

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