SOLVENT EXTRACTION OF INDIUM WITH TRIALKYLPHOSPHINE OXIDE FROM SULFURIC ACID SOLUTIONS CONTAINING CHLORIDE ION

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In order to develop an effective separation process for tin (IV) from indium (III) to produce high purity indium free from tin contamination, basic investigations on solvent extraction of indium (III) from sulfuric acid solution containing chloride ion added for the purpose of suppressing precipitate of tin hydroxide were conducted at 30°C employing Cyanex 925 and trioctylphosphine oxide (TOPO) in toluene as the solvents. Cyanex 925 quantitatively and selectively extracted tin (IV) from indium (III) in the low concentration region of sulfuric acid. From the concentration dependencies of the reactant species, i.e., the reagents, hydrogen ion and chloride ion, on the distribution ratio, it was elucidated that indium (III) is extracted as the solvated complex of the type, H(InCl)2-Reagent. Co-extracting hydrogen ion with both of these extraction reagents and the equilibrium constants for the extraction reactions were evaluated. The value for Cyanex 925 was half of that for TOPO, which was attributed to the sterically hindered structure of alkyl radicals of the former reagent.

Introduction

Demand for indium is increasing rapidly in recent years as a raw material for various electronic devices such as indium phosphide semiconductors and indium solar batteries and indium tin oxide (ITO) transparent electrodes for liquid crystal displays along with the rapid advances of high-technology industries. Indium does not form minerals by itself and is mainly found together with lead-zinc, copper and tin ores. It is being extracted from various conversion products (cake, blue powder, roasting dusts, slimes, etc.) emitted from smelters of lead-zinc and copper where it becomes concentrated during the treatment of ores. At present, the majority of indium is being recovered from the above-mentioned feed materials by means of many repeats of dissolution and precipitation followed by cementation by zinc to produce sponge-indium as the final product. However, this conventional process is insufficient because of consumption of large amount of labor and energy and a long treatment time. Therefore, an alternative, more effective process using solvent extraction and/or ion exchange technology has been desired. For both purification and recovery of indium, its separation from tin is of prime importance because it is present together with indium in the majority of cases. In sulfuric acid solutions usually employed as the leach liquor for the above-mentioned feed materials, tin is apt to be hydrolyzed to form very fine precipitates even at high acid concentration. These fine precipitates give rise to the formation of stable crud at the interface between two phases and impedes phase separation and, consequently, the smooth operation of extraction.

Separation of indium from tin by means of solvent extraction techniques has been investigated as long as 30 years ago. Levin found that the extraction of both indium (III) and tin (II and IV) was greatly affected by the kind of hydrohalic acid from which they were extracted when dialkylphosphoric acids were employed as the extracting reagents. This result suggests that halide anion influences the extraction by giving rise to complexes with these metal ions in aqueous phase, which may also affect the formation of precipitate in the aqueous phase. As will be described in the following section, it was found that the addition of chloride ion suppresses the formation of the precipitation of tin hydroxide, which suggests the possibility of successful separation of these metals by means of solvent extraction free from crud formation.

Ross and White found that highly sterically hindered trialkylphosphine oxides can strongly and selectively extract tin (IV) from hydrochloric acid solution. In recent years, American Cyanamid Co. Ltd. developed a novel type of sterically hindered trialkylphosphine oxide under the trade name, Cyanex 925, the main and active component of which is di(2,4,4’-trimethylpentyl) octylphosphine oxide, as an effective commercial solvent extraction reagent for tin. It is expected that high purity indium free from tin contamination can be prepared by selectively removing small amounts of tin from large amounts of indium by means of solvent extraction with this reagent from sulfuric acid solution containing chloride or by means of adsorption on porous resin impregnated with this reagent. However, there is no information available about the extraction behavior of this reagent for indium from such acid solution.

In the present work, we investigated the basic aspects of the equilibrium distribution of indium (III) in

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1. Preliminary Experiments

Prior to the investigation of the equilibrium distribution of indium (III), preliminary experiments were carried out to obtain qualitative information about the precipitation of tin hydroxide in sulfuric acid solution containing chloride and solvent extraction of tin (IV) and indium (III) from sulfuric acid solution containing chloride.

Table 1 shows formation of a precipitate of tin hydroxide in various concentration of sulfuric acid solution containing chloride ion after leaving the solution containing tin as it is for more than 24 hours after dissolving tin (IV) chloride (SnCl₄·H₂O) in the corresponding sulfuric acid solution containing chloride. From this table, it is apparent that the tetravalent tin gives rise to a precipitate even in sulfuric acid solution as high as 2 mol·dm⁻³, but it can be considerably suppressed by adding chloride ion.

Figure 2 illustrates the plot of % extraction of tin (IV) and indium (III) against sulfuric acid concentration in the extraction with 80 mmol·dm⁻³ Cyanex 925 in toluene at 30 °C from sulfuric acid solution containing 0.2 mol·dm⁻³ ammonium chloride. From this figure, it is apparent that tin (IV) is nearly completely extracted over the whole concentration range of sulfuric acid, while indium (III) is also nearly completely extracted at high concentration of sulfuric acid though the extraction is only slight in the low concentration region. Consequently, tin (IV) can be separated from indium (III) by selectively extracting the former in some low concentration range of sulfuric acid solution in which some amount of chloride ion is added in order to suppress the precipitate of tin hydroxide.

2. Experimental

2.1 Reagents

Cyanex 925 and TOPO were kindly donated by American Cyanamid Co. Ltd. and Hokko Chemical Co. Ltd., respectively, and were used as received without further purification. A reagent grade of toluene was used as the diluent. The aqueous solutions were prepared by dissolving a reagent grade of tin (IV) chloride (SnCl₄·H₂O) or indium (III) nitrate into various concentrations of sulfuric acid solution containing chloride ion added as ammonium chloride.

2.2 Procedure

30 cm³ of aqueous phase and 20 cm³ of organic phase were shaken overnight in a flask immersed in a water bath incubator maintained at 30 °C to attain equilibrium. Metal concentrations in the aqueous phase before and after
the extraction were determined by using a SEIKO model SAS 7500 atomic absorption spectrophotometer. Metal concentrations extracted into the organic phase were calculated by mass balance of those in the aqueous phase before and after the extraction.

3. Results and Discussion

3.1 Concentration dependencies of the reagent species on the distribution ratio

Figure 3 illustrates the effect of the activity of hydrogen ion which was calculated from sulfuric acid concentration determined by titration and the activity coefficient on the distribution ratio in the extraction from varying concentration of sulfuric acid solution containing 0.24 mol dm$^{-3}$ of chloride ion and about 6 mmol-dm$^{-3}$ of indium (III) with 50 mmol-dm$^{-3}$ TOPO and Cyanex 925, respectively, in toluene. In this figure, plots lie on a straight line with a slope of unity which suggests that a unit ion of hydrogen is co-extracted accompanied by the extraction of a unit ion of indium (III). This is against the conclusion of Hasegawa et al. who reported that the extraction of indium (III) is independent of hydrogen ion concentration in the extraction from 4 mol-dm$^{-3}$ (H, Na) Cl solution but is partly in accordance with that by Navratil et al. who concluded that the participation of hydrogen ion in the extraction reaction cannot be ruled out.

Figure 4 illustrates the effect of the concentration of chloride ion on the distribution ratio in the extraction from 4 mol-dm$^{-3}$ sulfuric acid solution containing varying concentration of chloride ion and about 6 mmol-dm$^{-3}$ of indium (III) with 80 mmol-dm$^{-3}$ TOPO and Cyanex 925, respectively, in toluene. In this figure, the plots appear to lie on a convex curve; i.e., they are lying on a straight line with a slope of two in the low concentration region while they deviate downward from a straight line and tend to approach a constant value in the high concentration region. This is considered to be attributable to the variation of composition of indium (III)-chloro complexes in the aqueous phase by changing of chloride ion concentration as will be described in detail later.

Figure 5 illustrates the effect of the reagent concentration on the distribution ratio in the extraction from 4 mol-dm$^{-3}$ sulfuric acid solution containing 0.24 mol-dm$^{-3}$ chloride ion and about 6 mmol-dm$^{-3}$ of indium (III) with varying concentration of TOPO and Cyanex 925, respectively, in toluene. In this figure, the plots lie on a straight line with a slope of two over the whole concentration range.
Table 2. Evaluated equilibrium constants for the extraction of indium (III) with Cyanex 925 and TOPO

<table>
<thead>
<tr>
<th>Reagent</th>
<th>((K_i/β_j))</th>
<th>((β_j/β_{2j}))</th>
<th>((β_j/β_{2j})^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyanex 925</td>
<td>1.15 x 10^3</td>
<td>5.5</td>
<td>36</td>
</tr>
<tr>
<td>TOPO</td>
<td>2.4 x 10^3</td>
<td>1.28</td>
<td>33</td>
</tr>
<tr>
<td>TOPO*</td>
<td>-</td>
<td>1.15</td>
<td>1.48</td>
</tr>
</tbody>
</table>

* Reference (5)

which suggests that two molecules of the reagents take part in the extraction reaction. The second order dependency for the reagent is in accordance with the extraction from hydrochloric acid solution with TOPO in hexane and benzene reported by Hasegawa et al. [9] and Navratil et al. [9] respectively.

3.2 Analysis of the extraction reaction of indium (III)

From the experimental results mentioned above, it appears that there are no significant differences in the concentration dependencies of the reactant species observed between TOPO and Cyanex 925. Consequently, it may be considered that indium (III) is extracted according to the same stoichiometric relation with both reagents.

Concerning the concentration dependency of chloride ion, the formation of chloro-complexes in the aqueous phase expressed by Eq. (1) should be taken into consideration.

\[
\text{In}^{3+} + i\text{Cl}^− = \text{InCl}^{i-3}β_j \text{[i = 1–4] (1)}
\]

The concentration of the \(i\)-th chloro-complex is described as

\[
[	ext{InCl}^{i-3}] = β_j [\text{Cl}^−] \cdot C_{In} / \left(1 + \sum_j β_j [\text{Cl}^−]^j\right) (2)
\]

where \(C_{In}\) denotes the total concentration of indium (III) in the aqueous phase. From the concentration dependencies of reactant species mentioned earlier, the extraction reaction is considered to be described by the same stoichiometric relation for both extractants as follows:

\[
\text{In}^{3+} + \text{H}^+ + 2\text{Reagent} + 4\text{Cl}^− = \text{H}^+ \text{InCl}_4^- \cdot 2\text{Reagent}; K_j (3)
\]

where the equilibrium relation gives

\[
K_j = [\text{H}^+ \cdot \text{InCl}_4^- \cdot 2\text{Reagent}] / [\text{In}^{3+}] [\text{H}^+] [\text{Reagent}] [\text{Cl}^-]^4 (4)
\]

Combination of Eqs. (2) and (4) gives the following equation for the distribution ratio of indium:

\[
D = K_j [\text{H}^+] [\text{Reagent}] [\text{Cl}^-]^2 / \left(1 + \sum_j β_j [\text{Cl}^-]^j\right) (5)
\]

The second order dependency on the distribution ratio with respect to chloride ion is expected from Eq. (5) in the low concentration region of chloride ion where the chlorocomplex, \(\text{InCl}_{2+}^−\), is preeminent as follows:

\[
D = (K_j / β_2) [\text{H}^+] [\text{Reagent}]^2 [\text{Cl}^-]^2 (6)
\]

On the other hand, the distribution ratio is expected to tend to approach a constant value independent of chloride ion as follows:

\[
D = (K_j / β_2) [\text{H}^+] [\text{Reagent}]^2 (7)
\]

These are in accordance with the concentration dependencies of the reactant species observed in the present work. On the assumption that the species, \(\text{In}^{3+}\) and \(\text{InCl}^{3+}\), can be ignored in the concentration region of chloride ion of the present experiment, the distribution ratio is approximately expressed as follows:

\[
D = K_j [\text{H}^+] [\text{Reagent}]^2 [\text{Cl}^-]^2 / \left(1 + \sum_j β_j [\text{Cl}^-]^j + \beta_2 \cdot [\text{Cl}^-]^2\right) (8)
\]

where \(K_j = K_e / β_2\).

Based on Eq. (8), the values of \(K_j, β_j / β_2\) and \(β_j / β_2\) were evaluated for TOPO and Cyanex 925 using the data shown in Fig. 4 as listed in Table 2, together with the values evaluated by Hasegawa et al. for comparison. In respect of \(K_j\), the value for Cyanex 925 is about half of that for TOPO, which may be attributable to the sterically hindered structure of alkyl radicals of this reagent for complexation with indium (III). In respect of \(β_j / β_2\), the orders of magnitude are roughly equal among the three values. The value for TOPO especially is in good agreement with that evaluated by Hasegawa et al. for TOPO. On the other hand although the \(β_j / β_2\) values evaluated for each reagent are in good agreement each other, they are as much as about 20 times that evaluated by Hasegawa et al. This might be attributable to the difference between the effects of perchlorate ion and sulfate or bisulfate ions on the activity of tetrachloro complex of indium (III). The solid curves in Fig. 4 are calculated results according to Eq. (8) using the values evaluated in the present work. The plots are in good agreement with the calculated curves in this figure.

Nomenclature

- \(C_j\): concentration of species \(j\) [mol-dm\(^{-3}\)]
- \(D\): distribution ratio of indium (III) [-]
- \(K_j\): equilibrium constant of indium (III) with extractant [dm\(^3\)-mol\(^{-1}\)]
- \(K_e\): apparent equilibrium constant of indium (III) with extractant [dm\(^3\)-mol\(^{-1}\)]
- \(β_i\): stability constant of \(i\)-th chloro complex of indium (III) [dm\(^3\)-mol\(^{-1}\)]
- \(\text{organic phase}\)

Literature Cited

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