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Selective Recovery of Indium from Acid Sulfate Media with Solvent Impregnated Resin of Bis(4-cyclohexylcyclohexyl)phosphoric Acid as an Extractant

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ABSTRACT
The selective recovery of In^{3+} from the mixture of In^{3+}, Ga^{3+}, and Zn^{2+} was investigated in acidic sulfate media, employing a solvent impregnated resin (SIR). Bis(4-cyclohexylcyclohexyl)phosophoric acid (D4DCHPA) in toluene was impregnated into synthetic adsorbent based on methacrylic ester copolymer. The SIR has high selectivity for In^{3+}, and the order of selectivity is $In^{3+} > Ga^{3+} > Zn^{2+}$. The adsorption progresses *via* Langmuir mechanism and the maximum adsorption amounts of In^{3+}, Ga^{3+}, and Zn^{2+} are found to be 0.22, 0.22, and 0.14 mmol/g, respectively. The effective adsorption-elution can be achieved by the column operation, and In^{3+} can be selectively recovered from ternary metal solution.

Keywords: indium, zinc refinery residue, adsorption, D4DCHPA, solvent impregnated resin (SIR)

INTRODUCTION

Indium is one of the important materials in ITO (indium tin oxide) for transparent electrodes in liquid crystal displays. Since there is no ore containing indium as a major component, indium is mainly recovered as by-products of zinc refinery residue. The development of an effective recovery process for indium is therefore desirable to secure the rare metal resources, because the zinc refinery residue contains large amounts of zinc, iron, and aluminum, while the contents of indium are quite low[1,2].

Solvent extraction has been widely used as processes for separation, purification, and recovery of rare metals, due to its simplicity of equipment and operation, and many papers related to the selective recovery of indium by the solvent extraction was reported. Among the extractants, various kind of organophosphorus compounds have been applied, since the compounds have high extractability and selectivity for indium[3-6]. In a previous study, acidic organophosphorus compounds with bulky alkyl chain were synthesized, and the extraction equilibria of In^{3+}, Ga^{3+}, and Zn^{2+} were investigated. Bis(4-cyclohexylcyclohexyl) phosphoric acid as shown in Figure 1 (abbreviated as D4DCHPA hereafter) has higher extractability and enough selectivity for In^{3+} against Ga^{3+} and Zn^{2+}, compared with a commercial extractant, bis(2-ethylhexyl) phosphoric acid (D2EHPA), because the bulky cyclohexyl groups of extractant contributes to greater extractability and separation ability among the metal ions[7].

The disadvantage of solvent extraction, such as requirement of large amount of organic solvent, is recently pointed out, since the organic solvent may then be lost into the aqueous phase, owing to its own solubility in aqueous solution. The combination of solvent extraction with adsorption and/or ion exchange has been therefore investigated, for the second generation of the extraction system. There are two ways to bridge the gap between the adsorption and solvent extraction; solvent impregnated resins[8-10] and microcapsules[11]. The solvent impregnated resin (abbreviated as SIR hereafter) is usually

prepared by just treating the polymer resin with the organic solvent containing extractant, and thus possesses an advantage of easy preparation. Liu *et al.* reported selective separation of In^{3+}, Ga^{3+}, and Zn^{2+} from dilute solution using SIR of D2EHPA. Their results show In^{3+} can be separated at low pH region, while Ga^{3+} and Zn^{2+} were co-adsorbed at high pH region[12]. Inoue *et al.* reported the recovery of indium from spent panel of liquid crystal display, demonstrating that indium can be effectively separated from concentrated hydrochloric acid solution co-exiting several metal ions using SIR of trialkylphosphine oxide[13].

In present work, SIR of D4DCHPA was prepared to investigate the adsorption behavior of In^{3+}, Ga^{3+}, and Zn^{2+} from acid sulfate media, for developing the environmentally friendly process of selective recovery of In^{3+}. The SIR was firstly applied to the conventional batchwise adsorption. The SIR was then applied to the column operation for the separation of In^{3+} from Ga^{3+} and Zn^{2+}, to elucidate the performance of indium recovery from zinc refinery residue.
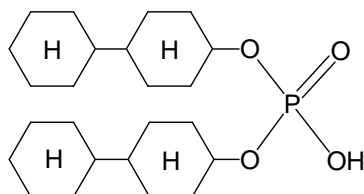

Figure 1 *Chemical structure of D4DCHPA.*

EXPERIMENTAL
Materials
All organic and inorganic reagents were supplied by Wako Pure Chemical Industries, as analytical-grade reagents. D4DCHPA was synthesized according to the procedure reported in the previous paper[14].
Impregnation procedure of D4DCHPA
A synthetic adsorbent, DIAION HP2MG is methacrylic ester copolymer and supplied by Nippon Rensui Co. Ltd. The specific surface area, pore volume, and pore radius of HP2MG are reported to be 500 m^2/g, 1.2 mL/g, and 200 Å, respectively, by the supplier. It was preliminary washed with methanol and was dried *in vacuo*. The washed resin of 3.5 g was immersed into 50 mL of toluene solution containing 0.1 mol/L of D4DCHPA for overnight. The solvent was evaporated completely and dried *in vacuo*. The impregnation amount of D4DCHPA was 0.90 mmol/g.

Leakage of the impregnated extractant into aqueous solution
The SIR of 50 mg was added to 10 mL of H_2SO_4 solutions. The mixture was shaken vigorously at 298 K for more than 12 h. The equilibrium pH was measured by a pH meter (Horiba F-23). The concentrations of phosphorus in the aqueous solutions were analyzed by an inductively coupled plasma atomic emission spectrometer (ICP-AES; Shimadzu ICPS-7000), to determine the leakage percentage of the extractant by material balance.
Batch adsorption
Aqueous solutions of metal ions were prepared by dissolving $In_2(SO_4)_3 \cdot nH_2O$, $ZnSO_4 \cdot 7H_2O$, $Ga(NO_3)_3 \cdot nH_2O$ in sulfuric acid solution for the single and ternary metal systems. The pH was adjusted by adding the appropriate amount of sulfuric acid solution to the HEPES [2-(4-(2-hydroxyethyl)-1-piperazinyl) ethane sulfonic acid] buffer aqueous solution. The SIR of 50 mg was added to 10 mL of aqueous feed solution. The mixture was shaken vigorously at 298 K for more than 12 h to attain equilibrium, since preliminary experiments indicated the extraction equilibria of all the metals achieved within 12 h. The equilibrium pH was measured by a pH meter. The concentrations of metal ions in the aqueous solutions were analyzed by ICP-AES, to determine the corresponding adsorption amounts, q_M, as follows.

$$q_M = \frac{([M]_{feed} - [M]) \cdot L}{w} \quad (1)$$

where $[M]_{feed}$ and $[M]$ are initial and equilibrium concentrations of each metal in the aqueous phase, L is volume of aqueous solution, and w is weight of adsorbent.
Column adsorption
The SIR was treated with sodium lauryl sulphate solution, prior to use for the column operation, for hydrophilizing the surface of SIR, because the SIR is difficult to be packed into column as it is, due to high hydrophobic surface. The treated SIR (wet volume = 5.0 mL) was packed into a column of 10 mm diameter, and was washed with deionized water. An aqueous feed solution containing In^{3+}, Ga^{3+}, and Zn^{2+} of pH = 2 was fed upward to the column at a flow rate of 0.4 mL/min (S.V. = 4.8), using a dual-plunger pump (FLOW, KP-11). After the break through of metal ions, deionized water was fed into the column to wash out the remained feed solution in the column. The loaded metal ions were then eluted with 3.0 mol/L HCl solution. The effluents were collected with a fraction collector

(EYELA, DC-1500). The pH values and metal concentration were measured by a pH meter and ICP-AES, respectively. Bed volume of the effluent is calculated by:

$$Bed\ Volume = \frac{v \cdot t}{V} \quad (2)$$

where v is flow rate of solution, t is supplying time of feed solution, and V is the wet volume of adsorbent.

RESULTS AND DISCUSSION
The leakage test of extractant from SIR
Figure 2 shows the effect of pH on the percentage leakage of extractant from SIR, which is defined as the ratio of the moles of phosphorus in the aqueous solution to those in SIR. The extractant was hardly leaked into aqueous solution, indicating that D4DCHPA possesses high affinity for HP2MG. The present SIR is therefore expected to be robust for iterative operation.
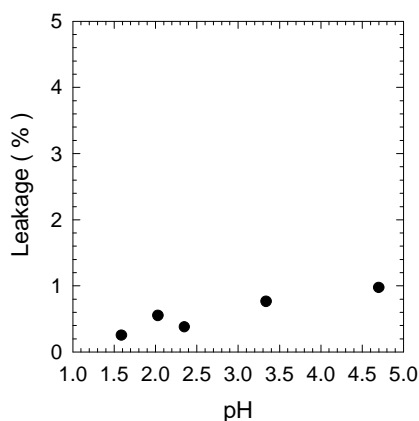

Figure 2 *The effect of pH on the percentage leakage of extractant from the SIR into aqueous solution.*

Batchwise adsorption of In³⁺, Ga³⁺, and Zn²⁺
The SIR was then applied to the batchwise adsorption. Figure 3 shows the effect of pH values on the adsorption amount of metal ions with the SIR in single metal systems. The adsorption amount of all metal ions increased with increasing pH, suggesting that the adsorption progresses *via* cation exchange mechanism. The present SIR possesses high adsorption ability for In³⁺, and the order of selectivity is In³⁺ > Ga³⁺ > Zn²⁺, in agreement with the solvent extraction system[7]. Figure 4 shows the adsorption isotherm of metal ions with the SIR at pH = 2.4 for In³⁺, pH = 3.1 for Ga³⁺, and pH = 4.7 for Zn²⁺, respectively. The
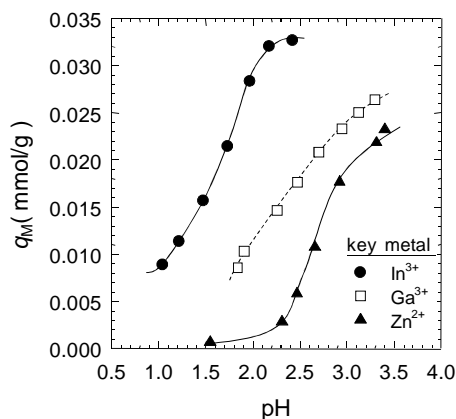

Figure 3 *The effect of pH on the adsorption amounts of In³⁺, Ga³⁺, and Zn²⁺ with the SIR in single metal systems. $[M]_{feed} = 0.17$ mmol/L.*

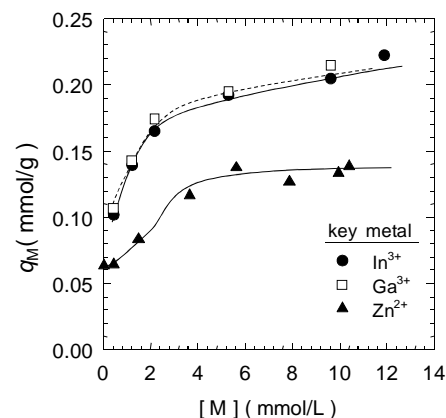**Figure 4** *Adsorption isotherm of In³⁺, Ga³⁺, and Zn²⁺. $pH_{In} = 2.4 \pm 0.01$, $pH_{Ga} = 3.1 \pm 0.09$, $pH_{Zn} = 4.7 \pm 0.11$.*

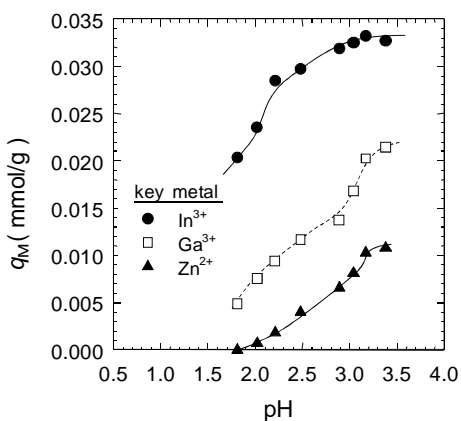**Figure 5** *The effect of pH on the adsorption amounts of In³⁺, Ga³⁺, and Zn²⁺ with the SIR in ternary metal systems. $[In^{3+}]_{feed} = [Ga^{3+}]_{feed} = [Zn^{2+}]_{feed} = 0.17$ mmol/L.*

adsorption of all metals with the SIR progresses with Langmuir type mechanism, and the maximum adsorption amounts of In^{3+}, Ga^{3+}, and Zn^{2+} were determined as 0.22, 0.22, and 0.14 mmol/g, respectively, while the impregnation amount of D4DCHPA is 0.90 mmol/g. The extraction equilibrium formulations are therefore changed in the cases of In^{3+} and Ga^{3+}, since the ratio of metal to D4DCHPA in the conventional extraction system was determined as 1 : 6 in the previous work[7]. This may be attributable to the appearance of new extracted species, which has been also reported in the microcapsule system containing extractant[15].

The adsorption behavior of the metals in ternary metal system was also investigated. Figure 5 shows the effect of pH on the adsorption amounts of the metal ions in ternary system. Since the adsorption of Ga^{3+} and Zn^{2+} was markedly suppressed by high selectivity for In^{3+}
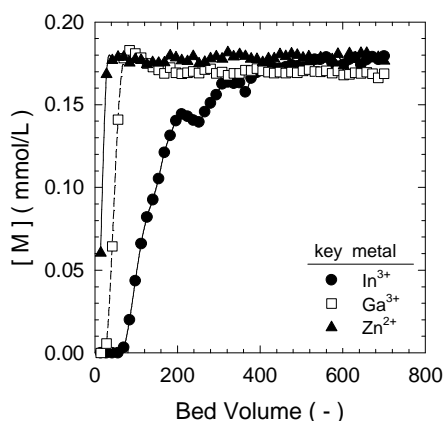

Figure 6 *Breakthrough profiles of In^{3+}, Ga^{3+}, and Zn^{2+}. pH = 2, $[In^{3+}]_{feed} = [Ga^{3+}]_{feed} = [Zn^{2+}]_{feed} = 0.17$ mmol/L.*

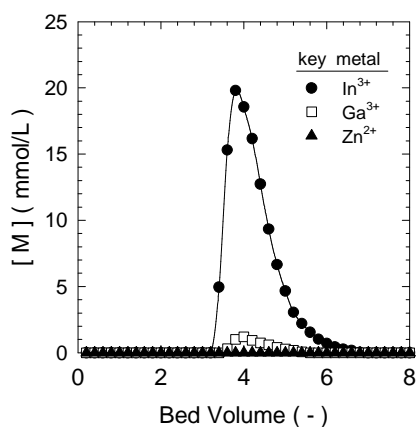**Figure 7** *Elution profiles of In^{3+}, Ga^{3+} and Zn^{2+}. [HCl] =3.0 mol/L.*

of the present SIR, the separation of In^{3+} from co-existing Ga^{3+} and Zn^{2+} is expected to be easily achieved by controlling of pH.

Column separation of In^{3+}

Based on the batchwise experiments, the column separation of In^{3+} from the ternary solution containing identical concentration of each metal was conducted. Figure 6 shows the breakthrough profiles of In^{3+}, Ga^{3+}, and Zn^+ at pH = 2 of the feed solution of 2. In^{3+} was selectively adsorbed as expected from the batchwise experiments, while Ga^{3+} and Zn^{2+} were scarcely adsorbed. Figure 7 shows the elution profiles of In^{3+}, Ga^{3+}, and Zn^{2+} using 3.0 mol/L HCl solution as a eluent. In^{3+} was quantitatively eluted with high purity of 92.5 % at bed volume of 3.8, while little Ga^{3+} and no Zn^{2+} were eluted. The SIR of D4DCHPA is therefore expected to possess high performance for the selective recovery of In^{3+} from the zinc refinery residue, because the concentration of Ga^{3+} is much lower than In^{3+} [2].

CONCLUSIONS

Selective recovery of In^{3+} from the acidic sulfate solution of In^{3+}, Ga^{3+}, and Zn^{2+} with SIR of D4DCHPA was investigated, with the following results. The adsorption of the metals with the SIR progresses with Langmuir type mechanism, and the selectivity of In^{3+} against Ga^{3+} and Zn^{2+} was elucidated. The adsorption of Ga^{3+} and Zn^{2+} was significantly suppressed in ternary metal systems. In column operation, In^{3+} can be selectively recovered with high purity from the acidic sulfate solution co-existing Ga^{3+} and Zn^{2+}. The present SIR has high potential as an adsorbent for recovery of In^{3+} from liquor of zinc refinery residue.

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