Removal and Recovery of Gallium and Indium Ions in Acidic Solution with Chelating Resin Containing Aminomethylphosphonic Acid Groups

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SYNOPSIS

Removal and recovery of gallium and indium ions in acidic solution with the macroreticular chelating resin containing aminomethylphosphonic acid groups was investigated. The resin (RMT-P) exhibited high affinity for gallium and indium ions in sulfuric acid solution. In the column method, gallium and indium ions in sulfuric acid solution (0.05 or 0.5 mol/dm^3) were favorably adsorbed on the RMT-P when the solution containing 27.6 mg/dm^3 of gallium ion or 51.4 mg/dm^3 of indium ion was passed through the RMT-P column at a space velocity of 15 h^{-1}. The gallium and indium ions adsorbed were eluted by allowing 1 mol/dm^3 sodium hydroxide or 4 mol/dm^3 hydrochloric acid to pass through the column. The proposed resin appears to be useful for the recovery of gallium and indium ions in sulfuric acid solution.

INTRODUCTION

In recent years, gallium and indium have attracted attention in electronic industry as material of Ga–As and In–As semiconductors.[1-3] Those metals have been recovered from the Bayer solution at the refining of aluminum, since there was not any ore which contained high concentrations of gallium and indium. For the increasing requirement of those metals in the future, a process is proposed to recover gallium and indium from acid-leaching solution of the residue at the smelting of zinc. We have prepared a macroreticular chelating resin with hard phosphonic acid groups.[4] In this article, the adsorption of hard gallium and indium ions in acidic solution is investigated with such a resin.

EXPERIMENTAL

Preparation of Macroreticular Chelating Resin

The macroreticular methyl methacrylate/divinylbenzene (5 vol %) copolymer beads were synthesized by suspension polymerization in the presence of 2,2,4-trimethylpentane (50 vol %/monomer) as diluent. The macroreticular copolymer beads (35–60 mesh, pore volume 0.47 cm^3/g, specific surface area 8.3 m^2/g, average pore radius 82 nm, 1 g) were aminated with triethylenetetramine (5 cm^3) at 175°C for 7 h. The aminated copolymer beads (1 g) were treated with phosphorous acid (2 g) and formalin (3 cm^3) in the presence of 20% hydrochloric acid (10 cm^3) as acid catalyst at 90°C for 5 h. The phosphor content of the resin obtained was 10.05%.

Measurement of Adsorption Capacity for Metal Ions

Batch Method

In a glass-stoppered Erlenmeyer flask were placed 0.125 g of the resin (H form) and 25 cm^3 of metal ion solution (1 mmol/dm^3) and the mixture was left at room temperature (about 25°C) for 48 h with occasional shaking. The concentration of the metal ion in the supernatant liquid was analyzed by spectrophotometric procedure based on oxine (8-hydroxyquinoline). The amount of metal ion adsorbed

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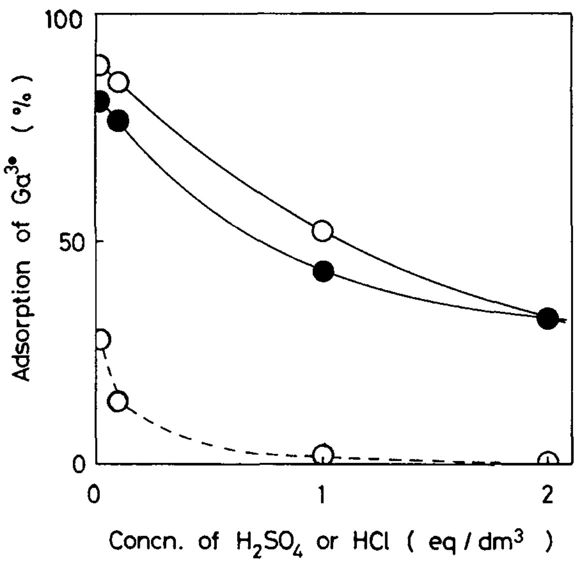

Figure 1 Effect of concentration of acid on the adsorption of Ga^{3+} on chelating resins: (○) sulfuric acid; (●) hydrochloric acid; (——) RMT-P; (---) Diaion CR 10.

on the resin was calculated by the change in the metal ion concentration. The metal ions adsorbed on the resin were then removed by shaking 0.125 g of the resin with 25 cm^3 of eluent at 30°C for 1 h. The amount of metal ion desorbed was quantified by the spectrophotometric analysis.

Column Method

A 2 cm^3 sample of the resin (H form) was packed in glass column (6 mmϕ × 200 mm). Resin height was about 70 mm. Metal ion solution was passed through the resin bed at a space velocity[†] of 15 h^{-1}. The metal content in the effluent was determined by means of the spectrophotometric procedure based on oxine. Metal ion solutions were prepared from gallium nitrate and indium chloride of reagent grade. Gallium and indium ions adsorbed on the column were eluted by passing 1 mol/dm^3 sodium hydroxide or 4 mol/dm^3 hydrochloric acid through the resin at a space velocity of 7.5 h^{-1}. After elution, the resin was washed with 50 bed volumes of deionized water and then the resin was converted to H form by passing 10 bed volumes of 0.05 or 0.5 mol/dm^3 sulfuric acid solution through the column. The adsorption–elution procedure was repeated several times.

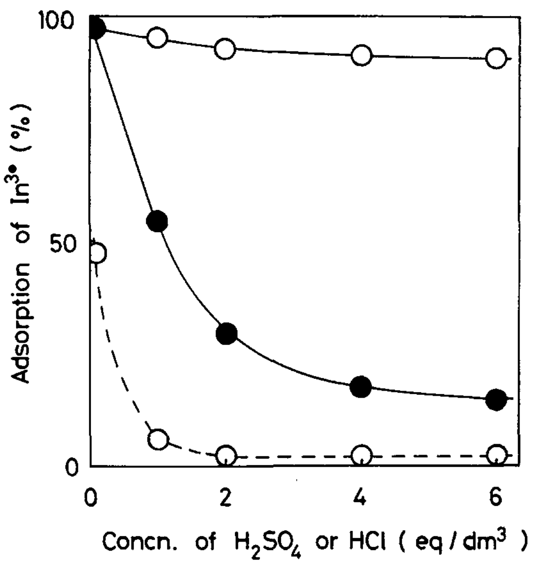

Figure 2 Effect of concentration of acid on the adsorption of In^{3+} on chelating resins: (○) sulfuric acid; (●) hydrochloric acid; (——) RMT-P; (---) Diaion CR 10.

RESULTS AND DISCUSSION

Adsorption Behavior of the Resin for Gallium and Indium Ions

The adsorption of the RMT-P for gallium and indium ions in acidic solution was investigated with hydrochloric acid or sulfuric acid solution. The results were shown in Figures 1 and 2. The value of

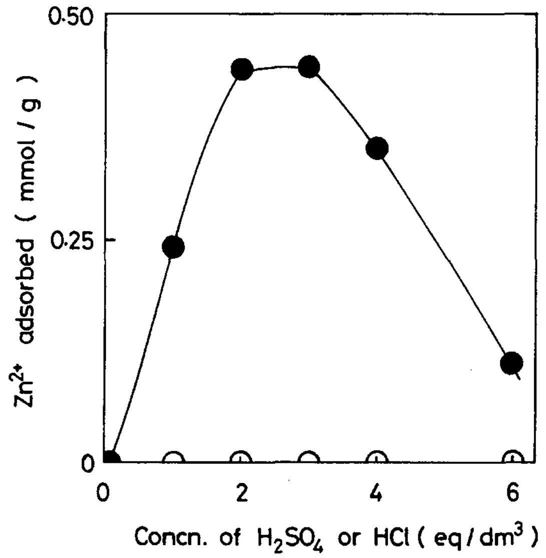

Figure 3 Effect of concentration of acid on the adsorption of Zn^{2+} on the RMT-P: (○) sulfuric acid; (●) hydrochloric acid.

[†] Volumes (cm^3) of loading solution per unit volume (cm^3) of resin hour.

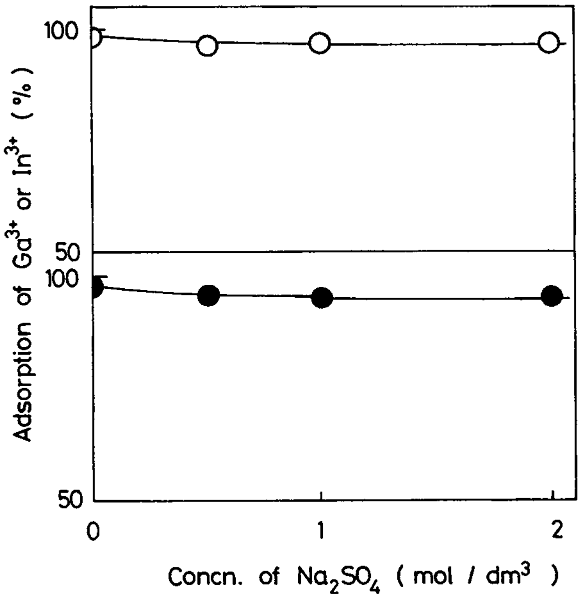

Figure 4 Effect of Na_2SO_4 on the adsorption of Ga^{3+} and In^{3+}: (○) Ga^{3+}; (●) In^{3+}.

commercial chelating resin containing iminodiacetic acid groups, Diaion CR 10 was also shown for comparison. The RMT-P exhibited high affinity for gallium and indium ions in comparison with the CR 10. From these results, it is clear that the RMT-P containing hard phosphonic acid groups is a chelating resin with a high affinity for hard gallium and indium ions in acidic solution. Indium ion capacity on the RMT-P in hydrochloric acid solution was remarkably different from that in sulfuric acid solution, indicating that the capacity rapidly decreased with an increase of the acid concentration. The decrease must be caused by the formation of chlorocomplex ion such as $InCl_4^-$. This fact suggests that the elution of indium ion adsorbed on the RMT-P shall be possible by using hydrochloric acid as eluent.

Figure 3 shows the adsorption capacities of the RMT-P for zinc ion in hydrochloric acid or sulfuric acid solution. The RMT-P did not show any affinity for zinc ion in sulfuric acid solution, whereas this resin showed an affinity that was probably due to the anionexchange adsorption of chlorocomplex ion for zinc ion in hydrochloric acid solution.

The results described above suggest that sulfuric acid is more suitable than hydrochloric acid for the extraction of gallium and indium from the residue at the smelting of zinc ore, in the case that the RMT-P is used to recover selectively gallium and indium ions in the acid-leaching solution.

Effect of Coexistent Ion on the Adsorption of Gallium and Indium Ions

As have been reported in a previous paper,[4] the RMT-P have not shown any affinity for Cu^{2+}, Pb^{2+}, Ca^{2+}, and Mg^{2+} at pH range less than 1. Hence, it seems that the RMT-P can selectively adsorb gallium and indium ions in the acidic solution which contains various coexistent ions such as Cu^{2+}, Pb^{2+}, Ca^{2+}, and Mg^{2+}.

The effect of coexistent salt on the adsorption of gallium and indium ions on the RMT-P was tested in the presence of sodium sulfate in concentration range of 0.5–2.0 mol/dm^3. The results were shown in Figure 4. From these results, it was proved that the adsorption ability of the RMT-P for gallium and indium ions were hardly affected by the presence of large amounts of sodium sulfate.

Table I Elution of Ga^{3+} Adsorbed on the Resin[a]

Eluent[b]	Ga^{3+} Added (mg)	Ga^{3+} Eluted (mg)	Recovery (%)
1 M[c] NaOH	6.92	5.90	85.3
2 M NaOH	6.91	5.93	85.8
3 M NaOH	6.92	5.89	85.1
4 M NaOH	6.90	5.80	84.1
6 M NaOH	6.91	5.86	84.8
4 M HCl	6.95	4.19	60.3
2 M H_2SO_4	7.19	4.42	61.5

[a] Adsorption conditions: 25 cm^3 of 0.01 mol/dm^3 $Ga(NO_3)_3$ acidic solution (0.05 mol/dm^3 H_2SO_4) per 0.125 g of resin, room temperature, 48 h.
[b] Elution conditions: 25 cm^3 of eluent, 30°C, 1 h.
[c] mol/dm^3.

Table II **Elution of In^{3+} Adsorbed on the Resin**[a]

Eluent[b]	In^{3+} Added (mg)	In^{3+} Eluted (mg)	Recovery (%)
1 M[c] HCl	13.03	6.64	51.0
2 M HCl	13.06	7.99	61.2
3 M HCl	13.12	8.66	66.0
4 M HCl	13.08	8.84	67.6
6 M HCl	13.17	8.70	66.1
2 M H_2SO_4	12.97	2.41	18.6
2 M NaOH	12.77	0	0

[a] Adsorption conditions: 25 cm^3 of 0.01 mol/dm^3 $InCl_3$ acidic solution (0.05 mol/dm^3 H_2SO_4) per 0.125 g of resin, room temperature, 48 h.

[b] Elution conditions: 25 cm^3 of eluent, 30°C, 1 h.

[c] mol/dm^3.

Elution of Gallium and Indium Ions Adsorbed on the Resin

In order to repeatedly use this resin for recovery of gallium and indium ions, it is necessary that gallium and indium ions adsorbed are eluted easily. The elution of gallium and indium ions adsorbed on the RMT-P was investigated by the batch method. Tables I and II show the recoveries of gallium and indium ions adsorbed on the RMT-P with various eluents. From those results, it proved that gallium and indium ions adsorbed on the resin could be effectively eluted by treating with 1–6 mol/dm^3 sodium hydroxide and 4 mol/dm^3 hydrochloric acid, respectively. Sodium hydroxide (2 mol/dm^3) was available for the elution of gallium ion, but it was not entirely available for that of indium ion. This difference may be due to the reason that gallium ion is capable of forming oxyacid ion such as GaO_3^{3-}. The remarkable difference in the behavior of gallium and indium ions adsorbed on the RMT-P in sodium hydroxide solution indicates that a separation of these ions shall be possible with the RMT-P.

The elution of gallium and indium ions adsorbed on the RMT-P was examined under practical column method. Figures 5 and 6 show the elution curves of gallium and indium ions, respectively. The elution of gallium ion adsorbed on the resin was almost

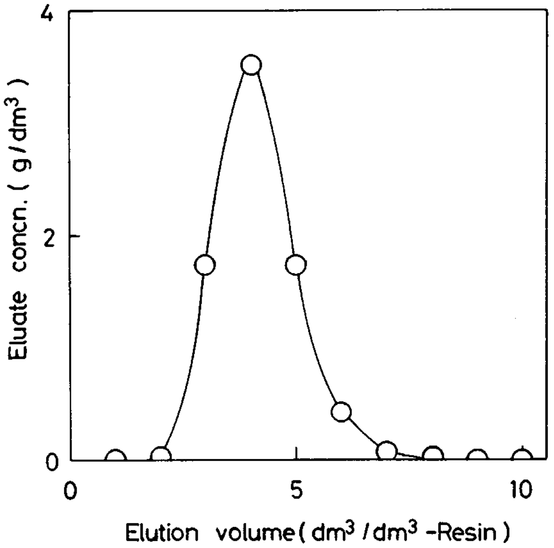

Figure 5 Elution curve of Ga^{3+}; eluent, 1 mol/dm^3 NaOH; flow rate, SV 7.5 h^{-1}.

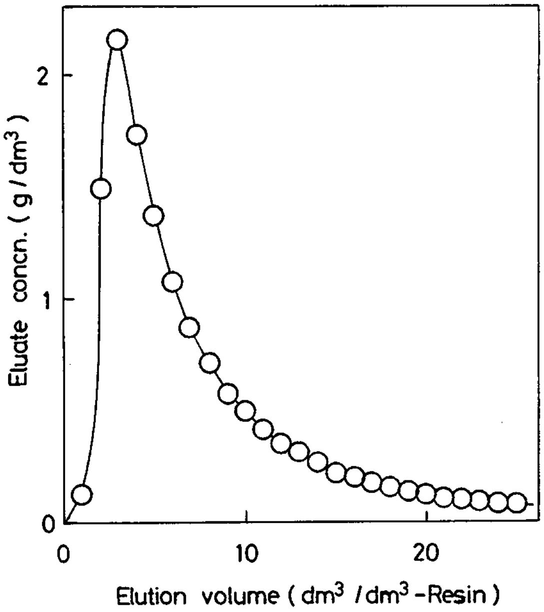

Figure 6 Elution curve of In^{3+}; eluent, 4 mol/dm^3 HCl; flow rate, SV 7.5 h^{-1}.

completed by passing 10 bed volumes of 1 mol/dm^3 sodium hydroxide solution through the column at a space velocity of 7.5 h^{-1}. The recovery ration of gallium ion was 99.2%. On the other hand, the elution of indium ion adsorbed on the resin was not completed by passing 4 mol/dm^3 hydrochloric acid solution through the column because of tailing phenomenon. The recovery ration of indium ion up to 10 bed volumes was 74.3%.

Recycle Test

Repeated adsorption and elution of gallium and indium ions in sulfuric acid solution was examined by the column method by using 1 mol/dm^3 sodium hydroxide solution and 4 mol/dm^3 hydrochloric acid solution as eluent, respectively. Figures 7 and 8 show the breakthrough curves of gallium and indium ions for several adsorption and elution cycles. A decrease of adsorption ability of the RMT-P for gallium ion was not observed on repeated cycling. On the other hand, a decrease of adsorption ability of the resin for indium ion was observed at the second cycle, since indium ion adsorbed on the resin was not eluted completely by passing 10 bed volumes of 4 mol/dm^3 hydrochloric acid solution through the column at a space velocity of 7.5 h^{-1}. However, the adsorption ability of the column for indium ion did not decrease at the subsequent cycles. From these results, it was proved that the RMT-P could be used repeatedly in order to recover gallium and indium ions in sulfuric acid solution.

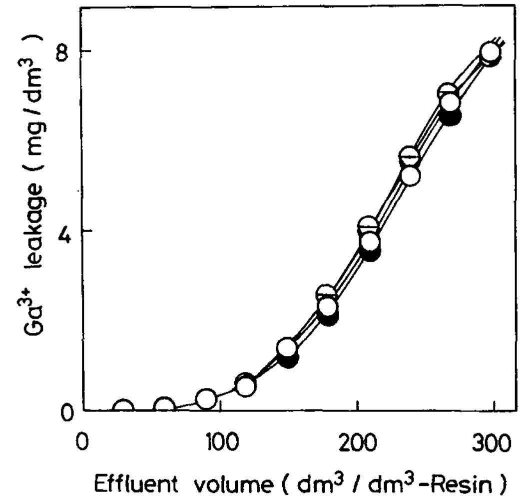

Figure 7 Recycle test; resin bed, RMT-P (H form) 2 cm^3 (6 mmϕ × 70 mm); loading solution, Ga^{3+} 26.6 mg/dm^3, H_2SO_4 0.05 mol/dm^3; flow rate, SV 15 h^{-1}; elution, 1 mol/dm^3 NaOH, 10 dm^3/dm^3 resin, SV 7.5 h^{-1}; cycle number: (○) 1; (●) 2; (⊖) 3; (◑) 4.

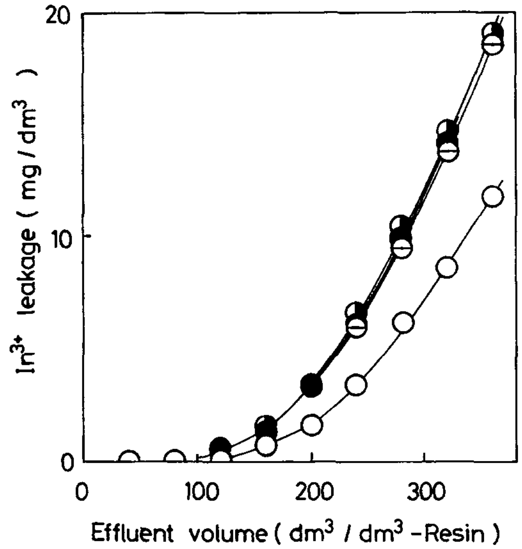

Figure 8 Recycle test; resin bed, RMT-P (H form) 2 cm^3 (6 mmϕ × 70 mm); loading solution, In^{3+} 43.4 mg/dm^3, H_2SO_4 0.5 mol/dm^3; flow rate, SV 15 h^{-1}; elution, 4 mol/dm^3 HCl, 10 dm^3/dm^3 resin, SV 7.5 h^{-1}; cycle number: (○) 1; (●) 2; (⊖) 3; (◑) 4.

From the results mentioned above, it is clear that the RMT-P containing aminomethylphosphonic acid groups is of practical use for the recovery of gallium and indium ions in sulfuric acid solution.

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