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The Separation and Concentration of Gallium(III) and/or Indium(III) Using Polystyrene Resins Functionalized with Complexane-Type Ligands

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Macroreticular styrene-divinylbenzene copolymers functionalized with iminodiacetic acid and diethylenetriamine-*N,N,N″,N″*-tetraacetic acid have been examined in order to apply them to the selective recovery of gallium(III) and/or indium(III) from acidic solutions. The equilibrium adsorption capacities, distribution coefficients, and metal-adsorption rates of the polymer resins for Group IIIb ions and other common metal ions have been studied. The selectivity sequence of the present resins are as follows: Fe(III)>In(III)>Ga(III)≈Cu(II)>Zn(II)>Al(III). The selective recovery of In(III) and/or Ga(III) from acidic solutions has been demonstrated using a column of the present resins.

In spite of the increasing requirement for gallium and indium in the electronic and semiconductor industries, the natural abundance of these metals is extremely small. Therefore, it is urgent to establish a process to recover gallium and indium selectively from low-grade ores or industrial scraps. For the recovery of less-common metals, there is a growing interest in the use of hydrometallurgical techniques which involve a leaching stage to dissolve the metals, followed by further stages to separate the metal ions of interest from other impurities. In 1976 a process based on solvent extraction was proposed to recover gallium from a sodium aluminate solution.[1] Chelating polymer resins containing a highly selective complexing group are one of the attractive candidates to apply to the metal separation procedure because of their operational flexibility and practical convenience.[2] Among the multidentate ligands, iminodiacetic acid (IDA) and ethylenediamine-*N,N,N′,N′*-tetraacetic acid (EDTA) are known to form extremely stable complexes with Ga(III)[3] and In(III)[4], hence, the chelating resins with these types of functional groups seem promising for the recovery of the metal ions from the leaching solutions.

We have prepared cross-linked polystyrene resins with complexane-type ligands structurally analogous to IDA or EDTA (Fig. 1). It was found that these chelating resins can adsorb Ga(III) and In(III) selectively from an acidic solution; the preliminary results have previously been reported briefly.[5] This paper presents full, detailed description dealing with the adsorption characteristics of the chelating resins and their use in the column separation of Ga(III) and/or In(III) from other common-metal ions.

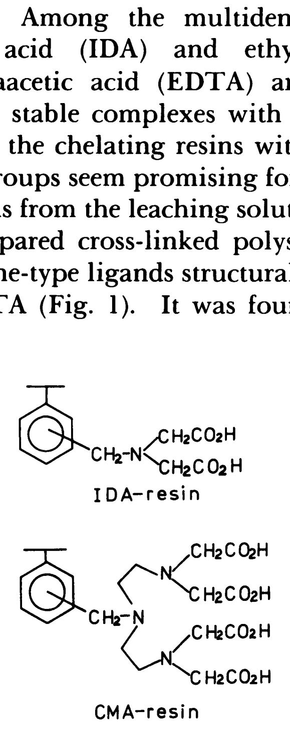

Fig. 1. Cross-linked polystyrene resins containing multidentate functional group.

Experimental

Materials. Reagent-grade $In(NO_3)_3 3H_2O$, $Ga(NO_3)_3$-$3H_2O$, and metallic gallium (99.99% grade) were used for the preparation of the stock solution. Metallic gallium was dissolved with *aqua regia,* and this solution was used for the column feed. Chloromethylated polystyrene beads (Cl, 17.1%, 60—100 mesh) were kindly donated by the Mitsubishi Chemical Co., Ltd. The resin matrix was macroreticular (MR) type styrene-10%-divinylbenzene copolymer with a surface area and mean pore diameter of 7.3 $m^2 g^{-1}$ and 720 Å, respectively.

IDA Resin. A suspension of chloromethylated polystyrene beads (45 g) and diethyl iminodiacetate[6] (85.6 g) in 450 cm^3 of dioxane was refluxed for 72 h with continuous stirring. The solid beads were then transfered to a Soxhlet extractor, extracted with ethanol, and then dried in vacuo. Yield, 76 g. To the dry beads (75 g) we then added a sodium hydroxide solution (20 g in 500 cm^3 of ethanol); the mixture was refluxed for 24 h under stirring. The beads were filtered off and washed successively with water, 2 M HCl ($M = mol\ dm^{-3}$), water, and then ethanol. Following a final washing with ether, the beads were dried at 50 °C in vacuo. Yield, 54.4 g. The nitrogen content of the IDA resin thus obtained was 3.7%, which corresponds to a ligand content of 2.6 mmol per gram resin.

CMA Resin. Polystyrene beads were functionalized with bis[2-(salicylideneamino)ethyl]amine[7] by the reaction of chloromethylated polystyrene and the Schiff base.[8] The resulting resin was hydrolyzed by treating it with 6 M HCl, yielding the diethylenetriamine-bound resin.[8] The carboxymethylation of the diethylenetriamine resin using the following procedures afforded the CMA resin.

To a solution of bromoacetic acid (213.6 g in 600 cm^3 of water) we added a sodium hydroxide solution (133 g in 600 cm^3 of water) drop by drop keeping the temperature of the reaction solution below 5 °C. To this solution we then added the diethylenetriamine resin (50 g), after which the mixture was gently shaken for 7 d at room temperature. The resin beads were collected, washed with water, and then treated with 2 M HCl. After having been washed successively with water, ethanol, and ether, the resin beads were dried in vacuo. Yield, 69.7 g. The nitrogen analysis of the resin (6.92%) indicates that the resin formally contains 1.65 mmol of the functional group per gram resin.

Determination of Adsorption Capacity. A batchwise technique was employed to determine the equilibrium adsorption capacity (amount of metal ion adsorbed on one gram of dry resin), with the metal ion always being in an excess over the ligand content. Typically, 500 mg of dry resin (H^+ form) was added to ca. 80 cm^3 of metal ion solution (0.02 M) of a certain pH, and the suspension was stirred at room temperature overnight. Then the mixture was transferred to a volumetric flask (100 cm^3) and finally diluted to the mark with water. The amount of the metal ion was determined with an atomic-absorption spectrometer. The capacity of the resins was calculated from the change in the metal concentration observed. The resin beads were placed in a glass column and washed thoroughly with water. The adsorbed metal ion was liberated from the resin beads by elution with 20 cm^3 of 2 M HCl, and the metal ion in the eluent was analyzed as has been described above. In most cases, a satisfactory material balance was observed between the metal ion liberated from the resin and that remaining in the solution.

Distribution Coefficients. The equilibrium distribution coefficients of the metal ions were determined by a batchwise procedure. A 500 mg portions of dry resin was immersed in 100 cm^3 of a metal ion solution (1 mM). The pH values from 3.0 to 5.0 were adjusted with an acetate buffer, while those below 3.0 were adjusted with perchloric acid. After shaking had continued for 5 d, the equilibrium pH and the amount of metal ion remain in the supernatant were determined. The results are expressed as the distribution coefficients, K_d=amount of metal adsorbed on one gram of the resin/amount of metal remaining in 1 cm^3 of the solution.

Adsorption Rate. The time-course of metal adsorption was monitored by measuring the change in the metal concentration in the solution. To a 1000 cm^3 portion of 1 mM metal solution (I=0.01, NaCl) at the given pH, we added 5 g of the chelating resin, which had been swollen with water in advance. While stirring, small portions of the metal solution were withdrawn at appropriate intervals and the change in the metal ion concentration was determined.

Column Separation of Metal Ion Mixture. A typical procedure is as follows: A 5-g sample of the CMA resin was swollen with water and poured onto a glass column (ϕ 1.2×10.2 cm). The metal ion solution containing Ga(III) (2.5 mM) and Al(III) (120 mM) was continuously passed through the column at a constant rate of 1.5 cm^3 min^{-1}. The effluent was fractionated into 17 cm^3 portions, and the amount of the metal ion was determined. The Ga(III) in the feed solution was adsorbed quantitatively on the column up to 1600 cm^3, while Al(III) was leaked out of the column. The adsorbed Ga(III) was liberated from the column by elution with 2 M HCl. The resin was regenerated by this procedure and can be used in the successive column operations. In a similar manner, Ga(III) and/or In(III) was selectively adsorbed from the solution containing excess amounts of Al(III), Ca(II), and Zn(II).

For the actual leaching solution, which often contains Fe(III) and Cu(II), H_2S was bubbled in at pH 1.0 and the precipitate was removed prior to column operation.

Measurements. The metal-ion concentration was determined with a Shimadzu atomic absorption/flame photometer, Model AA-610S.

Results and Discussion

Chelating Resins. The IDA resin was prepared by the treatment of the chloromethylated polystyrene with diethyl iminodiacetate, followed by the hydrolysis of the ester with a sodium hydroxide solution. The CMA resin was obtained by the *N*-carboxymethylation of the diethylenetriamine-bound resin, in which the amine is linked to polystyrene uniquely through the secondary nitrogen.[8] The IDA resin contains tridentate iminodiacetic acid, whereas the functional group of the CMA resin formally involves two sets of IDA groups, by analogy with EDTA. The IDA and CMA resins contain approximately 2.6 and 1.7 mmol, respectively of the functional group per 1

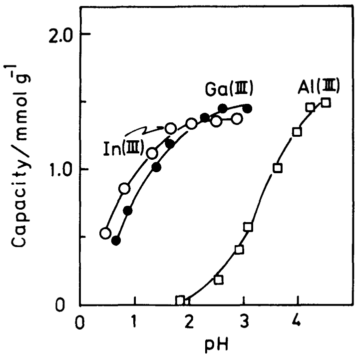

Fig. 2. Equilibrium adsorption capacity of the CMA resin for Al(III) (□), Ga(III) (●), and In(III) (○) as a function of pH.

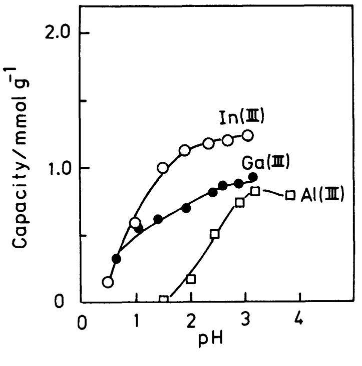

Fig. 3. Equilibrium adsorption capacity of the IDA resin for Al(III) (□), Ga(III) (●), and In(III) (○) as a function of pH.

Table 1. Maximum Adsorption Capacity of the Resins

Metal ion	Adsorption capacity/mmol metal g^{-1} (pH)	
	IDA resin	CMA resin
Al(III)	0.8 (4.0)	1.5 (4.2)
Ga(III)	0.9 (2.8)	1.5 (2.0)
In (III)	1.2 (2.0)	1.4 (1.8)
Fe(III)	0.7 (2.0)	1.5 (1.9)
Cu(II)	2.7 (4.0)	2.4 (4.0)
Zn(II)	2.3 (4.5)	2.2 (5.0)

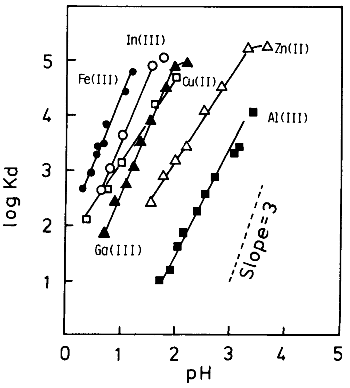

Fig. 4. Log K_d of the CMA resin for some metal ions as a function of pH.
Fe(III) (●), In(III) (○), Ga(III) (▲), Cu(II) (□), Zn(II) (△), Al(III) (■).

Table 2. Adsorption Rate of the Resins for Al(III), Ga(III), and In(III) ($t_{1/2}$, min)[a)]

Metal ion	pH	IDA Resin	CMA Resin
Al(III)	4.2	5	7
Ga(III)	2.0	30	25
In(III)	2.0	10	8

a) The time required to quench a half of the metal ion adsorbed at equilibrium. Metal ion concentration: 1 mM ($1000\,cm^3$), I=0.01 (NaCl) Resin; 5 g.

gram of the resin.

Equilibrium Adsorption Capacity. The present resins readily adsorb various kinds of metal ions from an acidic solution. The profiles of the adsorption capacities as a function of the pH for Al(III), Ga(III), and In(III) are given in Figs 2 and 3. The maximum adsorption capacities, including other common metal ions, are listed in Table 1, along with the equilibrium pH. The capacities of the CMA resin for most of the trivalent metal ions are around $1.5\,mmol\,g^{-1}$ resin; this value is comparable to the estimated ligand content, while those for the IDA resin are much lower than its ligand content. These results can be attributed to the difference in the dentate number of the functional groups. Each functional group in the CMA resin is expected to form 1:1 octahedral complexes in a fashion similar to those of EDTA complexes, whereas two sets of the IDA units are required for the IDA resin to form stable octahedral complexes. In contrast to homogeneous systems, such an opportunity must be considerably restricted when the IDA groups are fixed on a rigid polymer. For bivalent ions, such as Cu(II) and Zn(II), on the other hand, the adsorption capacities of the IDA resin are nearly equal to the ligand content, presumably because each IDA unit can form 1:1 complexes with these metal ions.

Distribution Coefficients. The distribution coefficients of the CMA resin for In(III), Ga(III), Fe(III), Cu(II), and Zn(II) were examined as a function of the pH; the results are given in Fig. 4. The slopes in the linear plots are approximately 3.0 for the adsorption of trivalent ions, whereas for Cu(II) and Zn(II) the slopes are close to 2.0. These results indicate that the adsorption of trivalent metal ions is accompanied by the release of three protons, while for bivalent ions two protons are liberated from the CMA resin. These observations are consistent with the expectation that each functional group in the CMA resin forms a 1:1 complex with trivalent metal ions.

Although the log K_d vs. pH profiles of the CMA and the IDA resins resemble each other, those of the CMA resin appear in a relatively lower pH region than those of the IDA resin, irrespective of the metal ions examined. This demonstrates that the CMA resin can form much more stable complexes than the IDA resin due to the chelating effect of the functional group.

The selectivity sequence of the CMA resin is; Fe(III)>In(III)>Ga(III)≃Cu(II)>Zn(III)>Al(III), which coincides with the order of the formation constants of the EDTA complexes.[9)] The apparent selectivity suggests the possibility of the column separation of Ga(III) and In(III) from the solution containing Zn(II) and Al(III). The K_d profile also suggests that Fe(III) and Cu(II) would greatly interfere with the adsorption of Ga(III) and In(III).

Adsorption Rate. Although the equilibrium capacity and the K_d values are of fundamental importance in characterizing the chelating resin, the rate of adsorption is extremely important from a practical point of view. The time-course of the adsorption of Al(III), Ga(III), and In(III) was examined at their optimal pH region by monitoring the metal ion concentration in the batch systems. The time required to adsorb a half of the metal ion adsorbed at the equilibrium ($t_{1/2}$) is listed in Table 2. The adsorption rates for these metal ions are, in any case, sufficiently rapid to allow a continuous column

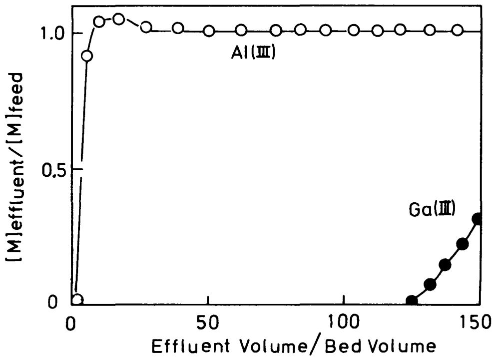

Fig. 5. Column breakthrough profile for the separation of Ga(III) and Al(III). Bed resin: CMA resin (5 g, 13 cm^3). pH: 1.8. $[M]_{feed}$: Al(III) (120 mM), Ga (III) (2.5 mM).

operation. The rate sequence is; Al(III)$\gtrsim$In(III)$>$Ga(III) under the present experimental conditions. The rate of adsorption has been claimed to be determined by the diffusion process inside the matrix in most of the ion-exchange systems.[10] On the basis of the electrophoresis experiments for the CMA resin, it was found that the resin beads are negatively charged at pH values higher than 2.0, where the carboxyl protons in the functional group may begin to dissociate.[11] The local charge density must be enriched inside the polymer beads with the sequential dissociation of protons; hence, the migration of positivily charged species into the polymer must be facilitated. The higher adsorption rate observed for Al(III) at pH 4.0 can be interpreted by this hypothesis. An opposed trend has been observed when the oxometalate anion (MoO_4^{2-}) was fed to the CMA resin and has been attributed to the charge repulsion between the resin and the incoming anion.[2e]

The observed rate sequence is almost independent of the nature of the anions present in the solution. Hence, provided that the chemical forms of Ga(III) and In(III) are not much different from each other under the given experimental conditions, the apparent difference in adsorption rate between them cannot be explained simply by the charge interaction mechanism. Although we have no clear explanation for the much slower rate for Ga(III) as compared to In(III), it should be noted that the rate sequence coincides with the order of lability of the metal ions.[12]

Column Separation. The apparent selectivity of the CMA resin suggests the possibility of the column separation of Ga(III) and In(III) from the solution of Al(III) or Zn(II). When a model solution (pH, 1.8) containing 2.5 mM of Ga(III) and 120 mM of Al(III) was passed through the column of the CMA resin, Ga(III) was quantitatively adsorbed on the resin, while Al(III) was found in the eluate, as is shown in Fig. 5. The amount of Ga(III) adsorbed on one gram of the resin at the breakthrough point (breakthrough capacity) was 0.95 mmol g^{-1}, approximately 65% of the equilibrium capacity. In a similar column operation using 1.7 mM of In(III) and 110 mM of Al(III), the breakthrough capacity for In(III) was found to be 0.8 mmol g^{-1}. The adsorbed Ga(III) or In(III) was liberated from the resin in a concentrated form on elution with 2 M HCl. Although a similar quantitative separation was achieved by using the IDA resin, the breakthrough capacity was much lower than in the case of the CMA resin, as is to be expected from the difference in their equilibrium capacities.

Among the metal ions commonly encountered in an acid-leaching solution of natural ores and industrial scraps, Fe(III) and Cu(II) compete most strongly in the adsorption of Ga(III) and In(III), as is to be expected from the K_d profiles. Therefore, it is preferable to remove these ions prior to the column operation. Interference from Cu(II) and Fe(III) can be considerably avoided by the treatment of the leaching solution with H_2S gas. By this procedure, Cu(II) can be eliminated from the solution as precipitate of CuS; at the same time, Fe(III) can be reduced to Fe(II), which has a much lower affinity for the present chelating resins than do In(III) and Ga(III).

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