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SELECTIVE ADSORPTION OF Ga(III) AND In(III) USING POLYSTYRENE RESINS WITH FUNCTIONAL GROUP HAVING BIS(CARBOXYMETHYL)AMINO MOIETY

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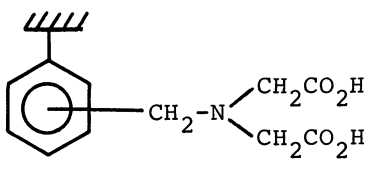
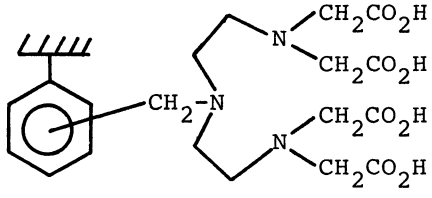
Adsorption characteristics of polystyrene resins containing bis(carboxymethyl)amino moiety for group IIIb ions have been studied. The selectivity order toward the present chelating resins is In(III) $\rangle$ Ga(III) $\rangle\rangle$ Al(III). Selective recovery of Ga(III) and/or In(III) from the acidic solution of Al(III) has been demonstrated by column operation using the present chelating resins.

Due to an increasing demand in the semiconductor manufacture, an efficient process is required to extract gallium and indium from low grade ores or industrial scraps. In 1976,a process based on solvent extraction has been proposed to recover gallium from sodium aluminate solution.[1] Recently solid-liquid system have attracted much attentions as a renewed hydrometallurgical process owing to the mechanical convenience over liquid-liquid systems.[2] We are searching for highly selective chelating resins which can be applicable to the recovery of gallium and indium. Amine-N-acetic acid such as ethylenediamine-*N,N,N',N'*-tetraacetic acid (EDTA) are known to form extremely stable complexes with Ga(III)[3] and In(III)[4] and hence the chelating resins having these types of ligands must be promising for the recovery of the ions from the acid-leaching solution. In this communication we describe the adsorption characteristics of the chelating resins containing bis(carboxymethyl)amino moiety for Al(III), Ga(III), and In(III) and the application for the selective recovery of Ga(III) and In(III).



IDA resin



CMA resin

The IDA resin was prepared by treatment the chloromethylated polystyrene[5] with diethyl iminodiacetate followed by hydrolysis of the ester. The CMA resin was obtained by carboxymethylation of *dien*-resin[6] in which diethylenetriamine (*dien*) is linked to polystyrene resin uniquely through the imino nitrogen. The polymer matrix used for the preparation of the *dien*-resin and the CMA resin was the same as that of the IDA resin. The functional group of the CMA resin consists of two sets of bis(carboxymethyl)amino moieties. Nitrogen analyses indicated that the IDA and the CMA resins formally contain 2.7 and 1.6 mmol of the functional group per gram resin, respectively.

Table 1. Maximum adsorption capacity of the resins / mmol metal g^{-1} resin (pH)

Metal ion \ Resin	IDA resin	CMA resin
Al(III)	0.7 (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)

Conditions: amount of resins; 500 mg in 100 cm^3, concentration of metal ions; 20 mM, treating time; 24 h (at room temperature).

Present resins readily adsorb Al(III), Ga(III), and In(III) from acidic solution while they showed little or no affinity for these ions at pH above 10. The equilibrium adsorption capacities for the metal ions were determined by batch-wise procedure under various pH with metal ion being excess over the resin capacity. The maximum adsorption capacities of the CMA resin for Al(III), Ga(III), and In(III) are comparable to the content of functional group (Table 1). On the contrary, the adsorption capacities of the IDA resin are much lower than the ligand content. It is suggested that each of the functional group in the CMA resin effectively forms 1 : 1 complex with these metal ions whereas two sets of the functional groups are required for the IDA resin to form octahedral complexes. However such an opportunity must be restricted when the ligands are immobilized on rigid polymer.

Figure 1 shows the log Kd vs. pH correlation of the CMA resin, where Kd is the distribution coefficient defined as : Kd = amount of metal ion adsorbed on one gram of resin / amount of metal ion remaining in 1 cm^3 of the solution. The slopes in the linear plots are approximately 3.0 irrespective of the metal ions indicating

that adsorption of the ions is accompanied by the release of three protons.[7] This result agrees with the expectation that each functional group in the CMA resin forms 1 : 1 complex with these metal ions.

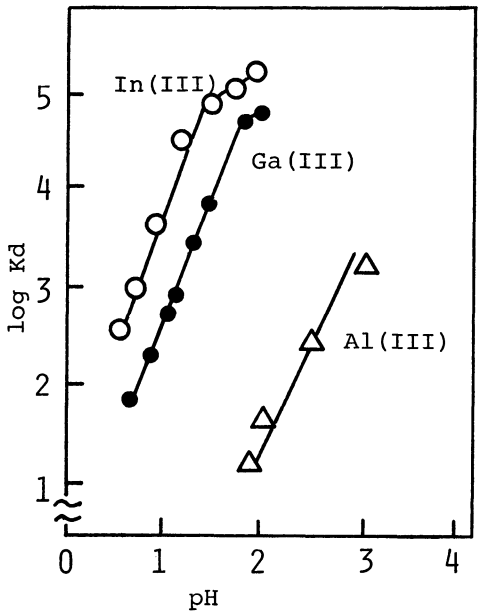


Fig. 1. Distribution coefficients of CMA resin for Al(III), Ga(III), and In(III).

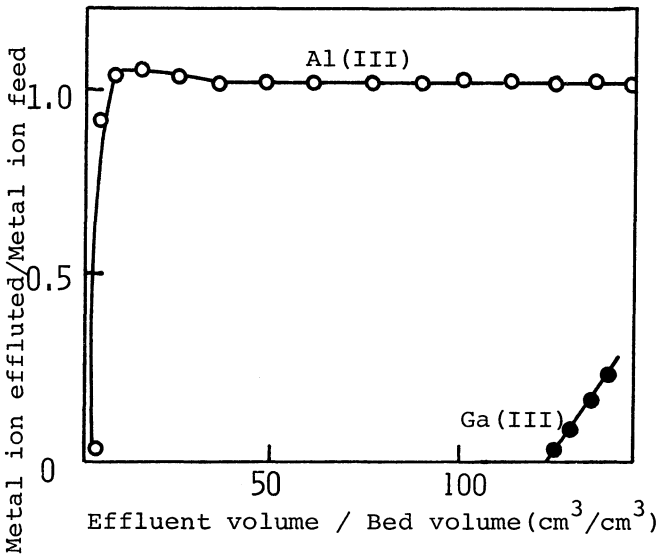


Fig. 2. Breakthrough curves for column separation of Ga(III) and Al(III) by using CMA resin.

Figure 1 clearly implies that the order of affinity for the CMA resin is In(III) $\rangle$ Ga(III) $\gg$ Al(III), which is in good accordance with the order of formation constants of EDTA complexes. The apparent selectivity suggests the possibility of column separation of Ga(III) and In(III) from the solution of aluminum.

For example, an aqueous solution (pH 1.8) containing Al(III) (120 mM, M=mol dm^{-3}) and Ga(III) (2.5 mM) was continuously passed through the column of the CMA resin (5 g, ϕ 1.2 x 10.2 cm) at a constant rate of 1.5 cm^3 min^{-1}, Ga(III) was quantitatively adsorbed on the resin while Al(III) was found in the eluate as given in Fig. 2. The amount of Ga(III) adsorbed on one gram of the resin at the breakthrough point (breakthrough capacity) was 0.95 mmol g^{-1} which was approximately 65% of the equilibrium capacity. When the mixture of In(III) (2.5 mM) and Al(III) (120 mM) was supplied to the similar column, In(III) was selectively adsorbed on the CMA resin as expected. The adsorbed Ga(III) and In(III) was liberated from the resin in concentrated form, i.e., hundreds-fold over the feed solution on elution with 2M HCl. The resin was regenerated by this procedure and

can be used in the successive operations. Although a similar quantitative separation was achieved by using the IDA resin, the breakthrough capacity was much lower than the CMA resin. The adsorption capacity of the present resins were almost reproducible over several adsorption-regeneration cycles.

Among the metal ions commonly encountered in the acid-leaching solution of natural ores and industrial scraps, Fe(III) and Cu(II) compete most strongly to the adsorption of Ga(III) and In(III) since the pH profiles of distribution coefficients are closely resemble to each other. Whereas other metal ions including alkaline and alkaline-earth metal ions, Al(III), Fe(II), Ni(II), Co(II), and Zn(II) do not interfere markedly with the adsorption of Ga(III) and In(III) at pH lower than 2.0. Interference from Cu(II) and Fe(III) can be avoided by treatment the leaching solution with H_2S bubbling prior to column operation, i.e., Cu(II) can be removed from the solution as precipitates of CuS and at the same time Fe(III) is reduced to Fe(II).

References

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