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TECHNICAL NOTE

Complexing Properties of Diphonix, a New Chelating Resin with Diphosphonate Ligands, Toward Ga(III) and In(III)

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ABSTRACT

The complexing properties of Diphonix, a new chelating ion-exchange resin, toward indium and gallium cations was investigated. Variables included bead size, contact time, solution pH, and the presence of competing cations. The resin, which contains diphosphonic acid ligands, displayed rapid rates of complexation and high selectivity under acidic conditions. Metal uptake from 1 M sulfuric acid solution under continuous flow conditions was 0.47 mmol/g (33.0 mg/g) for gallium and 0.76 mmol/g (87.8 mg/g) for indium. The resin may be regenerated by elution with 1-hydroxyethane-1,1-diphosphonic acid or hydrochloric acid.

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INTRODUCTION

The recovery of indium and gallium has received much attention due to utilization of these metals in the electronics industry. Since gallium and indium ores are not prevalent, recovery of these metals from Bayer solutions and acid-leach solutions from the smelting of zinc has been studied. Sulfuric acid has been used to remove gallium from Apex ore (1). In addition to solvent extraction (2, 3) with such complexing agents as 7-substituted hydroxyquinoline and di(2-ethylhexyl) dithiophosphoric acid, numerous papers have been devoted to the removal of Ga(III) and In(III) using chelating resins (4–9). These resins include amidoxime-containing polymers (4), Duolite ES-346 (5), alkylphenol-amineformaldehyde on alumina (6), and silica impregnated with high molecular weight carboxylic acids (7). Recently, the removal of Ga(III) and In(III) from sulfuric acid solutions with an aminomethylphosphonic acid resin was presented (8, 9).

We have introduced a new chelating resin which is stable in highly acidic solutions due to the absence of hydrolyzable bonds. This resin, named Diphonix, contains diphosphonic acid ligands (10). Its complexing properties toward gallium and indium form the subject of this report.

EXPERIMENTAL

Materials

Diphonix is prepared by the suspension polymerization of tetraethyl vinylidene diphosphonate with comonomers including styrene and divinylbenzene followed by chlorosulfonation (10). Before all contact studies, the resin is wet-sieved, conditioned, and pre-equilibrated with the appropriate sulfuric acid solution. The capacity of Diphonix is 1.71 mmol of phosphorus per gram of dry resin, its acid capacity is 6.43 mmol/g, and its moisture content is 71.3%. Stock solutions of metal salts (Aldrich) are prepared from indium nitrate (99.9%) and gallium chloride (99.99%). Other chemicals are analytical grade.

Batch Solution Method

Enough resin to give 0.1 mmol phosphorus is placed with 10 mL 0.001 M metal salt solution in a 20-mL vial and shaken for a given length of time. The solution is then filtered and its metal ion concentration determined by atomic emission at 403.3 nm for gallium and 451.1 nm for indium (Perkin-Elmer Atomic Absorption Spectrophotometer Model 3100). Solutions of 0.001 M In(III) in 1 M H_2SO_4 were also formulated with 0.001 M Zn(II), 0.001 M Cu(II), or 0.1 M Na(I) in order to determine the influence of these cations on In(III) sorption.

Continuous Column Method

Enough resin to give a bed volume of 11.5 mL (equivalent to 2 g dry weight) is placed in a fritted glass column (1 cm diameter, 30 cm length) and eluted with 0.001 M metal salt solutions in 1 M sulfuric acid at an hourly rate of 15 bed volumes. The effluent concentration was monitored by atomic emission. Gallium and indium ions complexed by the resin were eluted with 4 M HCl, 1 M NaOH, or 0.2 M 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) at an hourly rate of 8 bed volumes.

RESULTS AND DISCUSSION

The complexing properties of Diphonix toward In(III) and Ga(III) were investigated using 1.0 mM solutions of each metal in sulfuric acid of various concentrations. In(III) sorption as a function of bead diameter (Fig. 1) shows that particle size is not a significant variable on the sorption kinetics except in the most concentrated acid solution. The rate of com-

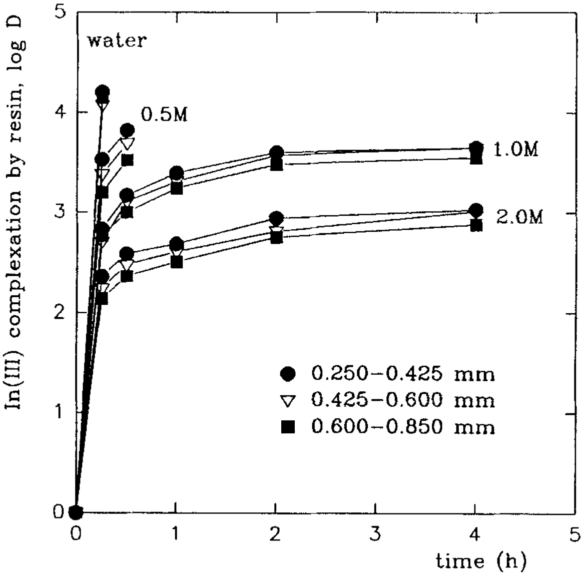

FIG. 1 Effect of sulfuric acid concentration [2.0, 1.0, 0.5, and 0.0 M (i.e., water)], contact time, and resin particle size on In(III) complexation.

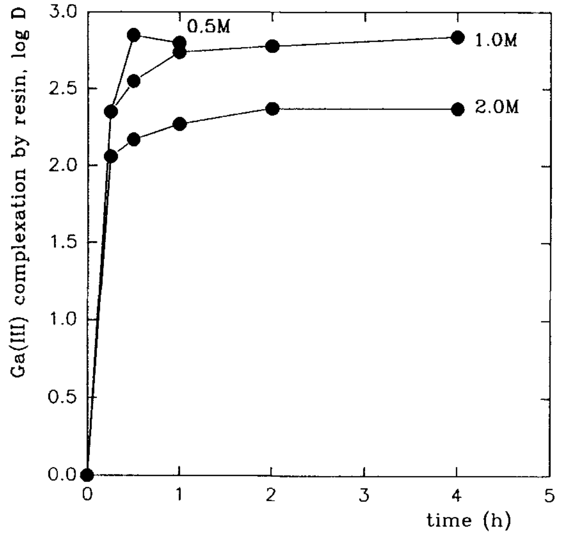

FIG. 2 Effect of sulfuric acid concentration (2.0, 1.0, 0.5, and 0.005 M) and contact time on Ga(III) complexation with 250–425 μm beads.

plexation is rapid even from concentrated acid solutions: approximately 90% of the total uptake occurs during the first 15 to 30 minutes of contact.

Ga(III) complexation by 250 to 425 μm Diphonix beads is found to be more strongly dependent on solution pH than indium (Fig. 2). This difference in resin behavior can be explained by the hardness of the In(III) cation which makes it less sensitive to changes in solution acidity (11).

Three additional experiments confirmed the resin's efficiency and selectivity in complexing a targeted ion from a multicomponent solution. First, the sorption of In(III) was investigated from a 1 M sulfuric acid solution which also contained 0.1 M sodium sulfate. After a 2-hour contact time, the resin complexed 95.8% In(III)—the same amount as in the absence of sodium ions. In a second experiment, a solution of 1 mM Zn(II)/1 mM In(III) in 1 M sulfuric acid was contacted with Diphonix. Complexation of 96.3% of the In(III) proved that the resin is highly selective under acidic conditions. The same result was found from a solution of 1 mM Cu(II)/1 mM In(III). As expected, the resin did not complex Zn(II) or Cu(II) from separate solutions of 1 mM Zn(II) and Cu(II) in 1 M sulfuric acid.

Results of column experiments are shown in Fig. 3. The metal ion concentration in the effluent is very low at the outset and, after the breakpoint, rapidly reaches 1 mM, indicating a rapid rate of complexation. The level

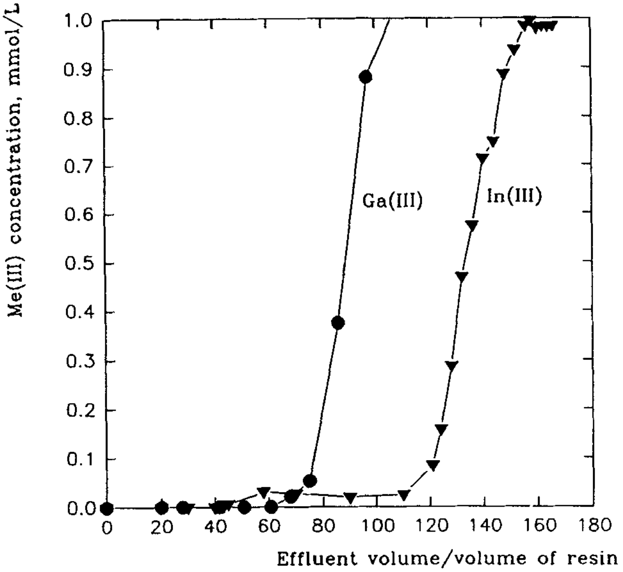

FIG. 3 Loading curves for gallium and indium.

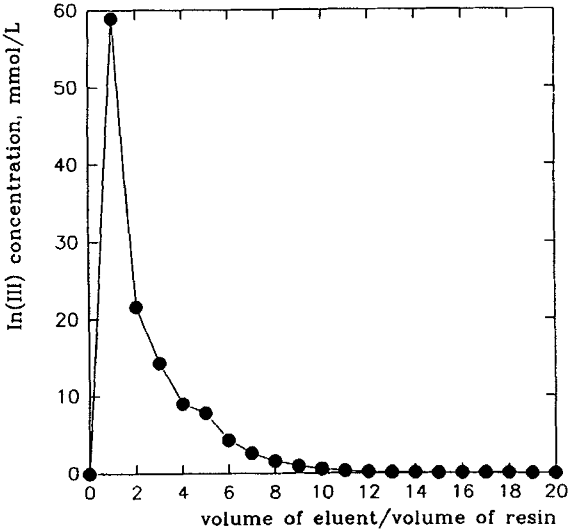

FIG. 4 Recovery of indium from Diphonix with 4 M HCl.

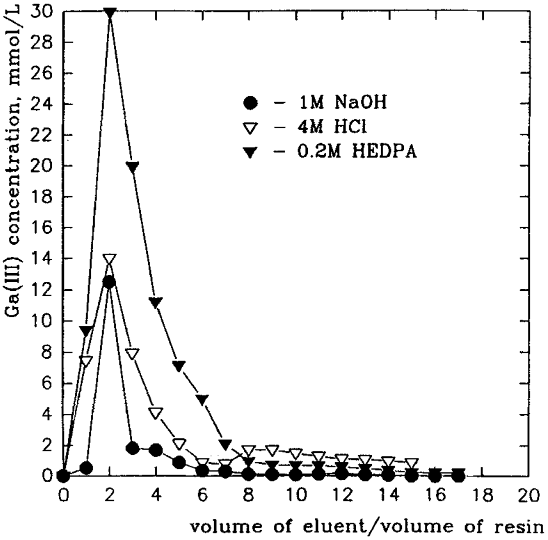

FIG. 5 Recovery of gallium from Diphonix.

of metal uptake is calculated to be 0.47 mmol/g (33.0 mg/g) for gallium and 0.76 mmol/g (87.8 mg/g) for indium.

Indium may be eluted from the resin with 4 M HCl (Fig. 4). The first volume of eluent contains the greatest amount of In(III) with almost complete recovery from the resin by the twelfth volume. Total recovery is 92.2%. Elution of Ga(III) is more difficult: 4 M HCl yields only 44.9% recovery. 1 M NaOH leads to only 24.2% recovery. Recovery is successfully accomplished, however, with a 0.2 M solution of HEDPA (Fig. 5) which yields 95.5% of the gallium on the resin.

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