

## Synthesis of Novel Type Resin Based on Calix[4]arene Carboxylate and Selective Separation of Lead from Zinc

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A novel type of resin derived from calix[4]arene carboxylate was synthesized and adsorption behavior for lead(II), zinc(II), copper(II), nickel(II), and cobalt(II) was investigated. Further, column separation of lead(II) from zinc(II) was also carried out. Adsorption equilibria of metal ions showed following order of selectivity series among metal ions: Pb(II)  $\gg$  Cu(II)  $>$  Zn(II)  $>$  Co(II) = Ni(II). Separation of lead and zinc using the packed column was sufficiently achieved.

Calixarene derivatives have peculiar complexation ability, however, their poor solubility in organic diluents makes them difficult to employ as extractants on commercial scale.<sup>1</sup> Hence, we have tried to develop the technology to employ them as ion exchangers.<sup>2,3</sup> The first trial was to chemically modify polymer matrix with the calixarene. That is, the calixarene carboxylate was introduced onto polyallylamine matrix, which has many active primary amine groups suitable for chemical modification.<sup>4</sup> This resin retained original metal complexation characteristics observed in the solvent extraction. Adsorption tests using packed column exhibited high selectivity to lead(II) over zinc(II) for mutual separation. However, this type of resin suffers from some disadvantages, one of which is low loading capacity of metal ions caused by low extent of introduction of calixarene onto the polymer matrix. In order to enhance the loading capacity, the content of the functional groups of calixarene should be increased. Thus, in the present work, we synthesized directly crosslinked calixarene with crosslinking reagent.

25,26,27,28-Tetrakis(carboxymethoxy)calix[4]arene was synthesized from debutylated calix[4]arene following a method similar to that of Gutsche et. al.<sup>5</sup> According to the synthetic route shown in Figure 1, the directly crosslinked calix[4]arene

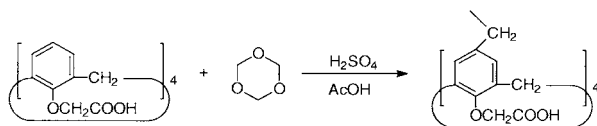


Figure 1. Synthetic route of the resin.

resin was prepared by means of condensation of the 25,26,27,28-tetrakis(carboxymethoxy)calix[4]arene using trioxane as a crosslinking reagent in  $\text{CH}_3\text{COOH}$  with  $\text{H}_2\text{SO}_4$  as a catalyst. That is, 25,26,27,28-tetrakis(carboxymethoxy)calix[4]arene and trioxane were dissolved in acetic acid and heated at  $80\text{ }^\circ\text{C}$  for 30 min. Then mixture of  $\text{H}_2\text{SO}_4$  and acetic acid was added dropwise to the solution for 30 min. The solution was heated at  $110\text{ }^\circ\text{C}$  for 8 h. After cooling, reaction mixture was poured into 5 wt% sodium hydrogen carbonate solution in small portions. Insoluble solid was collected by filtration and successively washed with hot-water,  $1\text{ mol dm}^{-3}$  HCl

and distilled water. Resulting solid was heated at  $80\text{ }^\circ\text{C}$  for 12 h in an oven. Crude resin was stirred in  $0.05\text{ mol dm}^{-3}$  sodium hydroxide solution for several hours to remove unreacted feed materials. The resulting solid was washed again with the above-mentioned solutions, then dried at  $80\text{ }^\circ\text{C}$  for 12 h in oven. The prepared resin was identified by IR spectra.

The adsorption experiments were carried out by conventional batch and column methods.<sup>6,7</sup> In the batch experiment, samples of aqueous solution were prepared by adjusting pH to desired values by mixing solutions of metal chloride individually dissolved in  $0.1\text{ mol dm}^{-3}$  HEPES buffer solution and  $0.1\text{ mol dm}^{-3}$   $\text{HNO}_3$  solution so as to maintain metal ion concentration constant at  $0.1\text{ mmol dm}^{-3}$ . The resin (0.02 g) was added to  $10\text{ cm}^3$  of the solution to be stirred for more than 3 h at  $30\text{ }^\circ\text{C}$ . After filtration, the metal ion concentration and pH in the aqueous solution were determined by using a Seiko model SAS-7500 atomic absorption spectrophotometer(AAS) and pH meter, respectively. In column operation, the aqueous feed solution was prepared by dissolving lead(II) and zinc(II) chloride into dilute hydrochloric acid solution pH of which was adjusted to 3.0 so as to keep the metal ion concentration constant at 100 ppm. The feed solution was passed through the column packed with 0.1 g resin supported by glass beads. After washing with distilled water, loaded metal was eluted with  $0.1\text{ mol dm}^{-3}$  hydrochloric acid solution. The feed rate of the solution was  $16.4\text{ cm}^3\text{ h}^{-1}$  in both of the breakthrough and elution tests. The metal ion concentration in solutions collected by fraction collector was determined by AAS.

The content of calix[4]arene carboxylate moiety of the resin was determined by neutralization titration.

Figure 2 shows relationship between equilibrium pH and percent adsorption of various metal ions. The sequence of

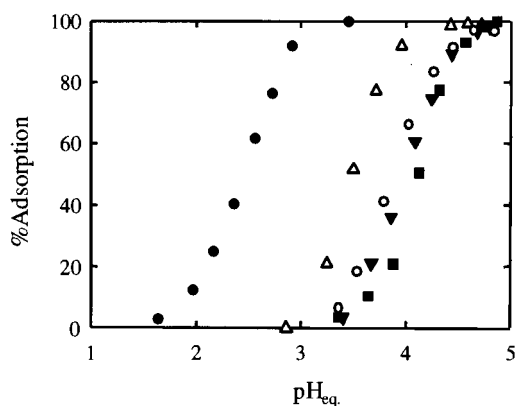
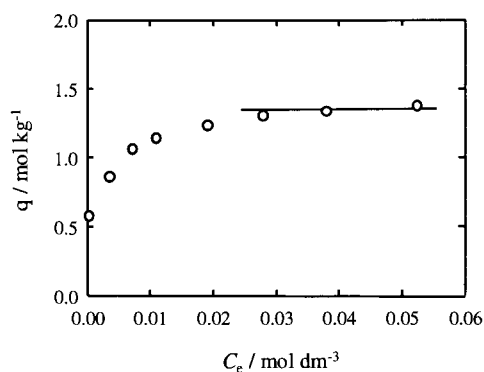


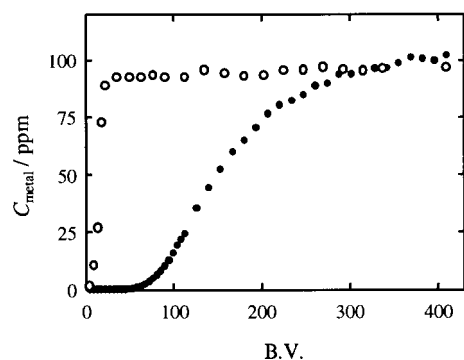
Figure 2. Effect of equilibrium pH on %Adsorption of various divalent metal ions. ●: Pb, △: Cu, ○: Zn, ▼: Co, ■: Ni, [metal]= $0.1\text{ mol dm}^{-3}$ .

adsorption selectivity is  $\text{Pb(II)} \gg \text{Cu(II)} > \text{Zn(II)} > \text{Co(II)} = \text{Ni(II)}$ , which is in accordance with those observed in the solvent extraction with *p*-tert-octylcalix[4]arene carboxylate.<sup>4</sup>

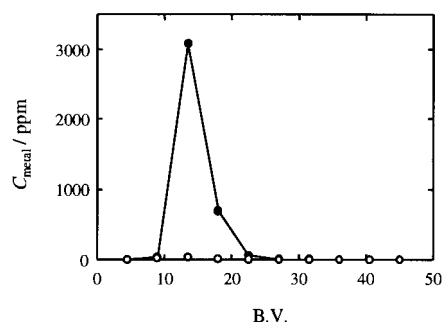
Figure 3 illustrates the adsorption isotherm of lead(II) ion, where the initial pH of the aqueous solution was kept at 3.50. As lead(II) ion concentration increases, the amount of lead adsorption increases and tends to approach a constant value, the maximum adsorption capacity,  $1.34 \text{ mol kg}^{-1}$ . Since the calix[4]arene moiety in the resin evaluated by means of the neutralization titration was  $1.30 \text{ mol kg}^{-1}$ , this value suggests that 1:1 complex formation takes place between lead(II) ion and calix[4]arene moiety. The maximum adsorption capacity of this resin was much improved compared with that of the polyallylamine resin chemically modified with calixarene mentioned earlier ( $0.62 \text{ mol kg}^{-1}$ ). Since the maximum adsorption capacity of commercial adsorbents is  $1\text{--}2 \text{ mol kg}^{-1}$ , that of the present resin is comparable with these commercial resins.



**Figure 3.** Adsorption isotherm of lead(II) ion. Weight of resin: 0.01g, pH=3.50 adjusted with  $0.1 \text{ mol dm}^{-3}$  HCl -  $0.1 \text{ mol dm}^{-3}$  HEPES.



**Figure 4.** Breakthrough profile of lead and zinc. ●: lead, ○: zinc, pH=3.00, Volume of resin:  $1.42 \text{ cm}^3$ , B.V.: Volume of feed solution represented by bed volume.



**Figure 5.** Elution profile of lead and zinc. ●: lead, ○: zinc,  $0.1 \text{ mol dm}^{-3}$  HCl, Volume of resin:  $1.42 \text{ cm}^3$ , B.V.: Volume of feed solution represented by bed volume.

Figures 4 and 5 show the separation and concentration of lead(II) from zinc(II) by the means of chromatographic operation using packed column. Figure 4 shows the breakthrough profile of lead(II) and zinc(II). Under this experimental condition, the breakthrough of lead(II) begins at about 60 B.V., while that of zinc(II) begins immediately after the initiation of the feed without being adsorbed on the resin. This result demonstrates the remarkable lead(II) selectivity of the resin as expected from the result of batchwise test shown in Figure 2. Figure 5 shows the elution profile of the loaded metal ions from the packed column by using  $0.1 \text{ mol dm}^{-3}$  hydrochloric acid solution. Lead(II) was completely eluted and concentrated as high as 30 times of the initial feed solution, while elution of zinc(II) was hardly observed, suggesting that complete mutual separation between two metal ions was able to be achieved.

In this study, high separation ability and adsorption capacity were obtained by mentioned method. In addition, the development of the resin with the high selectivity can be expected by the selection of the specific functional group for other metal ion.

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