Adsorptive Separation of Lead and Zinc Ions by Novel Type of Calix[4]arene Carboxylate Resin Immobilized with Polyallylamine

Keisuke Ohto,* Yuki Tanaka, and Katsutoshi Inoue
Department of Applied Chemistry, Faculty of Science and Engineering, Saga University, 1-Honjo, Saga 840

(Received March 24, 1997; CL-970213)

Novel type of calix[4]arene carboxylate resin immobilized with polyallylamine has been prepared to investigate the adsorption behavior for lead and zinc ions. It was found that the resin possesses significantly higher separation efficiency for lead away from zinc. In the separation by means of column chromatography, it was confirmed to highly selectively adsorb trace amount of lead ion over large excess amount of zinc ion.

Calixarene compounds are well-known as very attractive excellent ionophores. We have employed these compounds as selective extractants for the separation of metal ions and found various interesting extraction behaviors.[1-4] However, their poor solubility in organic diluents makes it difficult to use them as extractants on commercial scale. One option to avoid the draw back as such and to effectively use their properties characteristic for calixarenes as ionophores with high recognition ability is to immobilize them on some polymer matrices and to use as solid chelating ion exchangers for the purpose of highly selectively uptaking the trace amount of some specified metal ions away from large excess amount of other metal ions. Although the development of novel types of resins incorporated with macrocyclic ligands has much advanced in recent years,[5-7] only a few papers have been reported on the resin incorporated with calixarenes.[8-10] As well-known, lead is a toxic heavy metal and is desired to be much highly and severely separated and removed from environment. In nature, lead usually occurs together with zinc with similar chemistry and, consequently, it is very important from the above-mentioned point of view to selectively recognize and separate trace amount of lead coexisting in large excess amount of zinc.

The polymer matrices employed in the present work was polyallylamine (abbreviated as PAA), of the average molecular weight ca.10000, which involves many active primary amines fitting for a variety of chemical modification with various functional groups and is marketed by Nittobo Co. Ltd., as solid acetate salt under the trade name, PAA-AcOH-S; it was used without further purification.

From the above-mentioned view points, we prepared the novel type of calix[4]arene carboxylate resin immobilized on polyallylamine to investigate their adsorption behavior for lead and zinc ions.

Calix[4]arene 25,26,27,28-tetrol was esterified, hydrolyzed with base, and chloromethylated. The desired resin was prepared by interacting the resulting cone conformational 25,26,27,28-tetrakis(carboxymethoxy)-5,11,17,23-tetra(chloromethyl)calix[4]arene with PAA-AcOH-S in 2-propanol in the presence of sodium carbonate, taking care of followings; 1)quarternarization of amine, 2)formation of poly ion complexes, 3)formation of amide, 4)formation of ester, and so on. That is, PAA-AcOH-S was added into 2-propanol in the presence of sodium carbonate and reflux for 3 h. After cooling, chloromethylated compound was added to this solution and heated at 50°C for 48 h. After cooling to neutralize with hydrochloric acid, the resulting resin was washed with distilled water, and then dried. The prepared resin was identified by IR spectra. Figure 1 shows the synthetic route of the resin.

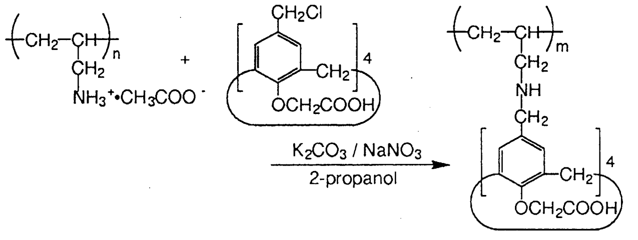

Figure 1. Synthetic route of the resin.

The adsorption experiment was carried out by conventional batch and column methods.[11] That is, in the batch experiment, aqueous solution was prepared by individually dissolving zinc chloride or lead chloride into 0.1 mol dm^{-3} nitric acid or 0.1 mol dm^{-3} HEPES buffer solution to 0.1 mmol dm^{-3}. Both solutions were arbitrarily mixed to adjust pH. To 10 cm^3 of the solution was added 0.02 g of the resin to be stirred for more than 2 h at 30 °C. After filtration, the metal concentration and pH in the aqueous solution were determined by atomic absorption spectrophotometer and pH meter, respectively. In the column experiment, the aqueous feed solution was prepared by dissolving zinc chloride and lead chloride into dilute nitric acid solution. The pH was 3.6 and the concentrations of zinc and leadwere 1130 and 9 ppm, respectively. The feed solution was passed through the packed bed of 0.3 g of the resin mixed together with 0.1 g of glass beads (average diameter = 1.3 mm). After washing with distilled water, the adsorbed metal was eluted with 1 mol dm $^{-3}$ nitric acid. The feed rate was 7.4 cm^3 h^{-1}. The metal concentration in the collected solutions were determined by atomic absorption spectro-photometer.

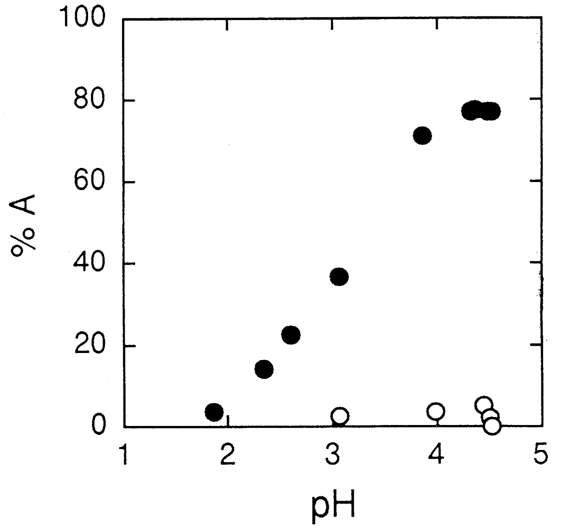

Figure 2. Effect of pH on percentage adsorption of lead and zinc on the resin. (●): lead , (○): zinc, 0.1 mol dm^{-3} HCl - 0.1 mol dm^{-3} HEPES, $[Pb^{2+}] = [Zn^{2+}] = 1.0 \times 10^{-4}$ mol dm^{-3}, weight of resin : 0.02 g.

Figure 2 shows the effect of pH on percentage adsorption of lead and zinc ions on the resin. It is apparent from Figure 2 that the resin can very effectively adsorb lead and hardly adsorb zinc under the present experimental condition.

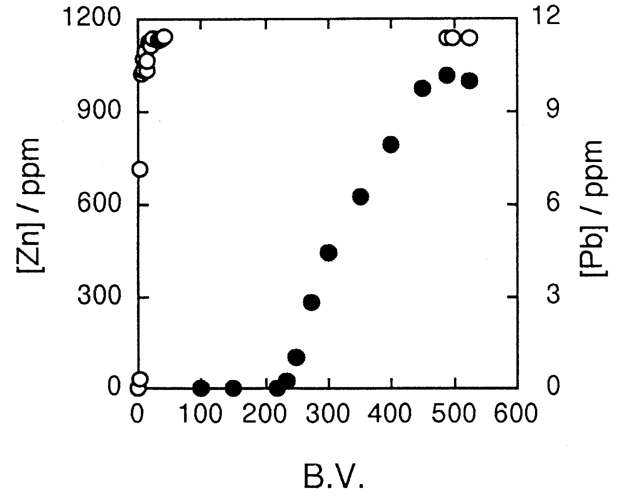

Figure 3(a). Breakthrough profile of zinc and lead. (●): lead , (○): zinc, 0.1 mol dm^{-3} HCl - 0.1 mol dm^{-3} HEPES, pH = 3.6, weight of resin : 0.30 g, Volume of resin: 4.9 cm^{3}, Feed rate: 7.4 cm^{3} h^{-1}. B.V.: Volume of feed solution represented by bed volume.

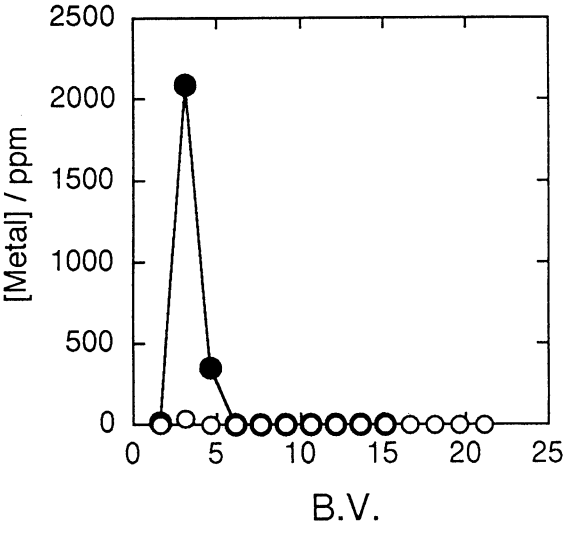

Figure 3(b). Elution profile of zinc and lead. (●): lead , (○): zinc, 1 mol dm^{-3} HNO^{3}, weight of resin : 0.30 g, Volume of resin: 4.9 cm^{3}, Feed rate: 7.4 cm^{3} h^{-1}. B.V.: Volume of feed solution represented by bed volume.

Since the high selectivity of the resin to lead over zinc is much superior to those of commercial resins, such as iminodiacetic acid, phosphonate, and sulfonate types of resins, it is sure that the resin is very much suitable for the removal of trace amount of lead from large excess amount of zinc. Subsequently, a small amount of lead ion was adsorbed on the resin to be separated away from 120 times excess amount of zinc ion by means of chromatographic operation using the packed column mentioned earlier to actually confirm the separation efficiency.

Figure 3(a) shows the breakthrough profile of zinc and lead. As expected from the result of batch experiment shown in Figure 2, zinc was broken through immediately after the initiation of the feeding without trapped in the bed, while the breakthrough of lead began to take place after as late as about 200 B.V., clearly suggesting that very complete separation of trace amount of lead away from zinc can be successfully achieved using the column backed with the resin immobilized with calixarene carboxylate.

Figure 3(b) shows the elution profile of loaded metal ions from the column with 1 mol dm^{-3} nitric acid. It demonstrates that lead can be concentrated as high as 200 times of the feed solution and free from zinc contamination.

The authors are grateful to Dr. Takashi Hayashita of Saga University (present address is Tohoku University) for the advise of the experiment.

This work was financially supported in part by a Grant-in-Aid for Scientific Research No.08875162 from the Ministry of Education, Science and Culture of Japan.

References

1 K. Ohto, M. Yano, K. Inoue, T. Yamamoto, M. Goto, F. Nakashio, S. Shinkai, and T. Nagasaki, *Anal. Sci.*, **11**, 893 (1995).
2 K. Ohto, E. Murakami, T. Shinohara, K. Shiratsuchi, K. Inoue, and M. Iwasaki, *Anal. Chim. Acta*, in press (1997).
3 K. Ohto, H. Yamaga, E. Murakami, and K. Inoue, *Talanta*, in press (1997).
4 K. Ohto, H. Ota, and K. Inoue, *Solv. Extr. Res. Dev. Jpn.*, in press (1997).
5 T. Hayashita, K. Yamasaki, X. Huang, and R. A. Bartsch, *Chem. Lett.*, **1993**, 1487.
6 T. Hayashita, K. Yamasaki, J. C. White, S. P. Kasprzyk, and R. A. Bartsch, *Sep. Sci. Tech.*, **31**, 2195 (1996).
7 R. M. Izatt, J. S. Bradshaw, R. L. Bruening, B. J. Tarbet, and M. L. Bruening, *Pure Appl. Chem.*, **67**, 1069 (1995).
8 S. Shinkai, H. Kawaguchi, and O. Manabe, *J. Polym. Sci., Part C, Polym. Lett.*, **26**, 391 (1988).
9 S. Hutchinson, G. A. Kearney, E. Horne, B. Lynch, J. D. Glennon, M. A. Mckervey, and S. J. Harris, *Anal. Chim. Acta*, **291**, 269 (1994).
10 R. Brindle, K. Albert, S. J. Harris, C. Treltzsch, E. Horne, and J. D. Glennon, *J. Chromatogr. A*, **731**, 41 (1996).
11 K. Inoue, H. Hirakawa, Y. Ishikawa, T. Yamaguchi, J. Nagata, K. Ohto, and K. Yoshizuka, *Sep.Sci.Tech.*, **31**, 2273 (1996).