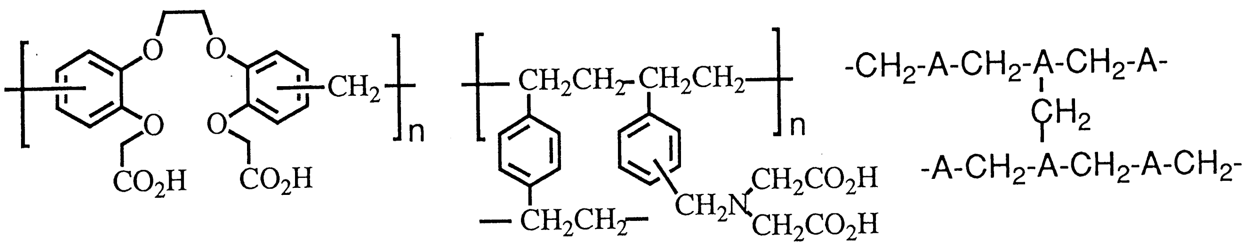
CHEMISTRY LETTERS, pp. 1487-1490, 1993.

Novel Dibenzopolyether Resin Possessing Dicarboxylic Acid Side Arm Functionality for Use in Specific Lead(II) Separation

Takashi HAYASHITA,* Kenji YAMASAKI, Xiaowu HUANG, † and Richard A. BARTSCH †
Department of Chemistry, Faculty of Science and Engineering, Saga University,
1 Honjo, Saga 840
† Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409

A novel dibenzopolyether resin possessing dicarboxylic acid side arm functionality (EDPAR) was synthesized by condensation polymerization of ethylenedi(oxy-*o*-phenoxyacetic acid) with formaldehyde in formic acid. The excellent sorption for Pb(II) over Cu(II) obtained with EDPAR was not observed with commercially available iminodiacetic acid resin (CR-10). For EDPAR, the percent sorption of Pb(II) exceeded 90% at pH 2.5, while Cu(II) sorption was less than 30% at this pH.

Selective separation and elimination of trace level of toxic metal ions from solutions containing other worthwhile metal ions is important for hydrometallurgical processing.[1)] Recently, we developed dibenzocrownether carboxylic acid resins which contain both ion-exchange and polyether binding sites for metal complexation.[2-4)] These resins exhibited excellent sorption selectivity and efficiency for alkali-metal ion separation. In the study, we also found that these resins have specific interaction with Pb(II) over other heavy metal ions. Even acyclicpolyether carboxylic acid resins exhibited a good sorption selectivity for Pb(II).[5)] This result indicates that the carboxylic acid resins possessing "hard" polyether binding sites would be potential for use in specific Pb(II) separation from solutions. In the present study, we synthesized ethylenedi(oxy-*o*-phenoxyacetic acid) resin (EDPAR) as a first example of



EDPAR **CR-10** **1**

Fig. 1. Structure of chelating resins.

polyether resin possessing dicarboxylic acid side arm functionality. The sorption of Pb(II) and Cu(II) from buffered aqueous solution of varying pH by EDPAR was determined and compared with that of commercially available iminodiacetic acid resin (Diaion CR-10, Mitsubishi Kasei Co. Ltd.).

Ethylenedi(oxy-*o*-phenoxyacetic acid) (EDPA) was synthesized from 1,2-di(*o*-hydroxyphenoxy)ethane and bromoacetic acid in THF in the presence of potassium tert-butoxide.[6] EDPAR was prepared by condensation polymerization of EDPA with formaldehyde in formic acid. The monomer (EDPA, 1.4 mmol) was dissolved in a solution of formic acid (5 cm^3) and formaldehyde (37% aqueous solution, 5 cm^3). The mixture was refluxed for 6 h. The formaldehyde (5 cm^3) was added to the mixture in succession, and the solution was refluxed another 6 h. To complete resin precipitation, a 5 cm^3 of formaldehyde was further added to the solution, and the mixture was refluxed for 6 h and cooled.[7] The precipitate resin was collected , washed with deionized water, methanol, and finally dried at 80℃. The resin was ground in powder form finer than 60 mesh, and the structure was characterized by IR spectroscopy and elemental analysis.[8] The structural representation of EDPAR imply polymers with no cross-linking. This is most certainly an overestimation since some level of cross-linking is anticipated. A possible structure for the partially cross-linked resin is given by **1** in which A is the dibenzopolyether unit (Fig. 1). The elemental analysis data agreed well with this formulation.

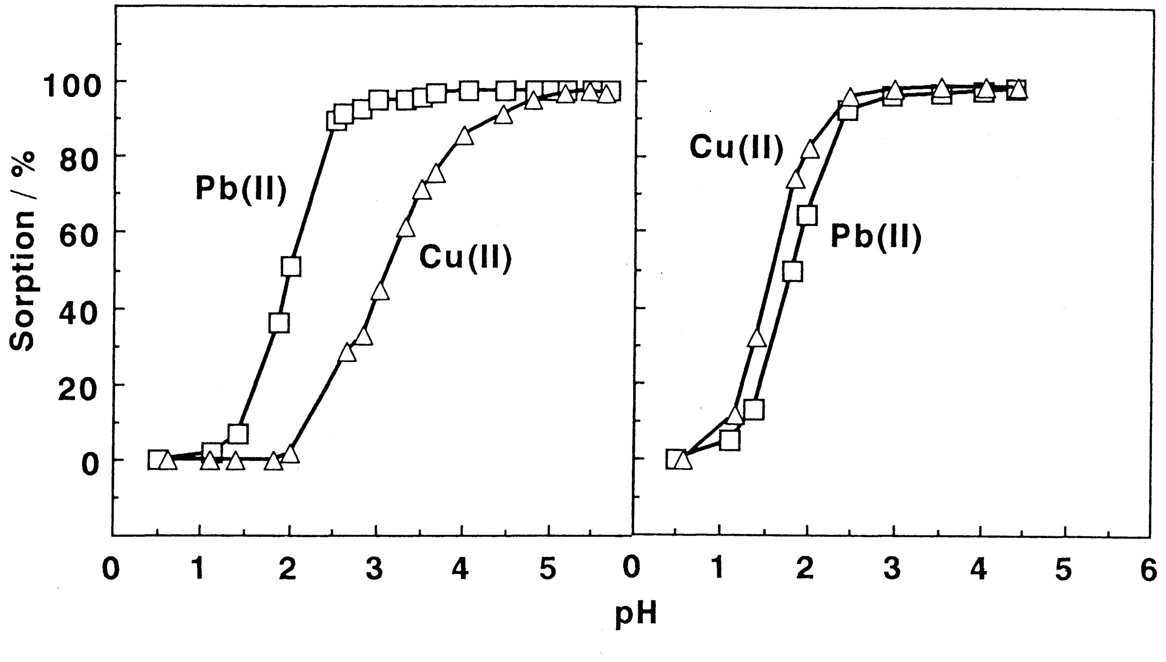


Fig. 2. Sorption of Pb(II) and Cu(II) by (a) EDPAR and (b) CR-10. Buffered aqueous solutions (5.0 cm^3) containing 1.0 $mmoldm^{-3}$ metal ions were shaken with 0.030 g of resin for 3.0 h.

The sorption behavior of Pb(II) and Cu(II) from aqueous solution into the resin was investigated by a batch analysis. An aqueous solution (5.0 cm^3) of 1 mmoldm^{-3} metal ions with nitric acid or 0.20 moldm^{-3} acetic acid/ tetramethylammonium hydroxide buffer for pH adjustment was mechanically shaken with 0.030 g of the resin for 3.0 h in a 10 cm^3 centrifuge tube. The aqueous phase was filtered and the equilibrium pH was measured. The sorption was evaluated by the percent sorption (S):

$$S(\%) = 100([M^{2+}]_i - [M^{2+}]_f)/[M^{2+}]_i \quad (1)$$

where $[M^{2+}]_i$ and $[M^{2+}]_f$ are the initial and the final metal concentration in the aqueous solution, respectively. The metal ion concentration was measured with atomic absorption spectro-photometer (Hitachi 170-30).

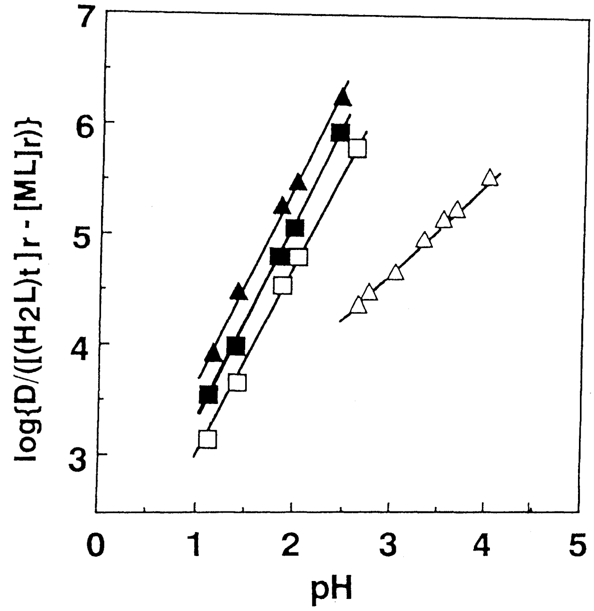


Fig. 3. Correlation of $\log\{D/([(H_2L)_t]_r - [ML]_r)\}$ and pH. Conditions are similar to those in Fig. 2. EDPAR: (□) Pb(II), (△) Cu(II); CR-10: (■) Pb(II), (▲) Cu(II).

The resultant sorption of Pb(II) and Cu(II) by EDPAR is shown in Fig. 2(a) as a function of the aqueous pH. For comparison, the metal sorption by commercially available imminodiacetic acid resin CR-10 was investigated (Fig. 2(b)). For both resins, the metal sorption is enhanced in the pH of the aqueous increased. This indicates that the ion-exchange sorption of metal ions is facilitated by deprotonation of the carboxylic acid groups in the resin. It is noted, however, that the sorption selectivity observed for EDPAR is different from that for CR-10. The CR-10 exhibited sorption selectivity for Cu(II) over Pb(II) in agreement with the reported selectivity.[9)] Thus the percent sorptions at pH 2.0 were 82% for Cu(II) and 64% for Pb(II), respectively. In contrast, EDPAR showed selective sorption for Pb(II) over Cu(II). The percent sorption of Pb(II) exceeded 90% at pH 2.5, while Cu(II) sorption was less than 30% at this pH. This is an interesting property of EDPAR possessing both carboxylic acid and polyether binding site for metal ion complexation.

When 1:1 complex formation between metal (M^{2+}) and ligand (H_2L) in the resin takes place, the sorption equilibrium is expressed by the following equations:

$$(H_2L)_r + (M^{2+})_a \overset{Kd}{\rightleftharpoons} (ML)_r + 2(H^+)_a \quad (2)$$

$$Kd = [ML]_r[H^+]_a^2/[H_2L]_r[M^{2+}]_a \quad (3)$$

where Kd, the subscripts "r" and "a" denote the sorption constant, the concentration in the resin and the aqueous phase, respectively. By introducing the distribution ratio of metal ion between the resin and the aqueous phase ($D = [ML]_r/[M^{2+}]_a$) into Eq. (3), the sorption equilibrium is logarithmically expressed as:

$$\log\{D/([(H_2L)_t]_r - [ML]_r)\} = 2pH + \log Kd \qquad (4)$$

where $[(H_2L)_t]_r$ represents an ion-exchange capacity (mol/g) of the resin and is determined by batch analysis (2.78 mmol/g for EDPAR, 2.58 mmol/g for CR-10). Equation (4) indicates that the plots of $\log\{D/([(H_2L)_t]_r - [ML]_r)\}$ against pH should give a straight line with a slope of 2, and log Kd value is obtained from an intercept of the straight line. The plots are shown in Fig. 3. With an exception of Cu(II) sorption by EDPAR, the plots are all linear with a slope of 2, indicating that the sorption depicted in Eq. (2) indeed took place. For Cu(II) sorption by EDPAR, a slope of the plot was 1.0. Thus the ion-exchange sorption accompanied by an anion from the aqueous phase may take place under the present condition. Apparently such difference in sorption mechanism between Cu(II) and Pb(II) enhances the Pb(II) selectivity for the sorption by EDPAR. The observed log Kd values were 1.1 (Pb(II)) for EDPAR, 1.5 (Pb(II)) and 1.9 (Cu(II)) for CR-10, respectively.

In conclusion, we found that the dibenzopolyether resin possessing dicarboxylic acid side arm functionality (EDPAR) exhibited an excellent sorption selectivity for Pb(II) over Cu(II) in solution. We already noticed that the sorptions of other heavy metal ions such as Ni(II), Zn(II), and Co(II) were much weaker than that of Cu(II). Thus EDPAR would be promising chelating resin for use in specific Pb(II) separation in hydrometallurgical processing.

References

1) A.Warshawsky, "Synthesis and Separations using Functional Polymers," Ed by D.C.Sherrington and P.Hodge, John Wiley&Sons, New York (1988), p.325 .

2) T.Hayashita, M-.J.Goo, J.C.Lee, J.S.Kim, J.Krzykawski, and R.A.Bartsch, *Anal.Chem.*, **62**, 2283 (1990).

3) T.Hayashita, M-.J.Goo, J.S.Kim, and R.A.Bartsch, *Talanta*, **38**, 1453 (1991).

4) T.Hayashita, J.H.Lee, M.G.Hankins, J.C.Lee, J.S.Kim, J.M.Knobeloch, and R.A.Bartsch, *Anal.Chem.*, **64**, 815 (1992).

5) T.Hayashita and R.A.Bartsch, unpublished results.

6) Yield 38% with mp 153-154 ℃. IR(KBr): 3426 (OH), 1739 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$+$CD_3S(O)CD_3$): δ 4.40-4.46 (t, 4H), 4.64-4.68 (d, 4H), 6.89-7.05 (m, 8H), 7.48 (S, 2H). Anal. Found: C, 59.52; H, 5.00%. Calcd for $C_{18}H_{18}O_8$: C, 59.67; H, 5.07%.

7) Though we investigated various conditions of formic acid/formaldehyde composition for resin synthesis, this stepwise addition of formaldehyde was found to be the best.

8) Yield 66%. IR(KBr): 3439 (OH), 1741 (C=O) cm^{-1}. Anal. Found: C, 61.00; H, 4.71%. Calcd for **1**: C, 61.17; H, 4.82%.

9) T.Itagaki, "Bunri-Yusou Kinouzairyou," Kyouritsu Shuppan (1992), p.401.

(Received May 31, 1993)