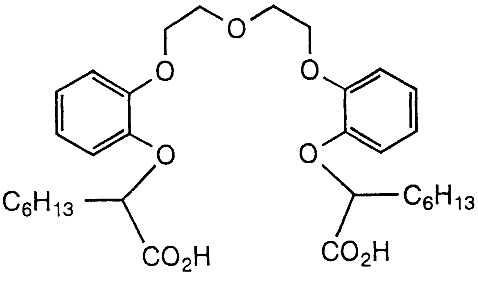
CHEMISTRY LETTERS, pp. 2385-2388 1994.

Separation of Lead(II) by Solvent Extraction and Membrane Transport with a Dibenzopolyether Dicarboxylic Acid Ionophore

Takashi HAYASHITA,* Takashi FUJIMOTO, Yuki MORITA, and Richard A. BARTSCH[†]
Department of Chemistry, Faculty of Science and Engineering, Saga University, Honjo, Saga 840
[†] Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409, U.S.A.

The lipophilic di-ionizable ionophore 1,5-Bis[2-(2'-carboxyheptyloxy)phenoxy]-3-oxapentane (**1**) provides a selective solvent extraction of Pb(II) from Cu(II). The stoicheometry of the extracted species is determined to be 1:1 by equilibrium analysis. Ionophore **1** also functions as a carrier in polymeric plasticizer membrane for separation of Pb(II) from Cu(II).


1

The development of chelating materials for the separation of toxic heavy metal ions from waste and processing solutions has been the subject of many investigations.1) However the selective removal of Pb(II) in environmental remediation remains an important objective.2-4) Recently we reported that a polymeric resin prepared from an acyclic dicarboxylic acid monomer gave efficient and selective sorption of Pb(II) from aqueous solutions containing other heavy metal ions.5) To determine if the "hard" oxygen binding sites in a structurally similar, soluble ionophore would also exhibit Pb(II) selectivity as an extractant and as a carrier in liquid membrane transport, the lipophilic dibenzopolyether dicarboxylic acid **1** was designed. The synthesis of this ionophore and its propensities for Pb(II) separation by solvent extraction and membrane transport are now reported.

1,5-Bis[2-(2'-carboxyheptyloxy)phenoxy]-3-oxapentane (**1**) was synthesized by reaction of 1,5-bis(2-hydroxyphenoxy)-3-oxapentane with sodium hydride then 2-bromooctanoic acid in THF. The crude product was purified by chromatography on silica gel. The structure of **1** was confirmed by ^{1}H NMR, IR, and combustion analysis.6) Since lipophilic ionophore **1** has two chiral carbons in the polyether framework, it can exist as a meso compound and a pair of diastereomers which are enantiomers of each other. Even though ionophore **1** gave a single spot on thin layer chromatography, it is most certainly a mixture of stereoisomers.7) No further attempt was made to separate the stereoisomers.

The complexation properties of ionophore **1** toward heavy metal ions were first evaluated by solvent extraction of Pb(II) and of Cu(II) into chloroform from buffered aqueous solutions. For conventional chelating reagents, Cu(II) generally shows the highest complexation in the Irving-Williams order.8) Therefore extractions of Pb(II) and Cu(II) were compared. A chloroform solution (9.0 cm^3) containing 1.0 mM (1 M = 1 mol dm^{-3}) **1** and 9.0 cm^3 of buffered aqueous solution (0.010 M sodium acetate) containing 0.10 mM Pb(II) or Cu(II) were combined in a 50-mL centrifuge tube and vigorously shaken for 30 min at room temperature (23-25 °C). In the present system, a shaking time of 15 min was found to be sufficient to achieve extraction equilibrium. After phase separation by centrifuging for 10 min (2000 rpm), the equilibrium pH and the heavy metal ion concentration of the aqueous phase were measured with an Orion Model 720A pH meter and a Hitachi 170-30 atomic absorption spectrophotometer, respectively. A 0.50-cm^3 portion of the organic phase was transferred to a 5.0-mL volumetric flask and diluted to the mark with chloroform. The absorbance at 274 nm was measured with a Shimadzu UV-2100 spectrophotometer to determine the ionophore concentration in the chloroform phase.

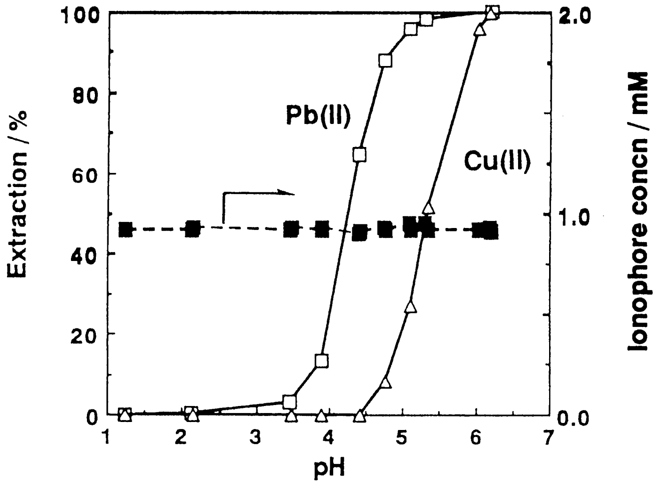


Fig. 1. Extraction of Pb(II) and Cu(II) with ionophore **1** from buffered aqueous solutions of varying acidities into chloroform. □: Pb(II), △: Cu(II), ■: Ionophore concentration in the chloroform phase after the extraction.

Results for the solvent extraction of Pb(II) and of Cu(II) with ionophore **1** from aqueous solution of various acidities into chloroform are presented in Fig. 1. The dashed line in the figure shows the ligand concentration in the chloroform phase after extraction. It is apparent that ionophore **1** is sufficiently lipophilic to avoid loss of the extractant into aqueous phase. At pH 4.7, the extraction of Pb(II) has reached 90%, but the extraction of Cu(II) was less than 10%. Thus it is shown that from an aqueous solution at an appropriate pH, ionophore **1** exhibits good extraction selectivity for Pb(II) over Cu(II).

When a 1:1 complex of the metal ion (M$^+$) and ionophore **1** (H_2L) is extracted into the organic phase, the extraction equilibrium is expressed by the following equations:

$$(H_2L)_o + (M^{2+})_a \overset{K_{ex}}{\rightleftharpoons} (ML)_o + 2(H^+)_a \qquad (1)$$

$$K_{ex} = ([ML]_o[H^+]_a^2)/([H_2L]_o[M^{2+}]_a) \qquad (2)$$

where K_{ex}, the subscripts "o" and "a" denote the overall extraction constant and the concentrations in the organic and the aqueous phase, respectively. By incorporation of the distribution ratio of metal ion between the organic and the aqueous phase ($D = [ML]_o/[M^{2+}]_a$) into Eq. 2, the extraction equilibrium may be expressed logarithmically as:

$$\text{Log } D = 2\text{pH} + \log [H_2L]_o + \log K_{ex} \qquad (3)$$

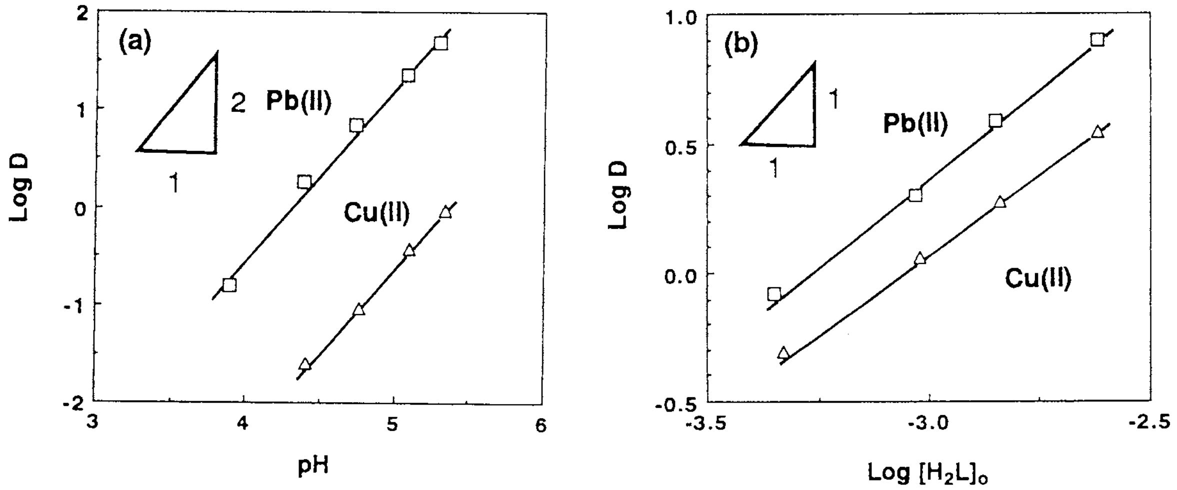


Fig. 2. Log-log plots of distribution ratio of metal ions against (a) pH and (b) ionophore concentration. (a) Aqueous phase, acetate buffer containing 0.10 mM metal ions; Organic phase, chloroform containing 1.0 mM **1**. (b) Aqueous phase, 0.10 mM Pb(II) solution (pH 4.38) and 0.10 mM Cu(II) solution (pH 5.38); Organic phase, chloroform containing **1**.

From Eq. 3 it is seen that plots of log D vs. pH and log $[H_2L]_o$ should be linear with slopes of 2 and 1, respectively. Results are shown in Fig. 2a and 2b. In both plots, the slopes of the lines obtained for Pb(II) and Cu(II) are consistent with the values anticipated from Eq. 3. Thus formation of 1:1 complexes between ionophore **1** and the divalent heavy metal ions is established for this solvent extraction process. From these plots, pK_{ex} (-log K_{ex}) values are determined to be 5.37 ± 0.12 for Pb(II) and 7.66 ± 0.08 for Cu(II), respectively.

To apply the observed propensity for Pb(II) extraction to a membrane separation process, novel polymeric plasticizer membrane was prepared according to the procedure reported by Sugiura et al.[9] Cellulose triacetate (0.20 g) as the membrane support, 0.60 g of *o*-nitrophenyl octyl ether (NPOE) as the plasticizer, and 0.16 g of ionophore **1** (0.46 mmol of **1**/g of NPOE) as the carrier were dissolved in 10 cm^3 of chloroform. Of this solution 5 cm^3 was poured into a glass culture dish (9.0 cm in diameter). After one day at room temperature, cold water was added and the membrane was peeled away from the dish. A stable, transparent film of 120 μm thickness

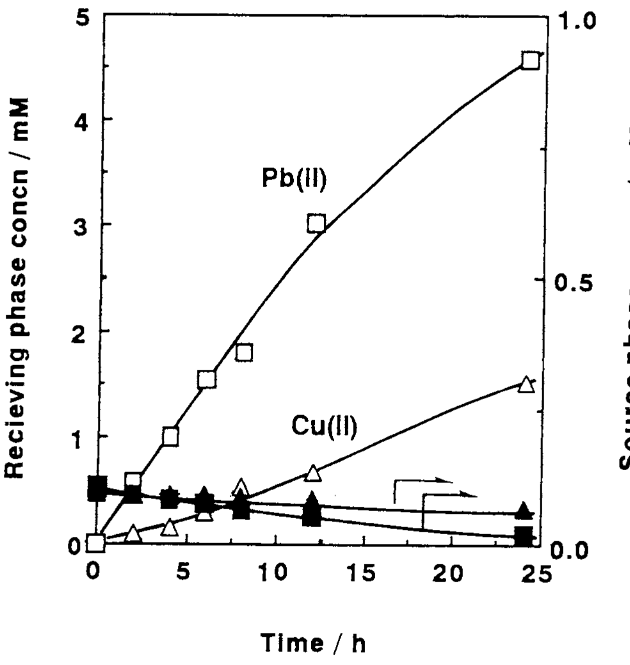


Fig. 3. Permeation behavior of Pb(II) and Cu(II) through polymeric plasticizer membrane. Source phase pH, 4.70. Membrane area, 0.79 cm^2.

was obtained. The membrane transport experiments were conducted in a cylindrical dialysis cell.[10)] The source phase solution was a 250 cm^3 of buffered aqueous solution (10 mM sodium acetate) which contained 0.10 mM Pb(II) and Cu(II). The receiving phase was 5.0 cm^3 of 0.10 M nitric acid.

When the pH of the aqueous source phase was 4.7, the competitive heavy metal ion transport results presented in Fig. 3 were obtained. As can be seen, selective permeation of Pb(II) over Cu(II) was observed in this system. Compared with its initial source phase concentration, the concentration of Pb(II) in the receiving phase was 43 times higher after 24 h permeation. Upon reduction of the source phase pH from 4.7 to 3.9, the concentration of Pb(II) in receiving phase after 24 h decreased from 4.6 to 3.9 mM. However, no Cu(II) could be detected in the receiving phase after 24 hours when the source phase pH was 3.9. This influence of the source phase acidity upon the propensity for transport of Cu(II) can be rationalized by consideration of the extraction data presented in Fig. 1. At pH=3.9, extraction of Cu(II) from the source phase into the membrane phase is expected to be very poor.

In conclusion, we have found that lipophilic dibenzopolyether dicarboxylic acid **1** is an effective extractant for Pb(II) in solvent extraction and carrier for Pb(II) in transport across a polymeric plasticizer membrane. In both separation systems, good selectivity for Pb(II) over Cu(II) was achieved under appropriate conditions.

The structure of the carrier and composition of the polymeric plasticizer membrane are expected to be important parameters for the transport system. Detailed investigations of the influence of these and other experimental variables upon the selectivity and efficiency of Pb(II) transport are underway.

This work was partly supported by The Salt Science Research Foundation and Nissan Science Foundation, which are gratefully acknowledged.

References

1) C. Kantipuly, S. Katragadda, A. Chow, and H. D. Gesser, *Talanta*, **37**, 491 (1990).
2) K. U. Damu, M. S. Shaikjee, J. P. Michael, A. S. Howard, and R. D. Hancock, *Inorg. Chem.*, **25**, 3879 (1986).
3) K. Hiratani, H. Sugihara, K. Kasuga, K. Fujiwara, T. Hayashita, and R. A. Bartsch, *J. Chem. Soc. Chem. Commun.*, **1994**, 319.
4) T. Hayashita, K. Yamasaki, K. Kunogi, K. Hiratani, X. Huang, Y. Jang, D. E. McGowen, and R. A. Bartsch, *Supramol. Chem.*, submitted.
5) T. Hayashita, K. Yamasaki, X. Huang, and R. A. Bartsch, *Chem. Lett.*, **1993**, 1487.
6) The detailed synthetic procedure will be described elesewhere. White solid with mp 60.0-62.3 °C. ^1H NMR ($CDCl_3$): δ 0.88 (t, 6H), 1.26-1.34 (m, 12H), 1.52-1.61 (m, 4H), 1.92-1.97 (m, 4H), 3.91-3.95 (m, 4H), 4.15-4.21 (m, 4H), 4.48-4.52 (m, 6H), 6.92-7.03 (m, 8H), 7.26 (s, 2H). IR (KBr): 3420 (O-H), 1710 (C=O) cm^{-1}. Elemental analysis, Found: C, 66.90; H, 8.10%. Calcd for $C_{32}H_{46}O_9$: C, 66.88; H, 8.07%.
7) A 0.47% solution (by weight) of ionophore **1** in acetonitrile showed no optical activity.
8) H. Irving, R. J. P. Williams, *J. Chem. Soc.*, **1953**, 3129; *Nature*, **162**, 746 (1948).
9) M. Sugiura, M. Kikkawa, and S. Urita, *J. Membr. Sci.*, **42**, 47 (1989).
10) T. Hayashita, T. Kurosawa, S. Ohya, T. Komatsu, and M. Igawa, *Bull. Chem. Soc. Jpn.*, **63**, 576 (1990).

(Received September 14, 1994)