

Selective Sorption of Heavy Metal Thiocyanate Complexes on Crown Ether Resin

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Synopsis

The sorption behavior of heavy metal thiocyanate complexes was investigated for dibenzo-18-crown-6 (DB18C6) resin and bis[2-(*o*-methoxyphenoxy)ethyl]ether (BMPE) resin. The DB18C6 resin showed a high sorption ability and the degree of zinc sorption increased significantly with thiocyanate concentration. This behavior was not observed for BMPE resin. The sorption behavior was influenced by the counteraction species, and the degree of sorption of zinc ions showed the maximum when the potassium thiocyanate was used as a complexing salt. The sorbed species appear to be $KZn(SCN)_3$, $K_2Zn(SCN)_4$ in the potassium thiocyanate system, and $Zn(SCN)_2$ in the lithium thiocyanate system, respectively, according to analysis of the sorption equilibrium. Sodium and ammonium thiocyanate systems show an intermediate behavior of the two. The sorption selectivity for DB18C6 resin depended not only on the hydrophobic nature of heavy metal thiocyanate complexes but also on the stabilization of counter cation species with crown ether matrix, and the sorption selectively was found to be effectively controlled by counteraction species according to the cation-chelation mechanism.

INTRODUCTION

Many attempts have been made to achieve a selective metal separation. Solvent extraction is known as one of the useful metal separation method, but the volatility and toxicity of organic solvents sometimes pose problems in the practical application in industry. In spite of the above shortcomings, it was reported that solid polymers such as polyurethane foam were effective substitutes for organic solvents for the sorption or "extraction" of some ion-association complexes.^{1,2} Several heavy metal halogeno complexes are effectively extracted by unloaded polyurethane foams.³⁻⁶ In the course of our study, we have recently found that cellulose acetate polymers also revealed the selective sorption ability for several heavy metal halogeno complexes.⁷⁻⁹ We applied this behavior to the selective metal hyperfiltration systems. The principle is that (i) heavy metal ions are better converted in solution to halogeno (or pseudohalogeno) complexes, (ii) the heavy metal complexes are sorbed onto membrane matrix by forming ion-association complexes in a similar manner to an ordinary liquid-liquid extraction of heavy metals, and (iii) the sorbed heavy metal species is transported through the membrane by a coupling with a solvent flow. Among these, point (ii) constitutes the most important research field, since it relates to the development of new polymeric membrane

materials to achieve a specific interaction with the heavy metal complexes in solution. So far, however, very little has been done in this field.

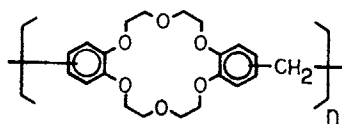
For a specific sorption (or extraction) of heavy metal species to the polymer matrix to take place, the polymer has to contain some structural units which specifically stabilize the complexes in ordinary liquid-liquid extractions. In the present study, we report some preliminary attempts to provide a polymer with a capability for specific interaction with ion-association complexes. We introduce a crown ether unit to a polymer chain for its specific interaction with a certain class of cations (alkali metal and ammonium), which in turn should cause an influence on the sorption selectivity (and possibly also on the structures) of anionic parts (anionic heavy metal complexes) in the sorption of ion-association complexes.

EXPERIMENTAL

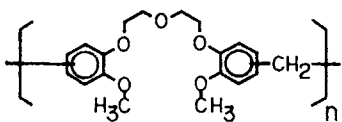
Reagents

The structures of the polymer used in this study are shown in Figure 1. Dibenzo-18-crown-6 (DB18C6) and bis[2-(*o*-methoxyphenoxy)ethyl]ether (BMPE) were prepared by a reaction of bis(2-chloroethyl)ether with pyrocatechol or *o*-methoxyphenol according to the published procedure.¹⁰ DB18C6 resin (1) and BMPE resin (2) were synthesized by condensation polymerization¹¹: DB18C6 (10.0 g, 0.028 mol) or BMPE (10.0 g, 0.035 mol) was dissolved in 300 mL formic acid solution. Formaldehyde (37% aqueous solution, 200 mL) was added in succession, and the mixture was refluxed for 24 h. The precipitate was collected and washed with formic acid, water, and finally dried. The resins were used in powder form (finer than 50 mesh). Amberlite CG-400 (Rohm & Haas Co. Ltd.) was used as a standard anion exchange resin. The resin was purified by treating with 1.0 mol dm⁻³ sodium hydroxide and 1.0 mol dm⁻³ hydrochloric acid and finally by washing with pure water. Other reagents were reagent-grade commercial products and used without further purification.

Stock solutions of 5 mmol dm⁻³ heavy metal nitrate and 1.0 mol dm⁻³ alkali metal thiocyanate were stored in polyethylene bottles. Magnesium



1



2

Fig. 1. Structure of the polymer: (1) DB18C6 resin; (2) BMPE resin.

thiocyanate solutions were prepared from Ba (SCN)₂ and MgSO₄ according to the reported procedure.¹² Solutions containing 1.0 mol dm⁻³ Ba(SCN)₂ were converted to 1.0 mol dm⁻³ Mg(SCN)₂ solutions by adding MgSO₄ to precipitate BaSO₄.

Sorption Experiment

Heavy metal thiocyanate solutions were prepared by mixing and diluting the stock solutions. An appropriate amount of the resin (0.1 g) was suspended in 20 mL of thiocyanate solution containing 1.0 mmol dm⁻³ heavy metal ions, and the mixture was mechanically shaken for 12 h at 25°C. A preliminary study indicated that a shaking time of 9 h is needed to achieve the sorption equilibrium. The pH of the solution was adjusted by HNO₃. The metal ion concentration in the solution was measured before and after the sorption by a standard atomic absorption spectrophotometry (Shimadzu AA-630-02). The sorption was evaluated by means of the degree of sorption (*E*) and the distribution ratio (*D*):

$$E = \frac{[M]_i - [M]_f}{[M]_i} \times 100 \quad (1)$$

$$D = \frac{[M]_i - [M]_f}{[M]_f} \times \frac{V_w}{W_m} \quad (2)$$

where $[M]_i$ and $[M]_f$ are the initial and final metal concentrations in the solution, respectively. V_w is a volume of the solution (mL), and W_m a weight of the resin (g).

RESULTS AND DISCUSSION

Sorption Behavior of Heavy Metal Thiocyanate Complexes

Figure 2 shows the sorption behavior of zinc under various thiocyanate concentrations. DB18C6 resin was found to have a considerable affinity (or capacity) to sorb zinc thiocyanate complexes. The degree of sorption (*E*) on DB18C6 resin increased with thiocyanate concentration. This suggests that complexes such as $K_{n-2}Zn(SCN)_n$ are the main species involved in the sorption. We have already reported that polymers of medium polarity such as cellulose acetate are efficient sorbents of ion-association complexes,^{7,8} and it is quite reasonable that DB18C6 resin, which is in effect a polyether polymer, exhibits such a property. However, BMPE resin, which is the corresponding open-chain polymer of DB18C6, showed only negligible capacity for the sorption of complexed zinc species. Hence the crown ether matrix is considered to work effectively for the sorption.

The effect of counter cation species on the sorption of zinc thiocyanate complexes are shown in Figure 3. It is seen that the sorption by DB18C6 resin indicates a strong dependency on the countercation species. The largest *D* value was obtained in the potassium salt system. Obviously, this reflects the presence of crown ether structure (18-crown-6) in the resin, since the interac-

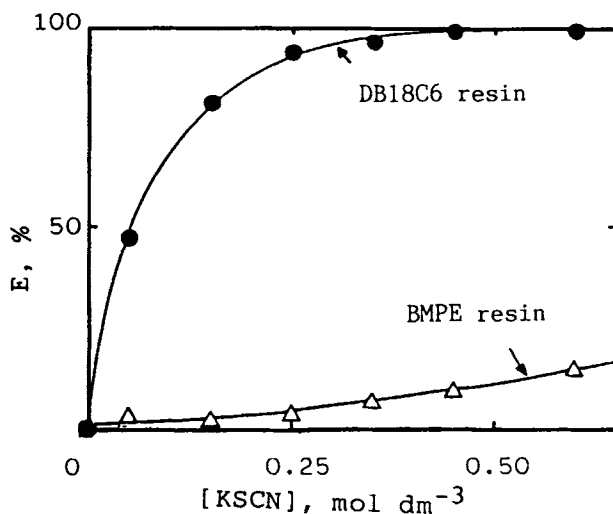


Fig. 2. Effect of potassium thiocyanate concentration on zinc sorption. Twenty milliliters of aqueous KSCN solution (pH 1.6 adjusted by HNO_3) containing $1.0 \text{ mmol dm}^{-3} \text{ Zn}(\text{NO}_3)_2$ were used. The amount of resin was 0.1 g. Sorption to DB18C6 resin (\bullet) and BMPE resin (Δ).

tion of potassium ion with DB18C6 is known to be large compared with that of other alkali metal cations.¹⁰ It is quite probable that anionic zinc thiocyanate complex and the cation in Figure 3 form an ion-association complex and become sorbed onto the polymer matrix. Recently, Hamon and co-workers described a "cation-chelation mechanism" in sorption with polyether type polyurethane foam, where a countercation selective sorption of heavy metal thiocyanate complexes was observed.⁴ The open-chain crown ethers did not

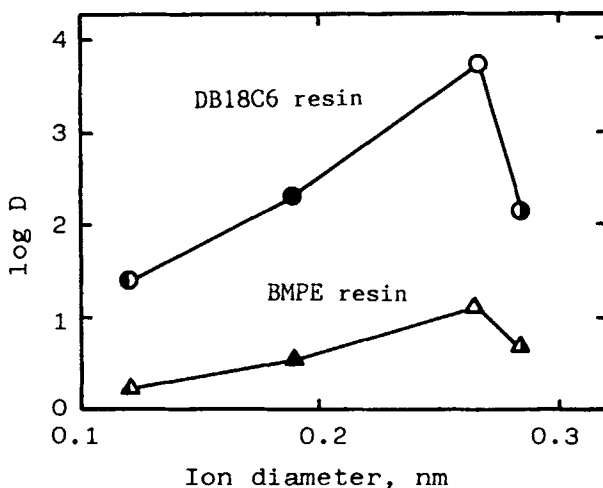


Fig. 3. Effect of counter cation species on sorption of zinc thiocyanate complex. Twenty milliliters of aqueous $0.45 \text{ mol dm}^{-3} \text{ RSCN}$ solution (pH 1.6 adjusted by HNO_3) containing $1.0 \text{ mmol dm}^{-3} \text{ Zn}(\text{NO}_3)_2$ were used. The amount of resin was 0.1 g. R: (\bullet , Δ) Li^+ ; (\bullet , \blacktriangle) Na^+ ; (\circ , Δ) K^+ ; (\bullet , Δ) NH_4^+ .

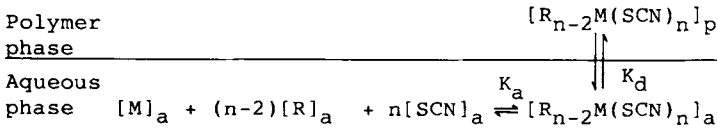


Fig. 4. Sorption equilibrium of heavy metal thiocyanate complexes.

effectively sorb the heavy metal complexes as is seen from Figures 2 and 3. Therefore, the sorption of the ion-association complex for DB18C6 resin is controlled by a countercation binding property with polymer matrix.

Mechanism of Sorption

Figure 4 shows a simplified expression of the sorption equilibrium, where the symbols M and R represent a divalent heavy metal ion and a monovalent alkali metal ion. The subscripts p and a refer to the polymer and aqueous phases, respectively. The heavy metal ions such as zinc form the thiocyanate complexes in an aqueous solution.¹³ The complex formation equilibrium are expressed as follows:

$$M + SCN = MSCN, \quad K_1 = [MSCN]_a/[M]_a[SCN]_a \quad (3-1)$$

$$MSCN + SCN = M(SCN)_2, \quad K_2 = [M(SCN)_2]_a/[MSCN]_a[SCN]_a \quad (3-2)$$

$$\vdots$$

$$M(SCN)_{m-1} + SCN = M(SCN)_m, \quad K_m = [M(SCN)_m]_a/[M(SCN)_{m-1}]_a[SCN]_a \quad (3-m)$$

where the charges are omitted for simplicity. K_m represents the m th successive complexation constant. The total concentration of heavy metal ions in the aqueous solution ($[(M)_t]_a$) is mostly expressed as a summation of the concentrations of the free heavy metal ion and the heavy metal thiocyanate complexes. Therefore, the concentration of the free heavy metal ion ($[M]_a$) is written as

$$[M]_a = [(M)_t]_a/\beta \quad (4)$$

where

$$\beta = 1 + K_1[SCN]_a + K_1K_2[SCN]_a^2 + \dots + K_1K_2 \dots K_m[SCN]_a^m \quad (5)$$

The metal distribution ratio (D) is defined conventionally as follows:

$$D = [R_{n-2}M(SCN)_n]_p/[(M)_t]_a \quad (6)$$

From eqs. (4)–(6), the distribution ratio is expressed as

$$D = [R_{n-2}M(SCN)_n]_p/\beta[M]_a \quad (7)$$

From the figure, the concentration of the sorbed species is readily derived as

$$[R_{n-2}M(SCN)_n]_p = K_aK_d[M]_a[R]_a^{n-2}[SCN]_a^n \quad (8)$$

where K_a represents a constant of overall ion-association equilibrium in the aqueous solution, and includes the successive complexation constants of the

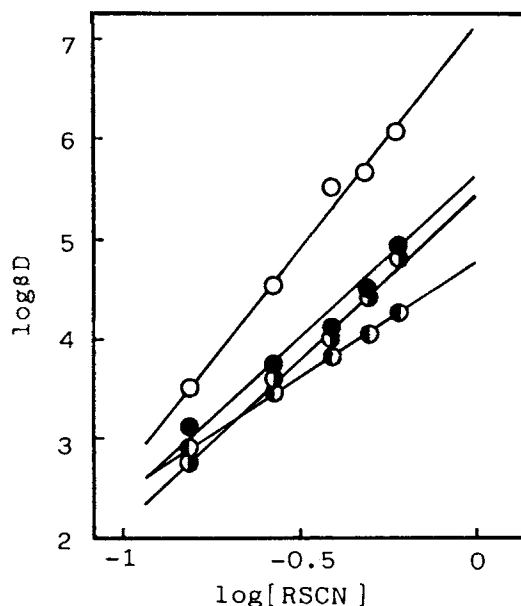


Fig. 5. Sorption of zinc thiocyanate complexes as a function of aqueous RSCN concentration. Plots according to eq. (10). Twenty milliliters of aqueous RSCN solution (pH 1.6 adjusted by HNO_3) containing $1.0 \text{ mmol dm}^{-3} \text{ Zn}(\text{NO}_3)_2$. The amount of DB18C6 resin was 0.1 g. R: (○) Li^+ ; (●) Na^+ ; (○) K^+ ; (●) NH_4^+ .

heavy metal thiocyanate complexes. K_d is a sorption constant of the ion-association complex sorbed onto the resin. From eqs. (7) and (8), the modified distribution ratio (βD) is expressed as

$$\beta D = K_a K_d [\text{R}]_a^{n-2} [\text{SCN}]_a^n \quad (9)$$

When thiocyanate salts are present in a large excess, i.e., $[(\text{R})_t]_a = [(\text{SCN})_t]_a = [(\text{RSCN})_t]_a \gg [(\text{M})_t]_a$, eq. (9) is more conveniently expressed as

$$\log \beta D = (2n - 2) \log [(\text{RSCN})_t]_a + \log K_a K_d \quad (10)$$

Equation 10 indicates that the coordination number (n) can be determined from log-log plots of βD against thiocyanate concentration.⁷ Figure 5 shows the plot for zinc thiocyanate sorption onto DB18C6 resin. The β values under various thiocyanate concentrations can be calculated by the reported values of the successive complexation constants [$\log K_m$ of Zn^{2+} : 1.5 ($m = 1$), 0.7 ($m = 2$), 0.2 ($m = 3$), -0.3 ($m = 4$)].¹³ The linear relationships are observed. The n values obtained from the slopes are summarized in Table I. It is seen that the number (n) varies with the counteranions used. This indicates that the structure of sorbed complex species is controlled by the nature of coexisting counteranion. This observation is important, since it suggests the possibility of attaining heavy metal selective sorption (and therefore heavy metal selective hyperfiltration) by changing the counteranionic components.

In the sorption to DB18C6 resin in the presence of potassium, the resin is expected to assume a nature of a "dynamic" anion exchanger because of a

TABLE I
Coordination Number (n) of Zinc Thiocyanate Complexes for DB18C6 Resin

RSCN	n	Sorbed species
KSCN	3.5	$RZn(SCN)_3, R_2Zn(SCN)_4$
NH_4SCN	2.7	$RZn(SCN)_3$
NaSCN	2.5	$RZn(SCN)_3, Zn(SCN)_2$
LiSCN	2.2	$Zn(SCN)_2$

strong interaction of potassium cations with the 18-crown-6 units in the resin. Therefore, the sorption of anionic complexes, such as $Zn(SCN)_3^-$ or $Zn(SCN)_4^{2-}$ is enhanced. On the other hand, lithium ion can have only a weak interaction with the crown ether matrix. The polymer is now no longer an anion exchanger, and a neutral complex such as $Zn(SCN)_2$ is the major species sorbed. Sodium and ammonium salts show an intermediate behavior of the two. Izatt et al. recently reported that the transport of heavy metal halogeno complexes by using dicyclohexano-18-crown-6 mediated emulsion membrane system were significantly influenced by the counter cation species.^{12,14} When magnesium thiocyanate was used as complexing salt in the source phase, only the neutral complex such as $Cd(SCN)_2$ was transported through the membrane.¹² However, in the presence of potassium salts, anionic heavy metal complexes were effectively transported.¹⁴ These results also support our findings that counter-cation-controlled sorption onto DB18C6 resin occurred.

Sorption Selectivity of Heavy Metal Thiocyanate Complexes

Sorption behavior of heavy metal thiocyanate complexes for DB18C6 resin is shown in Figure 6. The degree of sorption increases in the order, $Zn^{2+} > Fe^{3+}, Cd^{2+}, Co^{2+} > Ni^{2+}$. Similar selectivity was observed for the ion-association extraction systems.⁹ Hence the selectivity is considered to depend on the hydrophobic nature of thiocyanate complex. Zinc is complexed with thiocyanate ion as an N -coordinate form; the cadmium is complexed as a mixture of N - and S -coordinate forms. These differences affect the hydrophobic nature of heavy metal complexes and hence affect the sorption selectivity. The difference of complexation constants is also an important factor in determining the sorption selectivity. On the other hand, the counter-cation species is also considered to affect the sorption selectivity according to the sorption mechanism that was mentioned in the former sections. For the comparison, the competitive sorption of Zn^{2+} and Cd^{2+} was investigated for DB18C6 resin and anion exchange resin (CG-400). The data obtained were summarized in Table II. It is seen that the sorption selectivity for DB18C6 resin was enhanced in the binary system (Zn^{2+} and Cd^{2+} coexist in the solution) and drastically changed by the counter-cation species. The zinc thiocyanate complex was sorbed more selectively onto the DB18C6 resin in the presence of potassium ion. However, in the presence of magnesium ion, which can have little interaction with DB18C6 matrix, the degree of sorption decreased significantly. This was a typical properties of DB18C6 resin as a "dynamic" anion exchanger. Such behavior was not observed for CG-400 resin. In the case

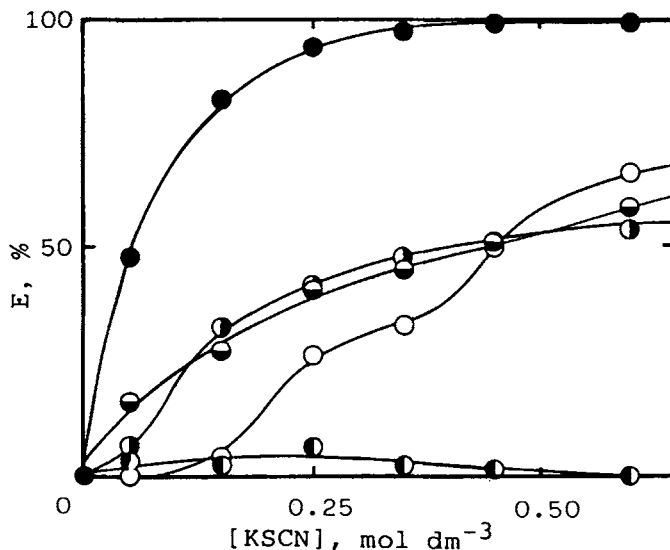


Fig. 6. Sorption behavior of heavy metal thiocyanate complexes on DB18C6 resin. Twenty milliliters of aqueous KSCN solution (pH 1.6 adjusted by HNO_3) containing 1.0 mmol dm^{-3} $\text{Zn}(\text{NO}_3)_2$. The amount of DB18C6 resin was 0.1 g. M: (●) Zn^{2+} ; (○) Co^{2+} ; (◐) Cd^{2+} ; (◑) Fe^{3+} ; (◒) Ni^{2+} .

TABLE II
Degree of Sorption (E) of Zn^{2+} and Cd^{2+} for DB18C6 Resin and CG-400 Resin^a

RSCN	[SCN] (M)	DB18C6 resin		CG-400 resin	
		Zn^{2+}	Cd^{2+}	Zn^{2+}	Cd^{2+}
	0.00	0	2	0	0
KSCN	0.25	87	1	100	91
KSCN	0.60	96	9	100	95
$\text{Mg}(\text{SCN})_2$	0.25	10	1	100	93
$\text{Mg}(\text{SCN})_2$	0.60	12	1	100	95

^a Twenty milliliters of aqueous RSCN solution (pH 1.6 adjusted by HNO_3) containing 1.0 mmol dm^{-3} $\text{Zn}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2$. The amount of resin was 0.1 g.

of CG-400 resin, both heavy metal complexes are sorbed completely on the anion exchange site regardless of the countercation species. These results indicate that the sorption selectivity is more controllable for the DB18C6 resin.

This sorption system is applicable to other metal halogeno complexes, and hence the more selective sorption would be expected. Study of the sorption for other metal halogeno complexes and the application of this system to the membrane separation are in progress.

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