The Solvent Extraction of Bivalent Metal Picrates by 15-Crown-5, 18-Crown-6, and Dibenzo-18-crown-6

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The overall extraction equilibrium constants (K_{ex}) for the 1 : 1 : 2 complexes of 15-crown-5 (15C5), 18-crown-6 (18C6), and dibenzo-18-crown-6 (DB18C6) with several bivalent metal picrates between benzene and water have been determined at 25 °C. The K_{ex} sequences of the bivalent metal ions with 15C5, 18C6, and DB18C6 are $Pb^{2+} > Sr^{2+} > Ba^{2+} > Ca^{2+}$, $Pb^{2+} \gg Ba^{2+} = Sr^{2+} > Hg^{2+} > Ca^{2+}$, and $Pb^{2+} > Hg^{2+} > Sr^{2+} > Ca^{2+}$ respectively. To clarify the role of the crown ether in the extraction process, the three constituent equilibria have been investigated: the stability and the extractability of the bivalent metal ion–crown ether complex, and the distribution coefficient of the crown ether. The extractability of the bivalent metal ion–crown ether complex about the same bivalent metal ion increases with increasing size of the crown ether, and appears to be dependent on the chemical nature of the bivalent metal ion trapped in the cavity of the crown ether.

The complex reaction between crown ethers and cations has been widely studied by different methods *e.g.* conductance,[1)] calorimetry,[2)] potentiometry,[3)] spectroscopy,[4)] and solvent extraction.[5)] It has been found that the crown ether has a remarkable capacity to form stable stoichiometric complexes with certain cations, particularly with the alkali and alkaline earths.

Solvent extraction is a useful method to investigate the complexing power of crown ethers towards cations, though it is not direct. Some solvent extraction studies of crown ether complexes with alkali metal ions have been reported,[5)] but there are very little data on bivalent metals. In terms of the analytical application, it is important to investigate the selectivity of crown ethers for various bivalent metal ions in solvent extraction systems. The present study was undertaken to determine the extraction constants for the crown ether–bivalent metal picrate systems between benzene and water, and to clarify the role of the crown ether in the extraction process. The crown ethers included in this work are 15-crown-5 (15C5), 18-crown-6 (18C6), and dibenzo-18-crown-6 (DB18C6). The sizes of these three compounds differ from one another. The cavity size of DB18C6 is equal to that of the 18C6,[3)] though the former has two benzo groups. In the cases of DB18C6 and 18C6, it is interesting to investigate the ligand ring substituent effect on the extraction equilibrium. Since a large anion is easily extracted into low dielectric constant solvents,[5d)] the picrate anion was used as the counter ion. Benzene was used as the diluent because of its nonpolar nature.

Experimental

Apparatus. Emission and absorption measurements were conducted on Seiko atomic absorption spectrophotometers, models SAS-720 and SAS-725. pH-measurements were made on a Hitachi-Horiba pH meter, model F-5.

Materials. 15C5 and 18C6 were obtained from Nisso Co., Ltd., and DB18C6 from Aldrich Chemical Co., Inc. 15C5 was used without further purification. 18C6 was recrystallized from petroleum ether twice, and dried in a vacuum oven before use. The method of purification of DB18C6 has been described in the literature.[1b)] Benzene, HNO_3, $Ca(NO_3)_2 \cdot 4H_2O$, $Sr(NO_3)_2$, $Ba(NO_3)_2$, $Hg(NO_3)_2 \cdot xH_2O$, and $Pb(NO_3)_2$ were special grade reagents from Wako-Pure Chemicals Ltd., and picric acid from Koso Chemical Co., Ltd. The purity of the bivalent metal nitrates and the concentration of the picric acid solution were determined by EDTA and basic titration, respectively. Benzene was washed twice with distilled water.

Procedure. The organic solution of the crown ether ($2 \times 10^{-5} - 3 \times 10^{-2}$ M), the aqueous solution of the bivalent metal nitrate ($5 \times 10^{-4} - 2.5 \times 10^{-2}$ M), picric acid ($1.5 \times 10^{-4} - 1.7 \times 10^{-2}$ M), and nitric acid (2×10^{-3} M) were placed in stoppered glass tubes (volume 30 ml). The initial volume of each phase was 10 ml in all cases. The two phases in the tubes were shaken in a thermostatted water bath for approx. 30 min at 25±0.2 °C, and centrifuged. An approx. 8 ml portion was removed from the aqueous phase, transferred to a 10 ml beaker and the hydrogen ion concentration determined by a pH meter. All extractions were conducted in the pH range 1.5—3.0. For the systems 15C5–Ca, Sr, Pb, and 18C6–Ca, Sr, Hg, Pb, a 8 ml portion was pipetted from the organic phase, transferred to a 50 ml beaker, and left for several days, until evaporation was complete. The residue was dissolved in 0.01 M nitric acid 8 ml, and the metal concentration determined by atomic absorption. In the 15C5 and 18C6–Ba, and DB18C6–Ca, Sr, Hg, Pb systems, the residue did not dissolve. Consequently, the bivalent metal in the organic phase was back-extracted into 1 M nitric acid 8 ml and the Ba concentration of this aqueous phase determined by flame photometry. For the 15C5–Hg system, it was impossible to extract any Hg into the organic phase. For the DB18C6–Ba system, turbidity was always found in the interface between benzene and water under all experimental conditions.

The Distribution Coefficient of the Crown Ether. A portion of the benzene solution containing the crown ether and an equal volume of distilled water were placed in a stoppered glass tube and shaken under the same conditions as before. The concentration ranges of 15C5 and 18C6 were from 5.1×10^{-2} to 3.3×10^{-1} M, and from 2.8×10^{-2} to 3.1×10^{-1} M, respectively. After the two phases had been separated by centrifuging, a portion of the organic phase 12 ml was transferred to a 10 ml beaker, left for several days until evaporation was complete, and the residue weighed. The average distribution coefficients determined in this way are listed in Table 1, together with the equilibrium constants of the bivalent metal ion–crown ether complexes.

Results

The overall extraction equilibrium between an aqueous phase containing the bivalent metal cation, M^{2+}, the picrate anion, A^-, and the hydrogen ion, H^+, and an organic phase of the crown ether, L, may be represented by the following equation:

$$M^{2+} + L_0 + 2HA_0 \rightleftarrows MLA_{2,0} + 2H^+$$

$$K_{ex} = \frac{[MLA_2]_0[H^+]^2}{[M^{2+}][L]_0[HA]_0{}^2}, \qquad (1)$$

where MLA_2 represents the ion pair between the bivalent metal–crown ether cation, ML^{2+}, and the picrate anion; the subscript "0" and the absence of subscript denote the organic phase and aqueous phase, respectively. The overall extraction equilibrium is thought to consist of the following equilibria:

○ the distribution of the free crown ether between the two phases

$$L \rightleftarrows L_0 \qquad K_{D,L} = \frac{[L]_0}{[L]}, \qquad (2)$$

○ the complex reaction of the bivalent metal ion with the crown ether

$$M^{2+} + L \rightleftarrows ML^{2+} \qquad K_{ML} = \frac{[ML^{2+}]}{[M^{2+}][L]}. \qquad (3)$$

Several stability constants of bivalent metal ion–crown ether complexes have been reported.[2a,2b,2c,4] They are listed in Table 1.

○The distribution of picric acid between the two phases

$$HA \rightleftarrows HA_0 \qquad K_{D,HA} = \frac{[HA]_0}{[HA]}, \qquad (4)$$

○ the association of picric acid

$$H^+ + A^- \rightleftarrows HA \qquad K_{HA} = \frac{[HA]}{[H^+][A^-]}, \qquad (5)$$

○ the association of the complexed cation with the picrate anion

$$ML^{2+} + 2A^- \rightleftarrows MLA_2 \qquad K_{MLA_2} = \frac{[MLA_2]}{[ML^{2+}][A^-]^2}, \qquad (6)$$

○ the distribution of the ion pair between the two phases

$$MLA_2 \rightleftarrows MLA_{2,0} \qquad K_{D,MLA_2} = \frac{[MLA_2]_0}{[MLA_2]}. \qquad (7)$$

Since benzene is a nonpolar solvent (ε=2.275 at 25 °C[6]), dissociation of the ion pair, MLA_2, has been assumed negligible. Thus,

$$K_{ex} = K_{D.L}^{-1}K_{ML}K_{D.HA}^{-2}K_{HA}^{-2}K_{ex'}, \qquad (8)$$

$$\text{where} \quad K_{ex'} = K_{MLA_2}K_{D.MLA_2} = \frac{[MLA_2]_0}{[ML^{2+}][A^-]^2}. \qquad (9)$$

The all-activity coefficients of the chemical species in this work have been assumed as unity.

The distribution ratio of the bivalent metal has been defined as follows and calculated from the experimental data,

$$D_M = \frac{[M]_{0,total}}{[M]_{total}},$$

where $[M]_{0,total}$ and $[M]_{total}$ are the total bivalent metal concentrations in the organic and aqueous phases, respectively. Assuming that the association between ML^{2+} and A^- is negligible in the aqueous phase;

$$D_M = \frac{[MLA_2]_0}{[M^{2+}]+[ML^{2+}]}. \qquad (10)$$

In the case of $[M^{2+}] \gg [ML^{2+}]$, Eq. 10 becomes

$$D_M = K_{ex}K_{HA}^2K_{D.HA}^2[A^-]^2[L]_0, \qquad (11)$$

where $K_{HA}K_{D,HA}$ is the extraction equilibrium constant of picric acid. The value of $K_{HA}K_{D,HA}$ in the benzene–water system at 25 °C has been determined to be 247 by spectroscopy using the association constant of picric acid, K_{HA}=1.95.[7] $[A^-]$ in Eq. 11 was calculated from Eq. 12, for the systems of 15C5–Sr, Ba, Pb, and 18C6–Sr, Ba, Hg, Pb, $[L]_0$ in Eq. 11 from Eq. 13 using the stability constants, $K_{ML'}$[2b] given in Table 2, and for the others $[L]_0$ by Eq. 14.

$$[A^-] = \frac{[HA]_{i.t.} - 2[MLA_2]_0}{1+(1+K_{D,HA})K_{HA}[H^+]}, \qquad (12)$$

$$[L]_0 = \frac{[L]_{i.t.} - [MLA_2]_0}{1+K_{D.L}^{-1}+K_{ML}K_{D.L}^{-1}[M^{2+}]}, \qquad (13)$$

$$[L]_0 = \frac{[L]_{i.t.} - [MLA_2]_0}{1+K_{D.L}^{-1}}, \qquad (14)$$

where $[HA]_{i.t.}$ and $[L]_{i.t.}$ are the initial total concentrations of picric acid and crown ether, respectively. $\log(D_M/[A^-]^2)$ *vs.* $\log[L]_0$ plots are illustrated in Figs. 1—3. Figures 1, 2, and 3 correspond to 15C5, 18C6, and DB18C6 respectively. From Figs. 1—3 it may be seen that the plots are linear with a slope of unity. $\log(D_M/[L]_0)$ *vs.* $\log[A^-]$ curves in Fig. 4 are linear with a slope of 2. It has then been concluded that the overall

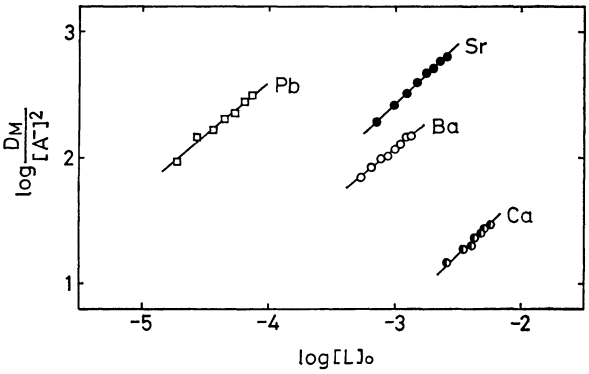

Fig. 1. Plots of $\log(D_M/[A^-]^2)$ *vs.* $\log[L]_0$ for the 15C5 system at 25 °C.

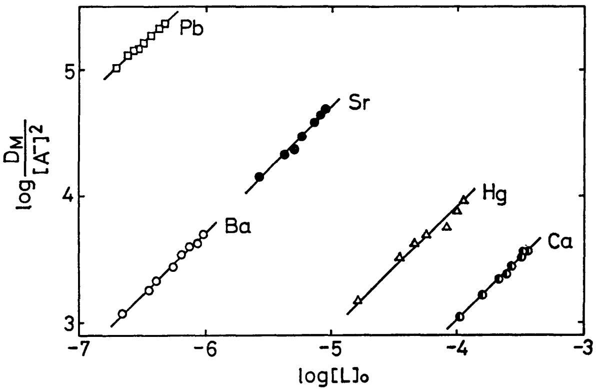

Fig. 2. Plots of $\log(D_M/[A^-]^2)$ *vs.* $\log[L]_0$ for the 18C6 system at 25 °C.

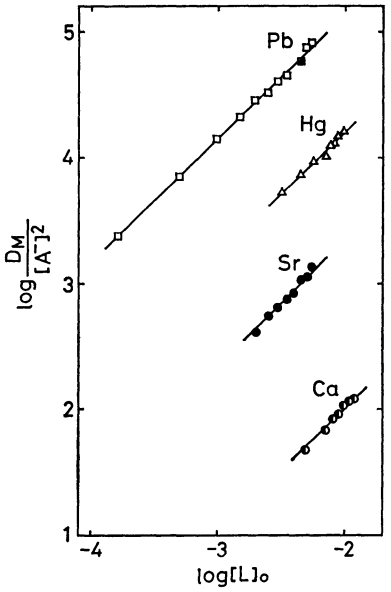

Fig. 3. Plots of log(D_M/[A^-]^2) *vs.* log[L]$_0$ for the DB18C6 system at 25 °C.

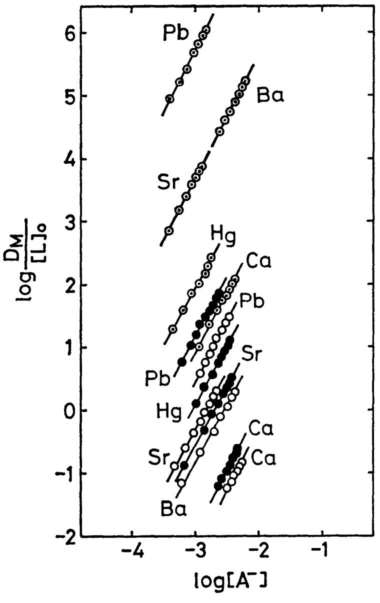

Fig. 4. Plots of log(D_M/[L]$_0$) *vs.* log[A^-] at 25 °C.
○: 15C5, ⊙: 18C6, ●: DB18C6.

extraction equilibrium, K_{ex}, in the present study is described by Eq. 1. For each system the value of the overall extraction equilibrium constant calculated from the data of Figs. 1—3 was found to agree well with that of Fig. 4. The K_{ex} values are given in Table 1.

Table 1. Equilibrium constants at 25 °C

Crown ether	$K_{D,L}$	Cation	logK_{ex}	logK_{ML}	log$K_{ex'}$
15C5	0.15_6	Ca^{2+}	−1.07	—	—
		Sr^{2+}	0.91	1.95[2b)]	2.94
		Ba^{2+}	0.41	1.71[2b)]	2.68
		Pb^{2+}	1.67	1.85[2b)]	3.80
18C6	0.063_4	Ca^{2+}	2.24	<0.5[2b)]	>5.33
		Sr^{2+}	4.93	2.72[2b)]	5.80
		Ba^{2+}	4.93	3.87[2b)]	4.65
		Hg^{2+}	3.18	2.42[2b)]	4.34
		Pb^{2+}	6.96	4.27[2b)]	6.28
DB18C6	800[5c)]	Ca^{2+}	−0.78	<0[4)]	>7.39
		Sr^{2+}	0.59	1.00[4)]	7.28
		Hg^{2+}	1.43	—	—
		Pb^{2+}	2.37	1.89[4)]	8.17

Table 2. Crystal ionic radii of bivalent metals and cavity radii of crown ethers (Å)

Cation	Crystal ionic radius	Crown ether	Cavity radius[3)]
Ca^{2+}	0.99[8)]	15-crown-5	0.85—1.1
Sr^{2+}	1.13[8)]	18-crown-6	1.3 —1.6
Ba^{2+}	1.35[8)]		
Hg^{2+}	1.10[8)]		
Pb^{2+}	1.20[9)]		

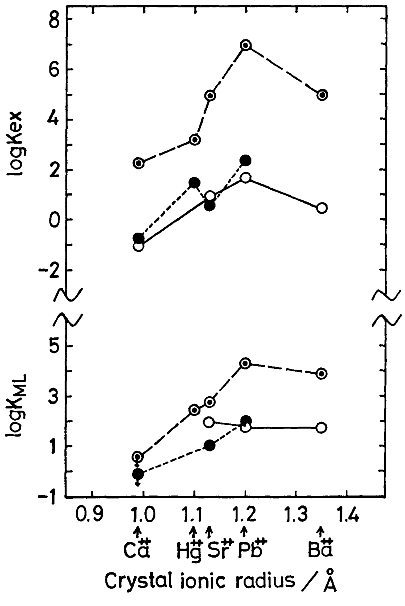

Fig. 5. Plots of logK_{ex} and logK_{ML} *vs.* crystal ionic radius of bivalent metal.
○: 15C5, ⊙: 18C6, ●: DB18C6.

Discussion

The crystal ionic radii of the bivalent metals and the cavity radii of the crown ethers are listed in Table 2. It may be noted from Tables 1 and 2 that for the 18C6 system logK_{ex} for Sr^{2+} is identical with that of Ba^{2+} which has a more optimum size for the 18C6 cavity than Sr^{2+}. The logK_{ex} and logK_{ML} values have been plotted *vs.* the crystal ionic radius in Fig. 5. As can be seen from Fig. 5, the logK_{ex} value of Ca^{2+}, whose crystal radius is much smaller than the cavity radius of 18C6 in comparison with the other bivalent metal ions (Table 2), is smallest for the 18C6 and the DB18C6 systems. For the 15C5 system, although the crystal radius of Ca^{2+} is nearly equal to the cavity radius of 15C5 (Table 2), the logK_{ex} value of Ca^{2+} is also the smallest. The size of Pb^{2+} is larger than the cavity size of 15C5, and Ba^{2+} fits more closely into the 18C6 cavity than Pb^{2+} (Table 2). In Fig. 5 however, 15C5 and 18C6 show the largest

$\log K_{ex}$ value for Pb^{2+}.

The most pronounced substituent effect of the two benzo groups attached to 18C6 on the extractability of Hg^{2+} and Sr^{2+} can be seen in Fig. 5, *i.e.* the $\log K_{ex}$ sequence for Hg^{2+} and Sr^{2+} with 18C6 is $Hg^{2+} < Sr^{2+}$, while that with DB18C6 is $Hg^{2+} > Sr^{2+}$, although the crystal radii of Hg^{2+} (1.10 Å[8]) and Sr^{2+} (1.13 Å[8]) are nearly equal.

From the data it appears that the ratio of the size of the bivalent metal ion to that of the crown ether cavity is not always the dominant factor in the extractability of the bivalent metal-crown ether picrate complex.

Equation 8 shows that the trend for K_{ex} for the same crown ether and different bivalent metal ions reflects the stability and the extractability of the bivalent metal ion–crown ether complex in the aqueous phase. The $\log K_{ex'}$ values calculated from Eq. 8 are given in Table 1. It is interesting that in each crown ether system the largest $\log K_{ex'}$ value is seen for Pb^{2+}. Table 1 shows that in the case of 15C5, the $\log K_{ex}$ sequence of Sr^{2+} and Ba^{2+} is $Sr^{2+} > Ba^{2+}$ and this sequence is determined by both the $\log K_{ML}$ and the $\log K_{ex'}$ sequences, and that the largest $\log K_{ex}$ value for Pb^{2+} is largely attributed to the largest $\log K_{ex'}$ value. In the case of 18C6 the larger $\log K_{ex'}$ value for Sr^{2+} entirely contributes to the larger and equal extractability of Sr^{2+} compared to Hg^{2+} and Ba^{2+}, respectively. It may be noted from Fig. 5 and Table 1 that for the 18C6–all the bivalent metal ions and the DB18C6–Ca^{2+}, Sr^{2+}, and Pb^{2+} systems, the $\log K_{ex}$ sequences largely depend on $\log K_{ML}$. The most remarkable extraction selectivities of 18C6 and DB18C6 for Pb^{2+} are due to the high stability and high extractability of the Pb^{2+}–crown ether complex.

The considerably different $\log K_{ex'}$ values for the bivalent metal ions about the same crown ether can be seen from Table 1, suggesting that the extractability of the bivalent metal ion–crown ether complex is not necessarily independent of the chemical nature of the bivalent metal ion trapped in the cavity of the crown ether.

Among the crown ethers, the $\log K_{ex'}$ value series about Sr^{2+} and Pb^{2+} are in the order 15C5<18C6<DB18C6, and about Ca^{2+} and Ba^{2+} 18C6<DB18C6 and 15C5<18C6, respectively (Table 1). The size sequences of the crown ethers are 15C5<18C6<DB18C6. These results indicate that the $\log K_{ex'}$ value of the same bivalent metal ion increases with an increase in the size of the crown ether.

The distribution coefficient of the crown ether, $K_{D,L}$, in Eq. 8 is also an important factor which determines the magnitude of K_{ex} for bivalent metal ions. Table 1 shows that about the same bivalent metal ion the difference between the $\log K_{ML}$ value of 15C5 and that of DB18C6 is not great and the difference in $\log K_{D,L}$ values of DB18C6 and 15C5 is comparable to that in $\log K_{ex'}$ value of DB18C6 and 15C5, indicating that the $\log K_{ex}$ values for 15C5 and DB18C6 are nearly identical (Fig. 5). About the same bivalent metal ion, the $\log K_{ML}$ value for 18C6 is larger than the others; the $\log K_{ex'}$ value of 18C6 is much larger than that of 15C5, and moreover the $\log K_{D,L}$ value of 18C6 is smaller than that of 15C5; the $\log K_{ex'}$ value of 18C6 is very small compared with DB18C6, however, the $\log K_{D,L}$ value of 18C6 is exceedingly small compared with DB18C6, indicating that the $\log K_{ex}$ value of 18C6 is consistently much larger than the others (Fig. 5).

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