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Solvent Extraction of Uni- and Bivalent Metal Picrates with 16-Crown-5 into Benzene

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Distribution constant ($K_{\mathrm{D,L}}$) of 16-crown-5 (16C5) and overall extraction equilibrium constants (K_{ex}) of uni- and bivalent metal picrates with 16C5 were determined between benzene and water at 25 °C. The K_{ex} values were analyzed by four fundamental equilibria, extraction constant of picric acid, $K_{\mathrm{D,L}}$, formation constant in water and ion-pair extraction constant ($K_{\mathrm{ex,ip}}$) with a picrate ion of the 16C5–metal ion complex. The K_{ex} value of 16C5 for the uni- and bivalent metal ions decreases in the order $\mathrm{Ag^+ > Na^+ > Tl^+ > K^+ > Rb^+ > Cs^+ > Li^+}$ and $\mathrm{Pb^{2+} > Ba^{2+} \geq Sr^{2+} > Ca^{2+}}$, respectively. Size-fit relationship holds for extraction-selectivity of 16C5 toward alkali metal ions, but it does not hold for that toward alkaline earth metal ions. Factors influencing extractability and extraction-selectivity of 16C5 for metal ions were discussed from the viewpoint of molecular grounds. $K_{\mathrm{ex,ip}}$ value of 16C5 varies with a cation of the same charge held in the cavity. $K_{\mathrm{ex,ip}}$ values of 16C5–metal picrate complexes were compared with those of 15-crown-5–metal picrate complexes. Various effects on ion-pair extractability of a 16C5–metal ion complex with a picrate anion were explained.

16-Crown-5 (16C5) and 15-crown-5 (15C5) have the same number of donor oxygen atoms. However, 15C5 has a symmetrical structure, whereas 16C5 has a less symmetrical structure, which is caused by an introduction of an extra methylene group into the 15C5 ring. It has been reported that 16C5 shows much higher selectivity for $\mathrm{Na^+}$ among alkali metal ions than 15C5 in both homogeneous[1)] and liquid–liquid extraction systems.[2)] The higher selectivity of 16C5 for $\mathrm{Na^+}$ was explained in terms of cavity size and orientation of the donor oxygen atoms through examination of CPK molecular models; namely, $\mathrm{Na^+}$ is better accommodated in the cavity of 16C5 than in the cavity of 15C5, and the donor oxygen atoms of 16C5 arrange more nicely around $\mathrm{Na^+}$ compared with 15C5.

In this study, in order to clarify the role of 16C5 in the metal ion-extraction process, overall extraction equilibrium constants of uni- and bivalent metal picrates with 16C5 were determined between benzene and water at 25 °C and analyzed by four constituent equilibria. The data on 16C5 were compared in detail with those of 15C5.

Experimental

Materials. The preparation of 16C5 was just the same as that described in the previous paper.[2a)] Benzene, picric acid, $\mathrm{LiOH \cdot H_2O}$, NaOH, KOH, $\mathrm{AgNO_3}$, $\mathrm{TlNO_3}$, $\mathrm{Mg(NO_3)_2 \cdot 6H_2O}$, $\mathrm{Ca(NO_3)_2 \cdot 4H_2O}$, $\mathrm{Sr(OH)_2 \cdot 8H_2O}$, $\mathrm{Ba(OH)_2 \cdot 8H_2O}$, and $\mathrm{Pb(NO_3)_2}$ were analytical-grade reagents. Rubidium and caesium hydroxides were reagent-grade. Benzene was washed three times with distilled water. The purities of $\mathrm{AgNO_3}$ and the other nitrates were determined by KCl and EDTA titrations, respectively. The concentrations of solutions of the hydroxides and picric acid were determined by neutralization titration.

The experimental procedures were almost the same as those described in previous papers.[3,4)] Extractions were conducted at 25±0.2 °C. Concentrations of 16C5, metal salts, and picric acid were 2.8×10^{-5}—7.9×10^{-2} M (1 M = 1 mol dm^{-3}), 4.1×10^{-3}—1.8×10^{-1} M, and 3.3×10^{-3}—1.1×10^{-2} M, respectively. For nitrate and Cs systems, the extractions were carried out at pH 2.2—2.9. For all the other systems, the extractions were performed at pH 6.8—12.1.[§] Concentrations of extracted Li, Na, K, Sr, and Ba were determined by a UV-spectrophotometer; those of extracted Rb, Cs, Ag, Tl, Ca, and Pb were determined by an atomic absorption spectrophotometer. It was impossible to extract any Mg into the benzene phase.

The Distribution Coefficient of 16C5. A 13 ml benzene solution of 16C5 (2.6×10^{-5}—1.5×10^{-3} M) and an equal volume of distilled water in a stoppered glass tube (volume 30 ml) were shaken in a thermostated water bath at 25±0.2 °C for 2 h and centrifuged. A portion 12 ml of the benzene phase and an equal volume of an aqueous solution (pH 10.7—11.3) containing NaOH (1.1×10^{-1} M) and picric acid (1.0×10^{-1} M) were placed in a stoppered glass tube (No. 1), agitated, and centrifuged. A portion $(12-2n)$ ml of the aqueous phase in the stoppered glass tube (No. n) and an equal volume of benzene were placed in a stoppered glass tube (No. $(n+1)$), shaken, and centrifuged. This procedure was repeated until $n=4$. The picrate in the benzene phase in the stoppered glass tube (No. n) was back-extracted into $(12-2n)$ ml of 0.01 M NaOH aqueous solution (volume ratio 1:1), and the picrate concentration was determined spectrophotometrically ($\lambda_{\mathrm{max}}=356$ nm, $\varepsilon=1.45\times10^{4}$ cm^{-1} M^{-1}). This procedure was repeated until $n=5$. The total concentration of the extracted 16C5–sodium picrate complex in a series of these extractions was calculated. The total concentration of the extracted 16C5 complex was assumed to be equal to the concentration of 16C5 which distributed itself into the 13 ml benzene phase. The distribution coefficient value of 16C5 is 0.397±0.004, which is the average of 22 measurements.

Results

In an equilibrium between a benzene solution of a

[§] These experiments were designed to study extraction of a 1:1 16C5:metal ion complex with a picrate ion.

crown ether (L) and an aqueous solution of a metal ion (M^{m+}) and a picrate ion (A^-), the equilibrium constants are defined as

$$K_{ex} = [MLA_m]_o[H^+]^m/[M^{m+}][L]_o[HA]_o^m, \tag{1}$$

$$K_{D,L} = [L]_o/[L], \tag{2}$$

$$K_{ex}(HA) = [HA]_o/[H^+][A^-], \tag{3}$$

$$K_{ML} = [ML^{m+}]/[M^{m+}][L], \tag{4}$$

$$K_{ex,ip} = [MLA_m]_o/[ML^{m+}][A^-]^m, \tag{5}$$

where the subscript "o" and the lack of subscript denote the organic and the aqueous phase, respectively. The overall extraction equilibrium constant (K_{ex}) can be written as

$$K_{ex} = K_{ML}K_{ex,ip}K_{D,L}^{-1}K_{ex}(HA)^{-m}. \tag{6}$$

The distribution ratio of the metal is represented by

$$D = [MLA_m]_o/([M^{m+}] + [ML^{m+}]). \tag{7}$$

In the case of $[M^{m+}] \gg [ML^{m+}]$, Eq. 7 is transformed into

$$D = K_{ex}K_{ex}(HA)^m[L]_o[A^-]^m. \tag{8}$$

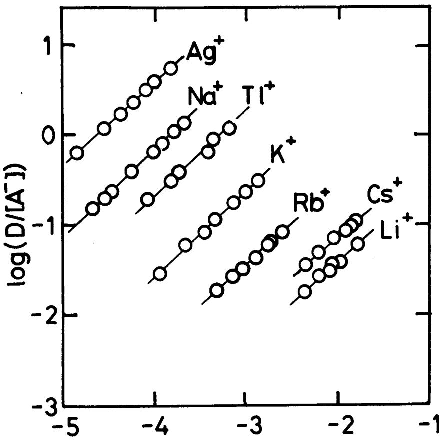

Fig. 1. Plots of $\log(D/[A^-])$ vs. $\log[L]_o$ for 16C5–univalent metal picrate systems at 25 °C.

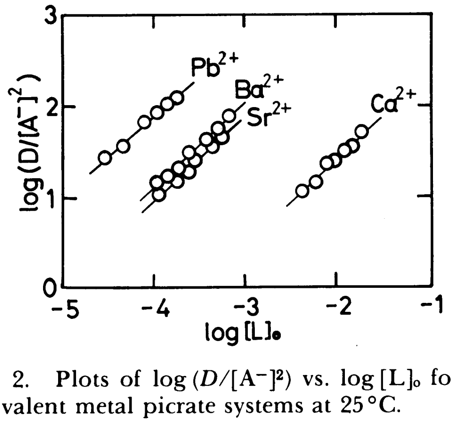

Fig. 2. Plots of $\log(D/[A^-]^2)$ vs. $\log[L]_o$ for 16C5–bivalent metal picrate systems at 25 °C.

For the univalent metal ion system, $\log(D/[A^-])$ vs. $\log[L]_o$ plot in Fig. 1 shows a straight line with a slope of 1 in every case. This indicates that 16C5 forms a 1:1 complex with the univalent metal ion. For the bivalent metal ion system, $\log(D/[A^-]^2)$ vs. $\log[L]_o$ plot in Fig. 2 always shows a line with a slope of 1. This indicates that 16C5 forms a 1:1 complex with the bivalent metal ion.

From the mass balances, $[L]_o$, $[M^{m+}]$, and $[HA]_o$ are given by

$$[L]_o = ([L]_t - [MLA_m]_o)/(\alpha + \beta[M^{m+}]), \tag{9}$$

$$[M^{m+}] = ([M]_t - [MLA_m]_o)/(1 + \beta[L]_o), \tag{10}$$

$$[HA]_o = ([HA]_t - m[MLA_m]_o)/\{1 + ([H^+]^{-1} + K_{HA})K_{ex}(HA)^{-1}\}, \tag{11}$$

where the subscript "t" denotes the total concentration, $\alpha = 1 + K_{D,L}^{-1}$, and $\beta = K_{ML}K_{D,L}^{-1}$. For all the systems except for the cases of Li^+, Rb^+, Cs^+, and Ca^{2+}, K_{ex} values were determined by using $[L]_o$ values of Eq. 9, $[M^{m+}]$ values of Eq. 10, and $[HA]_o$ values of Eq. 11; for the Li^+, Rb^+, Cs^+, and Ca^{2+} systems, K_{ex} values were determined, neglecting the terms, $\beta[M^{m+}]$ of Eq. 9 and $\beta[L]_o$ of Eq. 10. Values of $K_{ex}(HA)$ and K_{HA} at 25 °C are 247[3] and 1.9_5,[5] respectively, where K_{HA} is an association constant of picric acid in water and $K_{HA} = [HA]/[H^+][A^-]$. Equilibrium constants are summarized in Table 1.

Discussion

$\log K_{D,L}$ values at 25 °C of 12-crown-4 (12C4), 15C5, and 18-crown-6 (18C6) between benzene and water are -0.82,[8] -0.80_6,[3,4] and -1.19_8,[3,4] respectively. From $\log K_{D,L}$ values of 12C4, 15C5, 18C6, and 16C5, the contribution of an ether oxygen atom to $\log K_{D,L}$ (Π_o) at 25 °C between benzene and water can be evaluated by using the Π_{CH_2} value (0.48_5[9]), where Π_{CH_2} is the contribution of a methylene group to extraction constants of ion pairs of tetraalkylammonium ions with picrate anions at 25 °C between benzene and water; namely, $\Pi_o = (\log K_{D,L} - \Pi_{CH_2} \times a)/b$, a and b denoting the number of methylene groups and ether oxygen atoms, respectively. Π_o values are -1.17, -1.13_1, -1.16_9, and -1.147 for 12C4, 15C5, 18C6, and 16C5, respectively. They are nearly equal. The Π_o value is -1.15 on the average. From these empirical parameters, the $\log K_{D,L}$ value of 16C5 at 25 °C between benzene and water can be estimated to be -0.41_5. This is in accord with the experimental $\log K_{D,L}$ value of 16C5 (-0.401 ± 0.004).

The difference in $\log K_{D,L}$ values between 16C5 and

Table 1. Summary of Equilibrium Constants at 25 °C

Crown ether	$\log K_{D,L}$	Cation	Ionic radius (Å)[a]	$\log K_{ex}$	$\log K_{ML}$	$\log K_{ex,ip}$
16C5	−0.401±0.004	Li^+	0.74	−1.74±0.02	—	—
		Na^+	1.02	1.474±0.005	0.78[6]	2.68
		K^+	1.38	0.041±0.009	0.4[6]	1.63
		Rb^+	1.49	−0.84±0.01	—	—
		Cs^+	1.70	−1.49±0.03	—	—
		Ag^+	1.15	2.235±0.009	1.10[6]	3.13
		Tl^+	1.50	0.96±0.02	0.73[6]	2.22
		Ca^{2+}	1.00	−1.26±0.06	—	—
		Sr^{2+}	1.13	0.00±0.03	2.08[6]	2.61
		Ba^{2+}	1.36	0.07±0.02	1.84[6]	2.92
		Pb^{2+}	1.19	1.16±0.03	0.74[6]	4.81
15C5	-0.80_6[3,4]	Li^+		−1.10[4]	—	—
		Na^+		1.51[4]	0.70[7]	2.40[4]
		K^+		0.19[4]	0.74[7]	1.04[4]
		Rb^+		−0.25[4]	0.62[7]	0.72[4]
		Cs^+		−0.49[4]	0.8[7]	0.30[4]
		Ag^+		2.06[4]	0.94[7]	2.71[4]
		Tl^+		1.41[4]	1.23[7]	1.77[4]
		Ca^{2+}		−1.07[3]	—	—
		Sr^{2+}		0.91[3]	1.95[7]	2.94[3]
		Ba^{2+}		0.41[3]	1.71[7]	2.68[3]
		Pb^{2+}		1.67[3]	1.85[7]	3.80[3]

a) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B,* **25**, 925 (1969).

15C5 corresponds to Π_{CH_2}. It is interesting that the difference (0.40_5) between the two neutral crown ethers is consistent with the Π_{CH_2} value (0.48_5) determined by ion-pair extraction constants of tetraalkylammonium picrates.

Table 1 shows that $\log K_{ex}$ value of 16C5 for the univalent metal ions decreases in the order $Ag^+ > Na^+ > Tl^+ > K^+ > Rb^+ > Cs^+ > Li^+$. This indicates that, for the alkali metal ions, the more closely the metal ion fits into the 16C5 cavity (cavity radius 0.9 Å[1]), the more extractable the 16C5-metal ion complex is (size-fit concept); Ag^+, which has a more favorable size for the 16C5 cavity than Tl^+, is more extractable with 16C5 than Tl^+. The $\log K_{ex}$-value sequence of 16C5 for the univalent metal ions is identical with that of 15C5. However, 16C5 shows higher extraction selectivity for Ag^+ and Na^+ than for the other univalent metal ions, compared with 15C5; furthermore, extraction selectivity of 16C5 is higher for Ag^+ than for Na^+, compared with 15C5. For univalent metals M_1 and M_2, and crown ethers L_1 and L_2, $\Delta(\Delta\log K_{ex}(M_1-M_2))(L_1-L_2)$, $\Delta(\Delta\log K_{ML}(M_1-M_2))(L_1-L_2)$, and $\Delta(\Delta\log K_{ex,ip}(M_1-M_2))(L_1-L_2)$ are defined as follows; $\Delta(\Delta\log K_{ex}(M_1-M_2))(L_1-L_2) = (\Delta\log K_{ex}(M_1-M_2))_{L_1} - (\Delta\log K_{ex}(M_1-M_2))_{L_2}$, where $(\Delta\log K_{ex}(M_1-M_2))_L = (\log K_{ex}(M_1))_L - (\log K_{ex}(M_2))_L = (\Delta\log K_{ML}(M_1-M_2))_L + (\Delta\log K_{ex,ip}(M_1-M_2))_L$, where $(\Delta\log K_{ML}(M_1-M_2))_L = \log K_{M_1L} - \log K_{M_2L}$ and $(\Delta\log K_{ex,ip}(M_1-M_2))_L = (\log K_{ex,ip}(M_1))_L - (\log K_{ex,ip}(M_2))_L$, where $(\log K_{ex}(M))_L$ and $(\log K_{ex,ip}(M))_L$ are $\log K_{ex}$ and $\log K_{ex,ip}$ of a L-MA complex, respectively. $\Delta(\Delta\log K_{ML}(M_1-M_2))(L_1-L_2) = (\Delta\log K_{ML}(M_1-M_2))_{L_1} - (\Delta\log K_{ML}(M_1-M_2))_{L_2}$. $\Delta(\Delta\log K_{ex,ip}(M_1-M_2))(L_1-L_2) = (\Delta\log K_{ex,ip}(M_1-M_2))_{L_1} - (\Delta\log K_{ex,ip}(M_1-M_2))_{L_2}$. Thus, $\Delta(\Delta\log K_{ex}(M_1-M_2))(L_1-L_2) = \Delta(\Delta\log K_{ML}(M_1-M_2))(L_1-L_2) + \Delta(\Delta\log K_{ex,ip}(M_1-M_2))(L_1-L_2)$. Both positive $\Delta(\Delta\log K_{ML}(Ag-Na))(16C5-15C5)$ and $\Delta(\Delta\log K_{ex,ip}(Ag-Na))(16C5-15C5)$ values are responsible for higher extraction selectivity of 16C5 for Ag^+ than for Na^+, compared with 15C5.[§§] 16-Crown-5 shows higher extraction selectivity for Ag^+ or Na^+ than for Tl^+ and K^+ in comparison with 15C5. This is attributed to the fact that, although $\Delta(\Delta\log K_{ex,ip}(M_1-M_2))(L_1-L_2)$ value is negative, $\Delta(\Delta\log K_{ML}(M_1-M_2))(L_1-L_2)$ value is positive and $\Delta(\Delta\log K_{ML}(M_1-M_2))(L_1-L_2)$ is larger than $|\Delta(\Delta\log K_{ex,ip}(M_1-M_2))(L_1-L_2)|$ (M_1=Ag or Na; M_2=Tl or K; L_1=16C5 and L_2=15C5). From the above discussion, it can be concluded that higher extraction selectivity of 16C5 for Ag^+ than for Na^+, Tl^+, and K^+ and that for Na^+ than for Tl^+ and K^+ in comparison with 15C5 are dependent on higher selectivity in water of 16C5 for Ag^+ than for Na^+, Tl^+, and K^+ and that for Na^+ than for Tl^+ and K^+, compared with 15C5, respectively.

$\log K_{ex}$-, $\log K_{ML}$-, and $\log K_{ex,ip}$-value sequences of 16C5 for Na^+, K^+, Ag^+, and Tl^+ are identical ($Ag^+ > Na^+ > Tl^+ > K^+$), whereas it does not hold for

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[§§] Detailed explanations are as follows. The difference in $\log K_{ML}$ values of 16C5 between Ag^+ and Na^+ (0.32) is larger than the corresponding difference of 15C5 (0.24). The difference in $\log K_{ex,ip}$ values of 16C5 between Ag^+ and Na^+ (0.45) is larger than the corresponding difference of 15C5 (0.31). These two positive contributions are responsible for the fact that the difference in $\log K_{ex}$ values of 16C5 between Ag^+ and Na^+ (0.761) is larger than the corresponding difference of 15C5 (0.55).

15C5.

For a given metal ion, the following relationship can be derived from Eq. 6;

$$\log\{K_{ex}(L_1)/K_{ex}(L_2)\} = \log(K_{ML_1}/K_{ML_2}) + \log\{K_{ex,ip}(L_1)/K_{ex,ip}(L_2)\} - \log(K_{D,L_1}/K_{D,L_2}). \quad (12)$$

16-Crown-5 shows lower extractability for the univalent metal ion except for Ag^+ than does 15C5 (Table 1). For Na^+, K^+, and Tl^+, this is ascribed to the fact $\log(K_{D,L_1}/K_{D,L_2}) > \log(K_{ML_1}/K_{ML_2}) + \log\{K_{ex,ip}(L_1)/K_{ex,ip}(L_2)\}$; greater extractability of 16C5 for Ag^+ than that of 15C5 is attributable to the fact that $\log\{K_{ex,ip}(L_1)/K_{ex,ip}(L_2)\} > \log(K_{D,L_1}/K_{D,L_2})$ and the $\log(K_{ML_1}/K_{ML_2})$ value is positive, where L_1=16C5 and L_2=15C5.

$\log K_{ex}$-value sequences of 16C5 for the bivalent metal ions are $Pb^{2+} > Ba^{2+} \geq Sr^{2+} > Ca^{2+}$ (Table 1). The size-fit concept does not hold for the extractability of 16C5 for the alkaline earth metal ions. Although stability of the 16C5–Pb^{2+} complex in water is much lower than that of 16C5–Sr^{2+} and Ba^{2+} complexes, the 16C5–Pb^{2+} complex is the most extractable among all the 16C5–bivalent metal ion complexes. This is entirely due to much the largest $\log K_{ex,ip}$ value of the 16C5–Pb^{2+} complex. $\log K_{ex}$-value sequence of 16C5 for the bivalent metal ions except for Ba^{2+} is identical with that of 15C5. The value of $(\Delta\log K_{ML}(Sr-Ba))_L + (\Delta\log K_{ex,ip}(Sr-Ba))_L$ is negative when L=16C5 and positive when L=15C5, which are responsible for the slightly larger $\log K_{ex}$ value of Ba^{2+} of 16C5 than that of Sr^{2+} and the smaller $\log K_{ex}$ value of Ba^{2+} of 15C5 than that of Sr^{2+}, respectively.

Extractability of 16C5 for the bivalent metal ion is lower than that of 15C5. It can be seen from Table 1 and Eq. 12 that, for Sr^{2+}, Ba^{2+}, and Pb^{2+}, the term $\log(K_{D,L_1}/K_{D,L_2})$ plays a very important role in the lower extractability of 16C5 compared with 15C5, where L_1=16C5 and L_2=15C5; namely, the smaller $\log K_{ex}$ value of 16C5 than that of 15C5 is largely or completely due to the higher lipophilicity of 16C5 compared with 15C5.

$\log K_{ex,ip}$ value of 16C5 varies with a cation of the same charge (Table 1). The same trend is found for 15C5.

From Gibbs free energies of hydration ($\Delta G_h°$/kJ mol^{-1}) of Na^+ (−411.3) and K^+ (−338),[10] the interaction of Na^+ with water is much stronger than that of K^+. The interaction with water of Na^+ trapped in the 16C5 cavity is expected to be stronger than that of K^+. Association constant of Na^+ with a picrate ion in water is smaller than that of K^+.[11] Association constant with a picrate ion of Na^+ trapped in the 16C5 cavity is expected to be smaller than that of K^+. Hence, $K_{ex,ip}$ value of the Na^+–16C5 complex is anticipated to be smaller than that of the K^+ complex. However, $K_{ex,ip}$ value of 16C5 is larger for Na^+ than for K^+ (Table 1). From the structure of the 16C5 complex with the univalent metal ion trapped in the cavity, anion- and solvent-contact are possible in respective directions perpendicular to the plane of the 16C5 ring. Consequently, it is concluded from the above discussion that the larger $K_{ex,ip}$ value of the Na^+–16C5 complex than that of the K^+ complex is ascribed to negligible effect of water on association of the Na^+–16C5 complex with a picrate ion and/or weak interaction with water of the Na^+ complex. The same discussion holds for the cases of 15C5–Na^+ and -K^+ complexes. A Na^+ ion has a more suitable size for the 16C5 cavity than does a Ag^+ ion; $-\Delta G_h°$ of Ag^+ (479.1 kJ mol^{-1})[10] is larger than that of Na^+; but, $K_{ex,ip}$ value of 16C5 is greater for Ag^+ than for Na^+. The larger $K_{ex,ip}$ value of the Ag^+–16C5 complex may be attributed to the specific interaction with benzene of the Ag^+ ion[12] in the 16C5 complex and stronger association with a picrate ion and/or weaker interaction with water of the Ag^+ complex compared with the case of the Na^+ complex. The same discussion holds for the cases of 15C5–Na^+ and -Ag^+ complexes.

For a crown ether–bivalent metal ion complex, two picrate anion-contacts with the cation are possible in respective directions perpendicular to the plane of the ring. Sr^{2+} and Pb^{2+} are nearly equal in size and larger than the 16C5- and 15C5-cavity. Therefore, it can be considered that the size of the MLA_2 complex of Pb^{2+} is nearly equal to that of the corresponding MLA_2 complex of Sr^{2+}. $-\Delta G_h°$ values of Sr^{2+} (1447 kJ mol^{-1})[10] and Pb^{2+} (1497 kJ mol^{-1})[10] are almost the same. However, in each case of 16C5 and 15C5, $K_{ex,ip}$ is greater for Pb^{2+} than for Sr^{2+}. This is probably attributable to stronger interaction with the two picrate anions of the Pb^{2+} complex compared with the corresponding Sr^{2+} complex.

From Table 1, $K_{ex,ip}$ value of a univalent metal ion increases with an increase in the size of crown ether (15C5<16C5); but, it is not always true for the cases of the bivalent metal ions. The difference in $\log K_{ex,ip}$ values of a univalent metal ion between 16C5 and 15C5 is 0.28—0.59, which is roughly constant. This indicates that an increment of $\log K_{ex,ip}$ value per a methylene group is about 0.44 (on the average), which is nearly equal to the Π_{CH_2} value (0.48_5). $K_{ex,ip}$ consists of two fundamental equilibria, namely, $K_{ex,ip} = K_{MLA}K_{D,MLA}$ ($K_{MLA} = [MLA]/[ML^+][A^-]$, $K_{D,MLA} = [MLA]_o/[MLA]$). Since $K_{D,MLA}$ is a partition constant of a neutral complex MLA between benzene and water, an increment of $\log K_{D,MLA}$ per a methylene group is evaluated to be about 0.49 on the basis of Π_{CH_2} value (0.48_5). It thus appears from the above discussion that $\log K_{MLA}$ values of 16C5 and 15C5 complexes with the same univalent metal ion are roughly equal.

Since MLA_2 is a neutral complex, the K_{D,MLA_2} value probably increases with an increase in the size of the crown ether (15C5<16C5), where $K_{D,MLA_2} = [MLA_2]_o/[MLA_2]$. The differences in $\log K_{ex,ip}$ values between

16C5 and 15C5 for Pb^{2+} and Ba^{2+} are larger than and are comparable to the Π_{CH_2} value, respectively. This indicates that K_{MLA_2} values of 16C5 for Pb^{2+} and Ba^{2+} are greater than and roughly equal to those of 15C5, respectively, where $K_{MLA_2}=[MLA_2]/[ML^{2+}][A^-]^2$. Whereas, the log $K_{ex,ip}$ value of the 16C5–Sr^{2+} complex is smaller than that of the 15C5–Sr^{2+} complex. This indicates that the K_{MLA_2} value of the 16C5 complex is much smaller than that of the 15C5 complex.

For 15C5, log $K_{ex,ip}$ value of Sr^{2+} is larger than that of Ba^{2+}; but, the reverse is found for 16C5. It seems that, in each case of 16C5 and 15C5, the MLA_2 complexes of Sr^{2+} and Ba^{2+} are almost the same in size. Therefore, K_{D,MLA_2} values of Sr^{2+} and Ba^{2+} of the same crown ether can be expected to be nearly equal. It thus appears that the K_{MLA_2} value of Sr^{2+} for 15C5 is greater than that of Ba^{2+}, whereas the reverse is true for 16C5, which is caused by an extra methylene group in the 16C5 ring.

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