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Solvent Extraction of Various Metal Picrates with Benzo-18-crown-6 into $CHCl_3$

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Overall extraction equilibrium constants (K_{ex}) of various metal picrates (MA_m) with benzo-18-crown-6 (B18C6) and distribution constant ($K_{D,L}$) of B18C6 were determined at 25 °C between water and chloroform. The K_{ex} values were analyzed by constituent equilibria, e.g., $K_{D,L}$, formation constant in water and ion-pair extraction constant ($K_{ex,ip}$) with a picrate anion of the B18C6–metal ion complex. K_{ex} orders for univalent and bivalent metal ions are $Tl^+>K^+>Rb^+>Ag^+>Cs^+>Na^+$ and $Pb^{2+}\gg Sr^{2+}>Ca^{2+}$, respectively. Extraction selectivities of B18C6 for the alkali and alkaline earth metal ions are consistent with the size-fit concept; namely, the more closely a cation fits into a crown ether cavity, the more extractable the complex is. For a given B18C6–M^{m+} system, $K_{ex,ip}$ value is much larger than values of the other constituent equilibria. Thus, the magnitude of K_{ex} value is determined largely by that of $K_{ex,ip}$ value. $K_{ex,ip}$ value of B18C6 for univalent and bivalent metal ions increases in the order $Na^+<Ag^+<Cs^+<K^+<Rb^+<Tl^+$ and $Sr^{2+}<Ca^{2+}<Pb^{2+}$, respectively. Factors governing the magnitude of the $K_{ex,ip}$ value were discussed in detail.

Overall extraction equilibrium constant of a crown ether with a metal picrate consists of several constituent equilibria. In a series of our solvent-extraction studies regarding crown ethers,[1] the overall extraction equilibrium constants of metal picrates with crown ethers and some constituent equilibria have been measured, and the overall extraction equilibrium constants have been analyzed by the constituent equilibria in order to clarify factors governing selectivities and extractabilities of crown ethers for metal ions, and, moreover, obtain information on solute–solvent interactions of the crown ether complexes.

In this study, the overall extraction equilibrium constants of various metal picrates with benzo-18-crown-6 (B18C6) between water and chloroform were determined at 25 °C and analyzed by constituent equilibria. The role of B18C6 in the metal ion-extraction process was discussed.

Experimental

Materials. Benzo-18-crown-6 was prepared according to Pedersen.[2] The product was recrystallized four times from heptane and, prior to use, dried at 40 °C in a vacuum oven. Its purity was checked by melting point, elemental analysis, and NMR. Chloroform, picric acid, NaOH, KOH, $AgNO_3$, $TlNO_3$, $Ca(NO_3)_2$, $Sr(NO_3)_2$, and $Pb(NO_3)_2$ were analytical grade reagents. Rubidium and caesium hydroxides were reagent-grade. Chloroform was washed three times with distilled water. The other reagents were used without further purification.

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 B18C6, metal salts, and picric acid were 1×10^{-5}—7×10^{-3} M (1 M=1 mol dm^{-3}), 1×10^{-3}—5×10^{-2} M, and $(1—5)\times10^{-3}$ M, respectively. For hydroxide and nitrate systems, the extractions were performed at pH 11.2—12.1 and pH 2.4—3.1, respectively. For the Ba system, turbidity was always found in the interface between chloroform and water under all experimental conditions.

The Distribution Coefficient of B18C6. A 10 ml portion of a chloroform solution of B18C6 and an equal volume of distilled water were placed in a stoppered glass tube (volume 30 ml) and shaken in a thermostated water bath for 2 h at 25±0.2 °C. The concentration range of B18C6 was from 0.1 M to 0.2 M. After centrifugation, the B18C6 concentration of the aqueous phase was spectrophotometrically determined at 273 nm ($\varepsilon=2.49_5\times10^3$ cm^{-1} M^{-1}). The distribution coefficient value of B18C6 is 371±4, which is the average of twenty measurements.

Results

In an equilibrium between a chloroform solution of a 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

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

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 B18C6 forms a 1:1 complex with the univalent metal ion. For the bivalent metal ion system, $\log(D/[\mathrm{A}^-]^2)$ vs. $\log[\mathrm{L}]_\mathrm{o}$ plot in Fig. 2 always shows a line with a slope of 1. This indicates that B18C6 forms a 1:1 complex with the bivalent metal ion.

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

$$[\mathrm{L}]_\mathrm{o} = ([\mathrm{L}]_\mathrm{t} - [\mathrm{MLA}_m]_\mathrm{o})/(\alpha + \beta[\mathrm{M}^{m+}]), \tag{9}$$

$$[\mathrm{M}^{m+}] = ([\mathrm{M}]_\mathrm{t} - [\mathrm{MLA}_m]_\mathrm{o})/(1 + \beta[\mathrm{L}]_\mathrm{o}), \tag{10}$$

$$[\mathrm{HA}]_\mathrm{o} = ([\mathrm{HA}]_\mathrm{t} - m[\mathrm{MLA}_m]_\mathrm{o})/\{1 + ([\mathrm{H}^+]^{-1} + K_\mathrm{HA})K_\mathrm{ex}(\mathrm{HA})^{-1}\}, \tag{11}$$

where the subscript "t" denotes the total concentration, $\alpha = 1 + K_{\mathrm{D,L}}^{-1}$, and $\beta = K_\mathrm{ML}K_{\mathrm{D,L}}^{-1}$. The K_ex value was determined by using the $[\mathrm{L}]_\mathrm{o}$ value of Eq. 9, the $[\mathrm{M}^{m+}]$ value of Eq. 10, and the $[\mathrm{HA}]_\mathrm{o}$ value of Eq. 11. The value of $K_\mathrm{ex}(\mathrm{HA})$ was spectrophotometrically determined as 87.1±0.4 using the association constant ($K_\mathrm{HA} = 1.9_5$ at 25 °C[5]) of picric acid in water, $K_\mathrm{HA} = [\mathrm{HA}]/[\mathrm{H}^+][\mathrm{A}^-]$. Equilibrium constants are summarized in Table 1.

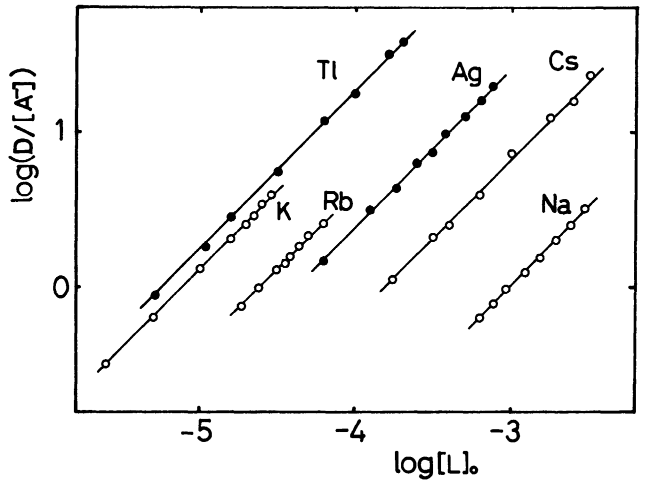

Fig. 1. Plots of $\log(D/[\mathrm{A}^-])$ vs. $\log[\mathrm{L}]_\mathrm{o}$ for B18C6–univalent metal picrate systems at 25 °C.

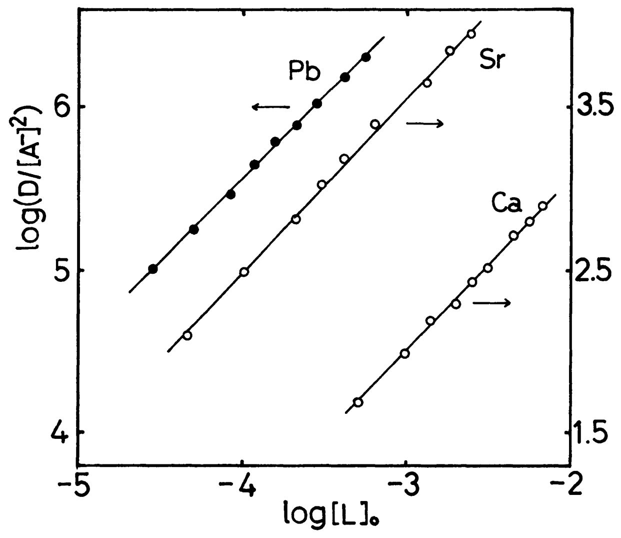

Fig. 2. Plots of $\log(D/[\mathrm{A}^-]^2)$ vs. $\log[\mathrm{L}]_\mathrm{o}$ for B18C6–bivalent metal picrate systems at 25 °C.

Table 1. Summary of Equilibrium Constants at 25 °C

Crown ether	$\log K_{\mathrm{D,L}}$	Cation	Ionic radius (Å)[a]	$\log K_\mathrm{ex}$	$\log K_\mathrm{ML}$	$\log K_{\mathrm{ex,ip}}$
B18C6	2.569±0.005	Na^+	1.02	1.08±0.02	1.38[6]	4.21
		K^+	1.38	3.17±0.02	1.744[6]	5.94
		Rb^+	1.49	2.67±0.01	1.15[6]	6.03
		Cs^+	1.70	1.90±0.02	0.88[6]	5.53
		Ag^+	1.15	2.46±0.02	1.83[6]	5.14
		Tl^+	1.50	3.29±0.05	1.68[6]	6.12
		Ca^{2+}	1.00	1.16±0.03	0.48[7]	7.13
		Sr^{2+}	1.13	2.74±0.03	2.41[6]	6.78
		Pb^{2+}	1.19	5.30±0.01	3.19[6]	8.56
18C6	0.78_6[8]	Na^+		1.53[8]	0.80[10]	3.46
		K^+		4.13[8]	2.03[10,11]	4.83
		Rb^+		3.71[8]	1.56[10]	4.88
		Cs^+		2.68[8]	0.99[10]	4.42
		Sr^{2+}		5.55[9]	2.72[10]	7.50
DB18C6	3.9[12]	Na^+		0.1_6[13]	1.1_6[16]	4.8_4
		K^+		2.6_6[13]	1.6_7[16]	6.8_3
		Rb^+		2.2_6[13]	1.0_8[16]	7.0_2
		Cs^+		1.2_6[13]	0.8_3[16]	6.2_7
		Ag^+		1.3_6[12]	1.4_1[16]	5.7_9
		Tl^+		2.7_6[14]	1.5_0[16]	7.1_0
		Sr^{2+}		1.0_2[15]	1.0_0[16]	7.8_0
		Pb^{2+}		2.7_2[15]	1.8_8[16]	8.6_2

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

Discussion

The contribution of an ether oxygen atom to $\log K_{D,L}$ (Π_o) and that of a methylene group to extraction constants of ion pairs (Π_{CH_2}) at 25 °C for the $CHCl_3$/water system are -0.79[8] and 0.47,[17] respectively. The contribution of a benzo group to $\log K_{D,L}$ ($\Pi_{C_6H_4}$) can be calculated to be 2.61 from the $\log K_{D,L}$ value of B18C6 by using the values of Π_o and Π_{CH_2} ($\Pi_{C_6H_4}=2.57-\{0.47\times 10+(-0.79\times 6)\}$). Values of $\Pi_{C_6H_4}$ are 2.5_9 for benzo-15-crown-5 (B15C5) and 2.4_4 for dibenzo-18-crown-6 (DB18C6).[8] They are nearly equal. The $\Pi_{C_6H_4}$ value is 2.5_4 on the average. From these empirical parameters, the $\log K_{D,L}$ value of B18C6 at 25 °C between $CHCl_3$ and H_2O can be estimated to be 2.5_0. This is consistent with the experimental $\log K_{D,L}$ value of B18C6 (2.569 ± 0.005). The same is true for the cases of B15C5 (2.3_5(calcd), 2.4(exptl)[18]) and DB18C6 (4.1_0(calcd), 3.9 (exptl)[13]).

From Table 1, the order of $\log K_{ex}$ of B18C6 for the univalent metal ions is $Tl^+>K^+>Rb^+>Ag^+>Cs^+>Na^+$. The extraction selectivity of B18C6 for the alkali metal ions is in accord with the size-fit concept; namely, the more closely a cation fits into a crown ether cavity, the more extractable the crown ether–cation complex is (cavity radius of 18-crown-6 (18C6)=1.38 Å (CPK model)[19]). Although $\log K_{ML}$ values of Ag^+ and Tl^+ are the largest and the third greatest of all the univalent metal ions, B18C6 shows the third lowest and the highest extractability for Ag^+ and Tl^+, respectively; this is attributed completely to the second smallest and the largest $\log K_{ex,ip}$ values of Ag^+ and Tl^+, respectively. $\log K_{ex}$ value sequences of B18C6 for the alkali metal ions are consistent with $\log K_{ML}$ value sequences except for Na^+ and $\log K_{ex,ip}$ value sequences except for K^+. Although $\log K_{ML}$ value of Na^+ and $\log K_{ex,ip}$ value of K^+ are the second largest of all the alkali metal ions, extractabilities of B18C6 for Na^+ and K^+ are the lowest and the highest, respectively; this is ascribed to the smallest $\log K_{ex,ip}$ value of Na^+ and the greatest $\log K_{ML}$ value of K^+, respectively.

For the bivalent metal ions, the $\log K_{ex}$ value of B18C6 decreases in the order, $Pb^{2+}\gg Sr^{2+}>Ca^{2+}$ (Table 1). The highest extractability of B18C6 for Pb^{2+} of all the metal ions in this study depends on both the greatest $\log K_{ML}$ and $\log K_{ex,ip}$ value.

For a given B18C6–M^{m+} system, $\log K_{ex,ip}$ value is much larger than $\log K_{ML}$, $\log K_{D,L}$, and $m\log K_{ex}(HA)$ value. Thus, the magnitude of $\log K_{ex}$ value is determined largely by that of $\log K_{ex,ip}$ value. The same is true for the cases of 18C6 and DB18C6 (Table 1). The K_{ex} value of a given metal ion among 18C6, B18C6, and DB18C6 increases with a decrease in the size of the crown ether; the same tendency is observed for the K_{ML} value of a metal ion among the crown ethers except for the case of a Na^+–18C6 complex; but, the reverse is true for the $K_{ex,ip}$ value except for the cases of Sr^{2+}–B18C6 and 18C6 complexes. Since the $K_{D,L}{}^{-1}$-value sequence is in the order DB18C6<B18C6<18C6, the K_{ex}-value sequence of a metal ion among the crown ethers depends on both the $K_{D,L}{}^{-1}$- and K_{ML}-value sequence (Eq. 6).

It can be seen from Table 1 that $\log K_{ex,ip}$ value of B18C6 varies with a cation of the same charge trapped in the cavity. The same is true for 18C6 and DB18C6. For alkali metal ions, $\log K_{ex,ip}$ value of B18C6 increases in the order, $Na^+<Cs^+<K^+<Rb^+$ (Table 1). The same trend is observed for the cases of 18C6 and DB18C6. This shows that, generally, a crown ether–metal ion complex, where the metal ion has a suitable size for the cavity, is more extractable as an ion pair with a picrate ion. From the structure of the crown ether complex with the univalent metal ion held in the cavity, anion- and solvent-contact are possible in respective directions perpendicular to the plane of the ring. It thus appears that strength of interaction between the central univalent metal ion and water molecules is one of the most important factors in determining the magnitude of $K_{ex,ip}$ value of the univalent metal ion. Consequently, the lowest $K_{ex,ip}$ value of Na^+ among all the alkali metal ions listed in Table 1 is probably attributed to the strongest interaction of Na^+ with water molecules. Gibbs free energies of hydration ($\Delta G_h{}^\circ$/kJ mol^{-1}) of K^+, Rb^+, and Cs^+ are -338, -320, and -297, respectively.[20] The interaction of Cs^+ with water is weaker than those of K^+ and Rb^+. The interaction with water of Cs^+ held in the crown ether cavity is expected to be weaker than those of K^+ and Rb^+. Association constant of Cs^+ with a picrate ion in water is larger than those of K^+ and Rb^+.[21] Association constant with a picrate ion of Cs^+ held in the crown ether cavity is expected to be greater than those of K^+ and Rb^+. However, $K_{ex,ip}$ value of a Cs^+–crown ether complex is smaller than those of the corresponding K^+– and Rb^+–crown ether complex. Judging from the structure of a crown ether–univalent metal ion complex. this may be attributable to negligible effect of water on association of the K^+– and Rb^+–crown ether complex with a picrate ion and/or very weak interactions with water of the K^+– and Rb^+–complex. The above discussion is supported by the following data. When L=18C6, B18C6, and DB18C6, differences in the numbers of water molecules coextracted into nitrobenzene among ML^+ complexes (M=K, Rb, Cs) are small, whereas those among uncomplexed K^+, Rb^+, and Cs^+ are relatively large.[22]

Ionic radii of Rb^+ and Tl^+ are nearly identical (Table 1); $-\Delta G_h^\circ$ value of Tl^+ (343 kJ mol^{-1})[20] is slightly greater than that of Rb^+; $K_{ex,ip}$ values of RbL^+ and TlL^+ complexes (L=B18C6 and DB18C6) are approximately equal. This indicates that strength of interaction with a picrate ion of the RbL^+ complex is nearly equal to that of the corresponding TlL^+ complex. The sizes of Na^+ and Ag^+ are smaller than those of B18C6- and DB18C6-

cavity; $-\Delta G_h°$ of Ag^+ (479.1 kJ mol^{-1})[20] is greater than that of Na^+ (411.3 kJ mol^{-1});[20] but, in each case of B18C6 and DB18C6, $K_{ex,ip}$ value of Ag^+ is larger than that of Na^+. Since specific interaction between Ag^+ and $CHCl_3$ is considered to be impossible, the higher $K_{ex,ip}$ value of Ag^+ may be caused by stronger association with a picrate ion and weaker interaction with water of the Ag^+ complex compared with the case of the corresponding Na^+ complex.

From the structure of a crown ether–bivalent metal ion complex, two picrate anion-contacts are possible in respective directions perpendicular to the plane of the ring. Sizes of Sr^{2+} and Pb^{2+} are almost the same; they are smaller than the B18C6- and DB18C6-cavity; $-\Delta G_h°$ value of Sr^{2+} (1447 kJ mol^{-1})[20] is nearly equal to that of Pb^{2+} (1497 kJ mol^{-1}).[20] However, in each case of B18C6 and DB18C6, $K_{ex,ip}$ value of Pb^{2+} is larger than that of Sr^{2+}. This may be ascribed to stronger interaction with two picrate anions of the Pb^{2+} complex compared with the corresponding Sr^{2+} complex.

$K_{ex,ip}$ value of a univalent metal ion increases with an increase in the size of crown ether (18C8<B18C6<DB18C6) (Table 1). However, it does not always hold for the bivalent metal ions. For a univalent metal ion, the difference in $\log K_{ex,ip}$ values between 18C6 and B18C6 is 0.75—1.15, which is approximately constant; that between B18C6 and DB18C6 is 0.6_3—0.9_9, which is approximately constant; they are roughly equal. This indicates that an increment of $\log K_{ex,ip}$ value per a benzo group is about 0.9 (on the average).

$K_{ex,ip}=K_{MLA}K_{D,MLA}$, where $K_{MLA}=[MLA]/[ML^+][A^-]$ and $K_{D,MLA}=[MLA]_o/[MLA]$. Since $K_{D,MLA}$ is a distribution constant of a neutral complex MLA between water and $CHCl_3$, an increment of $\log K_{D,MLA}$ per a benzo group is estimated to be about 2.5 on the basis of $\Pi_{C_6H_4}$ value (2.5_4). From an increment of $\log K_{ex,ip}$ per a benzo group (ca. 0.9), a decrement of $\log K_{MLA}$ per a benzo group is calculated to be 1.6. This indicates that the larger the size of a crown ether–univalent metal ion complex is, the smaller the $\log K_{MLA}$ value is. It is interesting from a structural point of view that the two-dimensional increase in the size of the crown ether–univalent metal ion complex causes the constant decrease in the $\log K_{MLA}$ value.

Since MLA_2 is a neutral complex, it seems reasonable to assume that the K_{D,MLA_2} value increases with an increase in the size of the crown ether (18C6<B18C6<DB18C6), where $K_{D,MLA_2}=[MLA_2]_o/[MLA_2]$. Consequently, the $K_{ex,ip}$-value sequences of a bivalent metal ion among the crown ethers may be determined chiefly by the K_{MLA_2}-value sequences, where $K_{MLA_2}=[MLA_2]/[ML^{2+}][A^-]^2$.

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