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The Solvent Extraction of Silver and Thallium(I) Picrates by Crown Ethers

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Extraction constants of silver and thallium(I) picrates and those of 12-crown-4 (12C4) and benzo-15-crown-5 (B15C5) with silver and thallium(I) picrates have been determined between benzene and water at 25 °C. Ion-pair complex-formation constants ($K_{\mathrm{MLA,o}}$) of 12C4 and B15C5 with silver and thallium picrates in the benzene solution have been calculated and compared with those of 15-crown-5 (15C5), 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6), and dibenzo-24-crown-8 (DB24C8). The $K_{\mathrm{MLA,o}}$ sequences of the crown ethers with Ag^+ and Tl^+ are 15C5, 18C6>DB18C6>B15C5>DB24C8≫12C4 and 18C6≫DB18C6>DB24C8>15C5>B15C5≫12C4, respectively. For both Ag^+ and Tl^+ systems, the relative sizes of the cation and the crown ether cavity, the number of donor oxygen atoms in the crown ether ring, the basicity of donor oxygen atom, and the flexibility of the crown ether are important factors in determining stabilities of the complexes with these crown ethers in the benzene solution.

Crown ethers form stable stoichiometric complexes with Ag^+ and Tl^+ as well as with alkali metal ions. The complexing-power of crown ethers for Ag^+ and Tl^+ has been investigated by solvent extraction.[1–5] In the present study, the extraction constants of silver and thallium(I) picrates and those of 12-crown-4 (12C4) and benzo-15-crown-5 (B15C5) with silver and thallium(I) picrates have been determined between benzene and water at 25 °C. Ion-pair complex-formation constants of 12C4 and B15C5 with silver and thallium picrates in the benzene solution have been calculated and compared with those of 15-crown-5 (15C5),[1] 18-crown-6 (18C6),[1] dibenzo-18-crown-6 (DB18C6),[2,4] and dibenzo-24-crown-8 (DB24C8)[5] in order to study the factors governing the stabilities of these complexes.

Experimental

The 12C4 (Wako-Pure Chemicals, Ltd.) was used without further purification. The method of purification of the B15C5 (Merck Japan Ltd.) has been described in the literature.[6] The purity of $AgNO_3$ and $TlNO_3$, and the concentrations of the picric acid solutions were determined by KCl, EDTA, and alkaline titrations, respectively. Analytical-grade benzene was washed twice with distilled water. All the experiments were conducted at 25±0.2 °C. Most of the experimental procedures were similar to those in the previous papers.[1,2] The concentrations of $AgNO_3$, $TlNO_3$, picric acid, 12C4, and B15C5 were $(2—6)\times10^{-3}$, $(1-9)\times10^{-3}$, $1\times10^{-3}-1.5\times10^{-2}$, $6\times10^{-3}-3.9\times10^{-1}$, and $5.9\times10^{-5}-3.9\times10^{-2}$ mol dm^{-3}, respectively. All the extractions were carried out in the pH range of 2.0—2.7.

Results

In an equilibrium between an aqueous solution of a univalent metal ion (M^+) and a picrate ion (A^-), and benzene, and its solution of a crown ether (L), the following equilibrium constants may be defined:

$$K_{\mathrm{ex}}(\mathrm{MA}) = [\mathrm{MA}]_{\mathrm{o}}[\mathrm{H}^+]/[\mathrm{M}^+][\mathrm{HA}]_{\mathrm{o}} \tag{1}$$

$$K_{\mathrm{ex}}(\mathrm{MLA}) = [\mathrm{MLA}]_{\mathrm{o}}[\mathrm{H}^+]/[\mathrm{M}^+][\mathrm{L}]_{\mathrm{o}}[\mathrm{HA}]_{\mathrm{o}} \tag{2}$$

$$K_{\mathrm{D,L}} = [\mathrm{L}]_{\mathrm{o}}/[\mathrm{L}] \tag{3}$$

$$K_{\mathrm{ex}}(\mathrm{HA}) = [\mathrm{HA}]_{\mathrm{o}}/[\mathrm{H}^+][\mathrm{A}^-] \tag{4}$$

$$K_{\mathrm{ML}} = [\mathrm{ML}^+]/[\mathrm{M}^+][\mathrm{L}] \tag{5}$$

$$K'_{\mathrm{ex}} = [\mathrm{MLA}]_{\mathrm{o}}/[\mathrm{ML}^+][\mathrm{A}^-], \tag{6}$$

where the subscript "o" and the lack of subscript denote the organic and the aqueous phase, respectively; square brackets indicate the molar concentrations. Thus, $K_{\mathrm{ex}}(\mathrm{MLA})$ can be written as follows:

$$K_{\mathrm{ex}}(\mathrm{MLA}) = K_{\mathrm{D,L}}{}^{-1}K_{\mathrm{ex}}(\mathrm{HA})^{-1}K_{\mathrm{ML}}K'_{\mathrm{ex}}. \tag{7}$$

In the absence of the crown ether, the distribution ratio of the metal may be written as

$$D = [\mathrm{MA}]_{\mathrm{o}}/[\mathrm{M}^+]. \tag{8}$$

The substitution of Eqs. 1 and 4 into Eq. 8 gives:

$$D = K_{\mathrm{ex}}(\mathrm{MA})K_{\mathrm{ex}}(\mathrm{HA})[\mathrm{A}^-]. \tag{9}$$

The $\log D$ *vs.* $\log[A^-]$ plot in Fig. 1 shows a straight line with a slope of 1. This indicates that the $K_{\mathrm{ex}}(\mathrm{MA})$ can be represented by Eq. 1. The value of $[A^-]$ in Eq. 9 was calculated from Eq. 10:

$$[\mathrm{A}^-] = ([\mathrm{HA}]_{\mathrm{t}}-[\mathrm{MA}]_{\mathrm{o}})/\{1+(K_{\mathrm{HA}}+K_{\mathrm{ex}}(\mathrm{HA}))[\mathrm{H}^+]\}, \tag{10}$$

where $K_{\mathrm{HA}}=1.9_5$,[7] $K_{\mathrm{ex}}(\mathrm{HA})=247$,[8] and the subscript "t" denotes the total concentration. When the extraction system contains a crown ether, D may be represented by:

$$D = [\mathrm{MLA}]_{\mathrm{o}}/([\mathrm{M}^+]+[\mathrm{ML}^+]). \tag{11}$$

In the case of $[\mathrm{M}^+]\gg[\mathrm{ML}^+]$, Eq. 11 becomes:

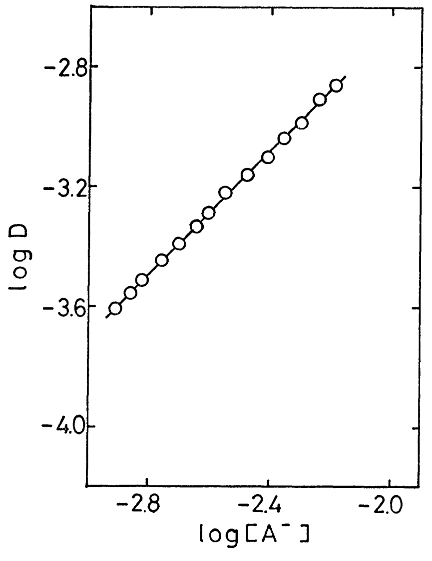

Fig. 1. Plot of $\log D$ *vs.* $\log[A^-]$ for the Tl^+ system.

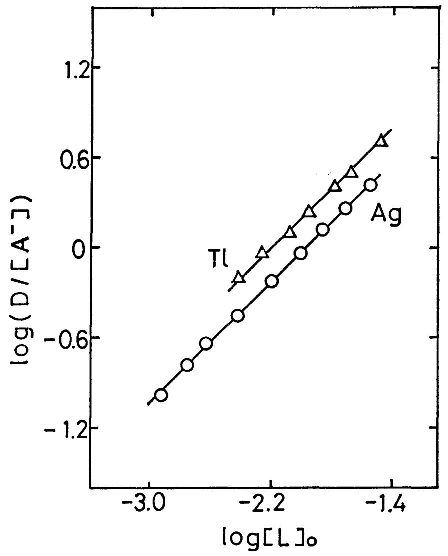

Fig. 2. Plot of $\log(D/[A^-])$ *vs.* $\log[L]_o$ for the 12C4–Ag^+ and Tl^+ systems.

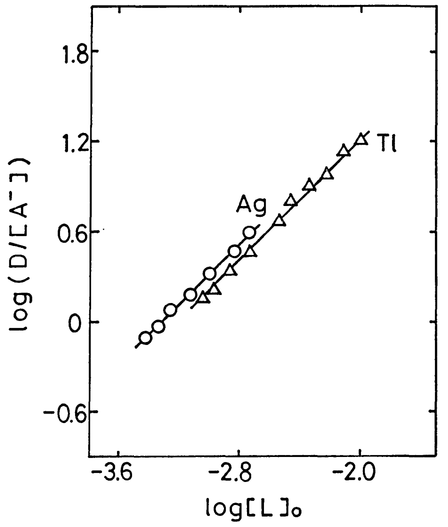

Fig. 3. Plot of $\log(D/[A^-])$ *vs.* $\log[L]_o$ for the B15C5–Ag^+ and Tl^+ systems.

$$D = K_{ex}(MLA)K_{ex}(HA)[A^-][L]_o. \qquad (12)$$

The $\log(D/[A^-])$ *vs.* $\log[L]_o$ plots in Figs. 2 and 3 show a linear relationship with a slope of 1 in every case, indicating that 12C4 and B15C5 form 1:1 complexes with Ag^+ and Tl^+. The values of $[A^-]$ and $[L]_o$ in Eq. 12 were calculated from Eqs. 13 and 14 respectively:

$$[A^-] = ([HA]_t - [MLA]_o)/\{1+(K_{HA}+K_{ex}(HA))[H^+]\} \qquad (13)$$

$$[L]_o = ([L]_t - [MLA]_o)/(1+K_{D,L}^{-1}). \qquad (14)$$

The equilibrium constants obtained from these data are listed in Table 1.

Discussion

Although a Ag^+ ion is much more strongly hydrated than a Tl^+ ion, for the benzene system, silver picrate is more extractable than thallium picrate and, for the chloroform system, the extractability of the former is equal to that of the latter (Table 1). In the cases of both Ag^+ and Tl^+, the picrate is more extractable by benzene than by chloroform. The reason why the Ag^+ ion is more extractable than the Tl^+ ion for the benzene system and the Ag^+ ion is more extractable by benzene than by chloroform may be due to the strong interaction of the Ag^+ ion with the π-electrons of a benzene molecule.

Table 1. Equilibrium constants at 25 °C

	$\log\{K_{ex}(MA)K_{ex}(HA)\}$	
	Benzene	Chloroform[3]
Ag^+	−0.26[2]	−1.33
Tl^+	−0.68	−1.33
	$\log K_{ex}(MLA)$ for benzene system	
	Ag^+	Tl^+
12C4	−0.43	−0.17
15C5[1]	2.06	1.41
B15C5	0.94	0.84
18C6[1]	2.05	3.91
DB18C6	1.17[2]	2.10[4]
DB24C8[5]	0.70	1.67
	$\log(K_{ML}K'_{ex})$ for benzene system	
	Ag^+	Tl^+
12C4	1.14	1.40
15C5[1]	3.65	3.00
B15C5	4.63	4.53

The crystal ionic radius of Ag^+ (1.26 Å[9]) is nearly equal to that of K^+ (1.33 Å[9]) and that of Tl^+ (1.40 Å[9]) is almost identical with those of K^+ and Rb^+ (1.48 Å[9]). However, in the cases of both 12C4 and B15C5, the $\log K_{ex}(MLA)$ value of Ag^+ is much larger than that of K^+ (12C4: −1.82,[10] B15C5: −0.46[6]) and that of Tl^+ is much greater than those of K^+ and Rb^+ (12C4: −2.10,[10] B15C5: −0.95[6]). The covalent bond[11] of Ag^+ and Tl^+ ions with oxygen atoms of the crown ether is one of the reasons for the above phenomena.

The $\log(K_{ML}K'_{ex})$ value sequences of 12C4, 15C5, and B15C5 with Ag^+ and Tl^+ are B15C5>15C5≫12C4 and B15C5≫15C5≫12C4, respectively (Table 1). Since both 12C4 and 15C5 are rigid and the sizes of Ag^+ and Tl^+ are larger than the cavity sizes of 12C4 (1.0—1.3 Å[12]) and 15C5 (1.7—2.2 Å[12]), the magnitude of the $\log K_{ML}$ value may largely depend on the number of donor oxygen atoms of the crown ether. Thus, for both Ag^+ and Tl^+, the $\log K_{ML}$ value for 15C5 is larger than that for 12C4. The size of the 15C5 complex with the same metal ion (Ag^+ and Tl^+) is larger than that of the 12C4 complex. Moreover, 15C5 may more effectively screen the surface charge of the metal ion trapped in its cavity than 12C4 because of its larger size. Consequently, for both Ag^+ and Tl^+, the $\log K'_{ex}$ value of 15C5 is larger than that of 12C4. The fact that the $\log(K_{ML}K'_{ex})$ value of 15C5 is greater than that of 12C4 is in agreement with the above discussion. In an aqueous solution, B15C5 complexes with Ag^+ and Tl^+ may be more unstable than 15C5 complexes owing to the two aromatic ether oxygen atoms. Since the B15C5 complex with the same metal ion has a larger molar volume than the 15C5 complex, the former may be more extractable by benzene than the latter. It thus appears that, in the case of both Ag^+ and Tl^+, the $\log(K_{ML}K'_{ex})$ sequences of B15C5 and 15C5 depend completely on the $\log K'_{ex}$ sequences.

$K_{ex}(MLA)/K_{ex}(MA)$ $(=K_{MLA,o})$ represents the ion-pair complex-formation constant of the crown ether with silver or thallium picrate in a benzene solution. Since the complex-formation reaction is an ion-pair complex-formation reaction, the anion has a large influence on the stability of the complex compared with the reaction between a free metal ion and a crown ether. The $\log K_{MLA,o}$ sequences of the crown ethers with Ag^+ and Tl^+ are 15C5, 18C6>DB18C6> B15C5 > DB24C8 ≫ 12C4 and 18C6 ≫ DB18C6 > DB24C8>15C5>B15C5≫12C4, respectively (Table 2). This indicates that, for both the Ag^+ and Tl^+ systems, the relative sizes of the cation and crown ether cavity; the number of donor oxygen atoms in crown ether ring; the basicity of donor oxygen atom; and the flexibility of the crown ether are important factors in determining the stabilities of the complexes.

Table 2. $\log (K_{MLA,o}/mol^{-1}\,dm^3)$ values in benzene at 25 °C

	Ag^+	Tl^+
12C4	2.22	2.90
15C5	4.71[2]	4.48
B15C5	3.59	3.91
18C6	4.70[2]	6.98
DB18C6	3.82[2]	5.17
DB24C8	3.35[2]	4.74

Although Ag^+ fits more closely into the 12C4 and B15C5 cavities than Tl^+, the $\log K_{MLA,o}$ value of Tl^+ is larger than that of Ag^+. This may be attributed to the fact that silver picrate is strongly solvated by benzene. However, in the case of 15C5, the Ag^+ complex is more stable than the Tl^+ complex. This can be considered to reflect the increase in basicity of the two donor oxygen atoms on going from B15C5 to 15C5. The reason why, in the cases of 18C6, DB18C6, and DB24C8, the Tl^+ complex is much more stable than the Ag^+ complex may be attributed to the strong solvation of silver picrate by benzene and the more optimal size of Tl^+ for each of the cavities of these crown ethers than Ag^+.

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