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The Solvent Extraction Study of a Dibenzo-18-crown-6 Complex with Silver Picrate

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Synopsis. The extraction constant of the silver ion–dibenzo-18-crown-6 (DB18C6) complex between benzene and water and the complex-formation constant of DB18C6 with silver picrate in benzene were determined at 25 °C. The Ag^+–DB18C6 complex is much more extractable than the Ag^+–18-crown-6 one. The Ag^+–DB18C6 complex is much more stable for benzene than for aqueous solutions.

The solvent extractions of uni- and bivalent metal ions with crown ethers to date have been investigated; these data show that the crown ethers form stoichiometrically stable complexes with the metal ions.[1] In some of these studies, the overall extraction equilibria have been analyzed by means of the constituent equilibria, and the extractability of the metal cation–crown ether complex as well as that of the metal cation have been discussed in detail.[1a–1d]

In the present study, the extraction constant values of the silver picrate and the silver picrate–dibenzo-18-crown-6 (DB18C6) systems have been determined between benzene and water, the overall extraction equilibrium of the latter system has been analyzed by means of the constituent equilibria, and the complex-formation constant values of DB18C6, 15-crown-5 (15C5), 18-crown-6 (18C6), and dibenzo-24-crown-8 (DB24C8) with the silver picrates in a benzene solution have been calculated using the extraction constant value of the silver picrate.

Experimental

The DB18C6 was obtained from the Aldrich Chemical Co., Inc. The $AgNO_3$ and picric acid were of an analytical grade and were from the Koso Chemical Co., Ltd. The method of the purification of DB18C6[2] and the determinations of the concentrations of $AgNO_3$ and the picric acid solutions[1d] have been described in the literature. Analytical-grade benzene (Wako-Pure Chemicals, Ltd.) was washed twice with distilled water. The benzene or the benzene solution of DB18C6 (4.0×10^{-4}–4.1×10^{-3} M; 1M=1 mol dm^{-3}) and the aqueous solution of $AgNO_3$ (3.0×10^{-3}—6.0×10^{-3} M) and the picric acid (1.9×10^{-3}—8.0×10^{-3} M) in stoppered 30-ml glass tubes were shaken in a thermostated water bath for approx. 30 min at 25±0.2 °C and then centrifuged. The initial volume of each phase was 10 ml in all cases. All the extractions were conducted in the pH range of 2.2—2.5. The Ag in the organic phase was back-extracted into a 1M nitric acid aqueous solution (8 ml), and the Ag concentration in the aqueous phase was determined by the use of a Seiko SAS-725 atomic absorption spectrophotometer.

Results

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

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

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

$$K_{D,L} = [L]_o/[L] (K_{D,L} = 800 \text{ for DB18C6}^{1a)}) \tag{3}$$

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

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

$$K_{ex}(3) = [MLA]_o/[ML^+][A^-] \tag{6}$$

where the subscript "o" and the lack of subscript designate the organic phase and the aqueous phase respectively; square brackets indicate the molar concentrations. Thus, $K_{ex}(2)$ can be written as follows:

$$K_{ex}(2) = K_{D,L}^{-1}K_{ex}(HA)^{-1}K_{ML}K_{ex}(3) \tag{7}$$

In the absence of crown ether, the distribution ratio of the metal may be represented by:

$$D_M = [MA]_o/[M^+] \tag{8}$$

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

$$D_M = K_{ex}(1)K_{ex}(HA)[A^-] \tag{9}$$

The log D_M *vs.* log$[A^-]$ plot for Ag^+ in Fig. 1 shows a linear relationship with a slope of 1, indicating that the $K_{ex}(1)$ in the present study can be described by Eq. 1. The value of $[A^-]$ in Eq. 9 was calculated from Eq. 10:

$$[A^-] = ([HA]_t - [MA]_o)/\{1+(K_{HA}+K_{ex}(HA))[H^+]\} \tag{10}$$

where the subscript "t" denotes the total concentration. The value of $K_{ex}(HA)$ was spectrophotometrically determined to be 247 by using the association constant of picric acid ($K_{HA}=1.9_5$[3]). When a crown ether exists in the extraction system, D_M may be represented by:

$$D_M = [MLA]_o/([M^+]+[ML^+]) \tag{11}$$

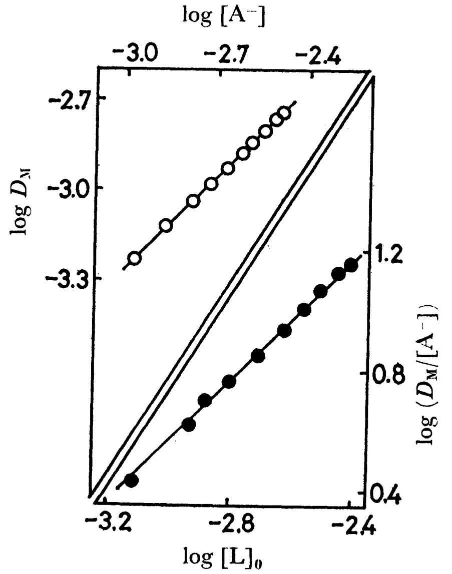

Fig. 1. ○: Plot of log D_M *vs.* log$[A^-]$ for the Ag^+ system at 25 °C. ●: Plot of log$(D_M/[A^-])$ *vs.* log$[L]_o$ for the Ag^+–DB18C6 system at 25 °C.

TABLE 1. $\log K_{ML}$ AND $\log\{K_{ex}(2)/K_{ex}(1)\}$ VALUES FOR Ag^+-CROWN ETHER SYSTEMS AT 25 °C

Crown ether	$\log K_{ML}$	$\log\{K_{ex}(2)/K_{ex}(1)\}$
15C5	0.94[4]	4.71[a]
18C6	1.50[4]	4.70[a]
DB18C6	1.41[5]	3.82
DB24C8	—	3.35[b]

a) The $\log K_{ex}(2)$ values for 15C5 and 18C6 are 2.06 and 2.05 respectively.[1d] b) $\log K_{ex}(2) = 0.70$.[1e]

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

$$D_M = K_{ex}(2)K_{ex}(HA)[A^-][L]_o \tag{12}$$

The $\log(D_M/[A^-])$ *vs.* $\log[L]_o$ curve in Fig. 1 is linear, with a slope of 1, indicating that DB18C6 forms a 1:1 complex with the Ag^+ ion. The values of $[A^-]$ and $[L]_o$ in Eq. 12 were calculated from Eqs. 13 and 14 respectively:

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

$$[L]_o = [L]_t - [MLA]_o \tag{14}$$

The values of $\log K_{ex}(1)$ and $\log K_{ex}(2)$ for the Ag^+ and the Ag^+–DB18C6 systems, as calculated from the data of Fig. 1, are −2.65 and 1.17 respectively.

Discussion

$K_{ex}(2)/K_{ex}(1)$ in Table 1 represents the formation constant for the 1:1:1 complex of the crown ether with the silver picrate in a benzene solution. Table 1 shows that the complex-formation constants are very much larger for benzene than for aqueous solutions. The stability of the 15C5 complex is the highest of all the crown ether complexes in a benzene solution; on the contrary, it is the lowest in an aqueous solution. The difference in the complex-formation constant values between 18C6 and DB18C6 considerably increases in going from water to benzene. The $\log\{K_{ex}(2)/K_{ex}(1)\}$ value of DB24C8 is the smallest, although it has the most donor oxygen atoms (eight) of all these crown ethers. The picrate anion was used as the only counter ion in this work. However, the anion effect on the complex-formation reaction in a low polar solvent may be very important, since an ion-pair complex-formation reaction, *e.g.*, $AgA + L \rightleftarrows AgLA$ in the present study, occurs in a solvent with a low dielectric constant.

As may be seen from Table 2, in the cases of both 18C6 and DB18C6, the $\log K_{ex}(3)$ values of K^+ and Tl^+, which have very much smaller $-\Delta G_h^\circ$ values and much more optimum sizes for the 18C6 and DB18C6 cavities (radius: 1.3—1.6 Å[1c]) than does Ag^+, are larger than that of Ag^+; the $\log K_{ex}(3)$ values of Rb^+ and Cs^+, which have very much smaller $-\Delta G_h^\circ$ values than Ag^+ and no more optimum sizes for the 18C6 and DB18C6 cavities than Ag^+ has, are larger than that of Ag^+; the $\log K_{ex}(3)$ value of Ag^+, which fits more closely into the 18C6 and DB18C6 cavities than Na^+, is larger than that of Na^+, although the $-\Delta G_h^\circ$ value of Ag^+ is much greater than that of Na^+. It has been found that the structure of the crown ether complex with the cation in the center of the crown ether ring does not require the stripping of the entire solvation shell of the ion, since solvent contacts are still possible in the direction perpendicular to the plane of the ring.[8] It thus appears that the extractability of the univalent metal ion complex with the same crown ether in this work is determined primarily by both the ratio of the ionic size to the cavity size of 18C6 and the interaction of the metal ion trapped in the cavity with water molecules. The remarkable substituent effect of the two benzo groups attached to 18C6 on the extractability of the Ag^+ complex can be seen in Table 2; *i.e.*, the difference in the $\log K_{ex}(3)$ values of Ag^+ and Na^+ markedly increases from 18C6 to DB18C6, while, on the contrary, that of Ag^+ and each of the others decreases and the Ag^+–DB18C6 complex, whose molar volume is much larger than that of the Ag^+–18C6 complex, is much more extractable than the Ag^+–18C6 one.

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TABLE 2. $\log K_{ex}(3)$ VALUES AND FREE ENERGIES OF HYDRATION, ΔG_h°, AT 25 °C AND CRYSTAL IONIC RADII OF METAL IONS

	Na^+	K^+	Rb^+	Cs^+	Ag^+	Tl^+
18C6[1d]	1.39	2.74	2.67	2.19	1.74	2.83
DB18C6	3.9[1a]	5.9[1a]	5.6[1a]	5.2[1a]	5.1	5.9[1b]
$-\Delta G_h^\circ$/kJ mol^{-1} [6]	411	338	320	297	479	343
Crystal ionic radius/Å[7]	0.95	1.33	1.48	1.69	1.26	1.40