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The Solvent Extraction of Alkali Metal Picrates by Benzo-15-crown-5

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Benzo-15-crown-5 (B15C5) extracted alkali metal picrates (MA) into benzene by forming M(B15C5)A or $M(B15C5)_2A$ complexes and moreover, in the presence of tributyl phosphate (B), B15C5 extracted rubidium and caesium picrates by forming M(B15C5)BA complexes. The extractability sequences of the M(B15C5)A, $M(B15C5)_2A$, and M(B15C5)BA complexes are $Na^+ > K^+ > Rb^+ > Li^+ > Cs^+$, $K^+ > Rb^+ > Cs^+$, and $Rb^+ > Cs^+$ respectively. The extraction equilibrium constants for these complexes have been determined at 25 °C, and the synergistic formation constants of the $M(B15C5)_2A$ and M(B15C5)BA complexes in the benzene solution have been calculated. The synergistic effects for the alkali metal ions for the B15C5 system were compared with those for the 15C5 system.

The solvent extractions of alkali metal ions with various crown ethers have been widely studied.[1] In the previous papers,[2,3] it was reported that 15-crown-5 (15C5) extracted alkali metal picrates (MA) into benzene by forming M(15C5)A or $M(15C5)_2A$ complexes and moreover, in the presence of tributyl phosphate (B), 15C5 extracted rubidium and caesium picrates by forming M(15C5)BA complexes.

In this paper, the solvent extraction of alkali metal picrates has been investigated between benzene and water at 25 °C in the presence of benzo-15-crown-5 (B15C5) or both B15C5 and B in order to compare with the case of 15C5. The synergistic formation constants of the $M(B15C5)_2A$ and M(B15C5)BA complexes in the benzene solution have been calculated.

Experimental

Materials. B15C5 and analytical-grade B were obtained from Merck Japan Ltd. and Wako-Pure Chemicals, Ltd. respectively. B15C5 was dissolved in heptane, and filtered while hot. Then it was recrystallized from heptane three times and, before use, dried at 40 °C in a vacuum oven. B was used without further purification. The concentrations of the alkali metal hydroxides and picric acid solutions were determined by means of acid and basic titrations respectively. Analytical-grade benzene was washed twice with distilled water.

Procedure. All the experiments were carried out at 25±0.2 °C. The experimental procedures were the same as those described in the previous papers.[3,4]

The Distribution Coefficient of B15C5. Most of the procedures were similar to those in the previous paper.[5] The average value of the distribution coefficient is 20.

Results

When an aqueous phase of an alkali metal ion (M^+) and a picrate ion (A^-), and a benzene phase of a crown ether (L) or both B and L are equilibrated, the equilibrium constants may be defined by the following equations:

$$K_{ex}(ML_mA) = [ML_mA]_o[H^+]/[M^+][L]_o^m[HA]_o \qquad (1)$$

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

$$K_{D,L} = [L]_o/[L] \qquad (3)$$

$$K_{ML} = [ML^+]/[M^+][L] \qquad (4)$$

$$K'_{ex} = [MLA]_o/[ML^+][A^-] \qquad (5)$$

$$K_{ex}(HA) = [HA]_o/[H^+][A^-], \qquad (6)$$

where the subscript "o" means organic and the lack of a subscript refers to the aqueous phase. Thus, $K_{ex}(MLA)$ can be written as follows:

$$K_{ex}(MLA) = K_{ML}K'_{ex}/K_{D,L}K_{ex}(HA). \qquad (7)$$

The $K_{ex}(HA)$ value was spectrophotometrically determined to be 247.

When the benzene phase contains only B15C5, the distribution ratio of the alkali metal may be represented by

$$D = [ML_mA]_o/[M^+]. \qquad (8)$$

In the case of $m=1$, Eq. 8 becomes

$$D = K_{ex}(MLA)K_{ex}(HA)[L]_o[A^-]. \qquad (9)$$

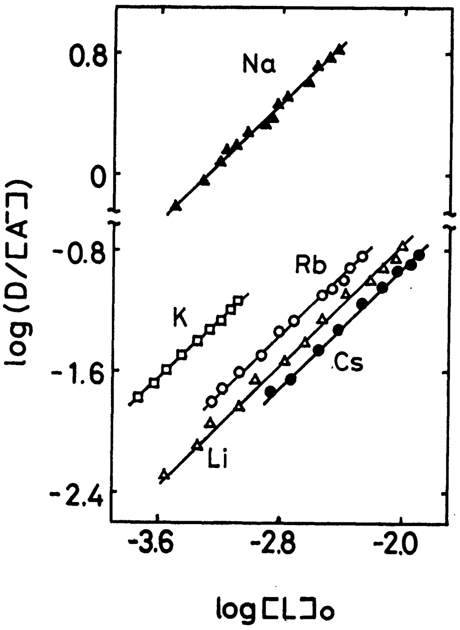

Fig. 1. Plots of $\log(D/[A^-])$ *vs.* $\log[L]_o$ for the MLA system.

The log $(D/[A^-])$ *vs.* log $[L]_o$ plot in Fig. 1 shows a linear relationship with a slope of 1 in every case, indicating that B15C5 forms the 1 : 1 complex with the alkali metal ion. The values of $[L]_o$ and $[A^-]$ in Eq. 9 were calculated by means of Eqs. 10 and 11 respectively:

$$[L]_o = ([L]_t - [MLA]_o)/(1 + K_{D,L}^{-1}), \qquad (10)$$

$$[A^-] = ([HA]_t - [MLA]_o)/\{1 + (K_{HA} + K_{ex}(HA))[H^+]\}, \qquad (11)$$

where the subscript "t" denotes the total concentration and K_{HA} is the association constant of picric acid ($K_{HA}=1.9_5$[6]). In the case of $m=2$, Eq. 8 becomes

$$D = K_{ex}(ML_2A)K_{ex}(HA)[L]_o^2[A^-]. \tag{12}$$

The log $(D/[A^-])$ *vs.* log $[L]_o$ plot in Fig. 2 shows a straight line with a slope of 2 in each case, indicating that B15C5 forms the 2 : 1 complex with the alkali metal ion. The values of $[L]_o$ and $[A^-]$ in Eq. 12 were calculated from Eqs. 13 and 14 respectively:

$$[L]_o = ([L]_t - 2[ML_2A]_o)/(1 + K_{D,L}^{-1}), \tag{13}$$

$$[A^-] = [HA]_t - [ML_2A]_o. \tag{14}$$

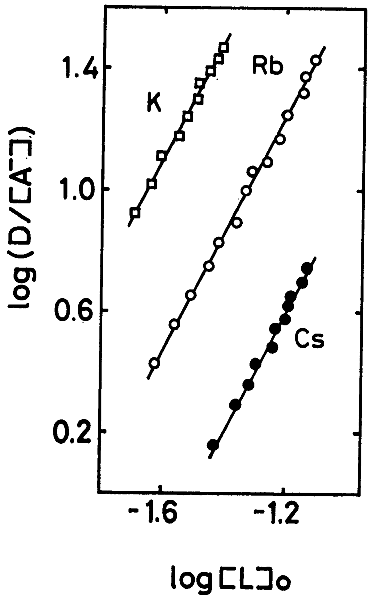

Fig. 2. Plots of log$(D/[A^-])$ *vs.* log$[L]_o$ for the ML_2A system.

When the benzene phase contains both B15C5 and B, D may be represented by

$$D = [MLBA]_o/[M^+]. \tag{15}$$

The substitution of Eqs. 2 and 6 into Eq. 15 gives

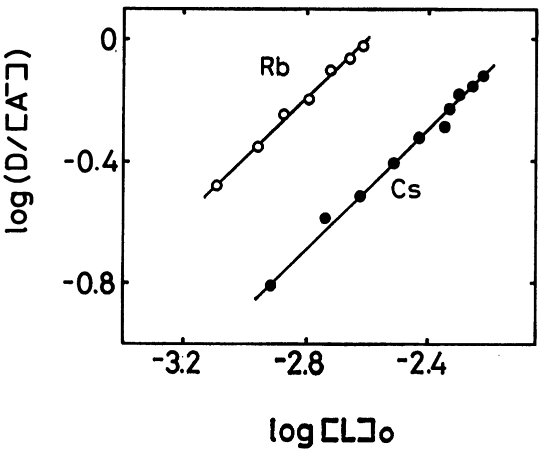

Fig. 3. Plots of log$(D/[A^-])$ *vs.* log$[L]_o$ for the MLBA system.

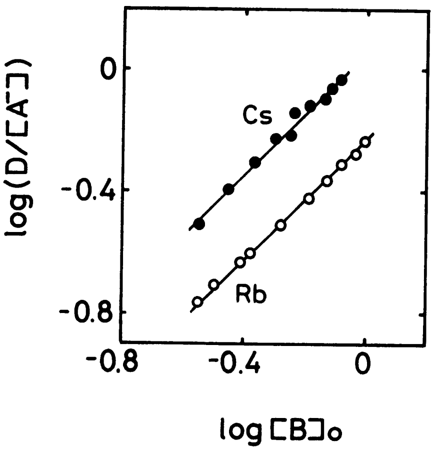

Fig. 4. Plots of log$(D/[A^-])$ *vs.* log$[B]_o$ for the MLBA system.

$$D = K_{ex}(MLBA)K_{ex}(HA)[L]_o[B]_o[A^-]. \tag{16}$$

The log $(D/[A^-])$ *vs.* log $[L]_o$ and log $[B]_o$ plots are given in Figs. 3 and 4 respectively. It may be seen from Figs. 3 and 4 that, in each case, the plots of both Rb and Cs have a slope of 1. Thus, the Kex(MLBA) in this work can be described by Eq. 2. The value of $[B]_o$ in Eq. 16 was supposed to be approximately equal to that of $[B]_t$ under the present experimental conditions, and those of $[L]_o$ and $[A^-]$ were calculated from Eqs. 17 and 18 respectively:

$$[L]_o = ([L]_t - [MLBA]_o)/(1 + K_{D,L}^{-1}), \tag{17}$$

$$[A^-] = [HA]_t - [MLBA]_o. \tag{18}$$

The extraction equilibrium constants obtained from these experiments are listed in Table 1, together with those from the literature.

TABLE 1. EXTRACTION EQUILIBRIUM CONSTANTS AT 25 °C

		15C5[2]	B15C5
$K_{D,L}$		0.15_6	20
log K_{ex} (MLA)	Li^+	−1.10	−1.13
	Na^+	1.51	0.90
	K^+	0.19	−0.46
	Rb^+	−0.25	−0.95
	Cs^+	−0.49	−1.31
log K_{ex} (MLBA)	Rb^+	0.56	0.37
	Cs^+	0.19	−0.15
log K_{ex} (ML_2A)	K^+	—	1.91
	Rb^+	2.15	1.22
	Cs^+	1.48	0.41
log ($K_{ML}K'_{ex}$)	Li^+	0.49	2.56
	Na^+	3.10	4.59
	K^+	1.78	3.23
	Rb^+	1.34	2.74
	Cs^+	1.10	2.38

Discussion

The $K_{D,L}$ value of B15C5, which is more bulky than 15C5, is much larger than that of 15C5.

The logK_{ex}(MLA) series for B15C5 and 15C5 are given by $Na^+ > K^+ > Rb^+ > Li^+ > Cs^+$ and $Na^+ > K^+ >$

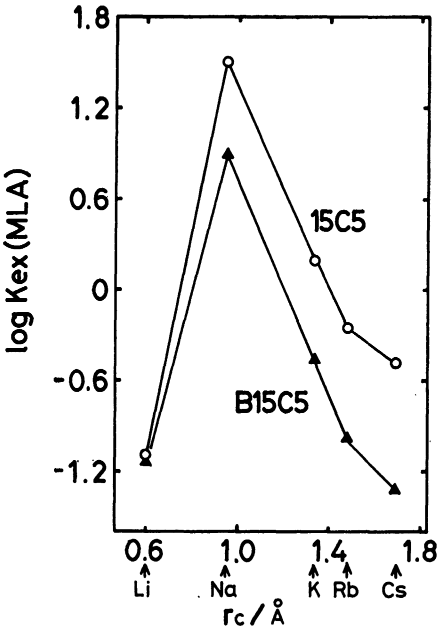

Fig. 5. Plots of log K_{ex}(MLA) *vs.* crystal ionic radii, r_c, of alkali metals for the B15C5 and 15C5 systems.
▲: B15C5, ○: 15C5.

$Rb^+ > Cs^+ > Li^+$ respectively (Table 1). The selectivity tendency of B15C5 (cavity radius: 0.85—1.1 Å[7]) for the alkali metal ions is not much different from that of 15C5 and agrees with the size-fit concept (Fig. 5). A possible explanation for the difference in the sequences of Li^+ and Cs^+ is as follows. The extractability of the crown ether complex with the univalent metal picrate depends on the interaction of the univalent metal ion trapped in the crown ether cavity with water molecules.[8] Since, for the alkali metal ion in the cavity, the interaction of the lithium ion with water molecules seems to be the strongest of all the alkali metal ions, the hindrance for the hydration of the B15C5 complex by the benzo group attached to 15C5 may be much more effective for the case of Li^+ compared to Cs^+. Thus, in the case of B15C5, Li^+ is more extractable than Cs^+. The following data may support the above discussion, though they have been obtained in the nitrobenzene–water system. The numbers of water molecules coextracted with the Li^+–15C5, Li^+–B15C5, Cs^+–15C5, and Cs^+–B15C5 complexes into the nitrobenzene phase are 2.0, 1.4, 0.2, and 0.4 respectively.[9] For the lithium complex, the number of water molecules decreases remarkably on moving from 15C5 to B15C5, while, for the caesium complex, it increases only slightly.

Equation 7 shows that $K_{D,L}$, K_{ML}, and K'_{ex} are important factors which determine the magnitude of K_{ex}(MLA) for the same alkali metal ion and different crown ethers. Although the log $(K_{ML}K'_{ex})$ sequence of B15C5 and 15C5 for the same alkali metal ion is B15C5>15C5, the log K_{ex}(MLA) value of B15C5 for Li^+ is nearly equal to that of 15C5 and that of B15C5 for the other alkali metal ion is smaller than that of 15C5. This is entirely attributed to the much greater $K_{D,L}$ value of B15C5 compared to 15C5 (Table 1). The basicity of the aromatic ether oxygen atom is lower than that of the aliphatic one. Since B15C5 has two aromatic ether oxygen atoms, the B15C5 complex with the same alkali metal ion may be more unstable than the 15C5 complex. The B15C5 complex with the same alkali metal ion may be more extractable than the 15C5 complex because of its larger size compared to 15C5. The log $(K_{ML}K'_{ex})$ value of B15C5 for the same alkali metal ion is larger than that of 15C5 (Table 1). It thus appears that the log $(K_{ML}K'_{ex})$ sequence of B15C5 and 15C5 depends completely on the K'_{ex} sequence. By way of example, in the case of K^+, the log K_{ML} values of B15C5 and 15C5 are 0.38[10] and 0.74,[11] and the log K'_{ex} values are 2.85 and 1.04,[2] respectively.

For the MLA, MLBA, and ML_2A systems, Rb^+ is more extractable than Cs^+, and, for the B15C5–ML_2A system, K^+ is the most extractable (Table 1). In the cases of the MLA, MLBA, and ML_2A systems, the difference in the extractabilities of Rb^+ and Cs^+ increases in going from 15C5 to B15C5.

When MLA undergoes further complex formation with B and L in the organic phase, the equilibria can be described as Eqs. 19 and 20 respectively:

$$\mathrm{MLA_o} + \mathrm{B_o} \rightleftharpoons \mathrm{MLBA_o},$$
$$K_{\mathrm{MLBA,o}} = K_{ex}(\mathrm{MLBA})/K_{ex}(\mathrm{MLA}) = [\mathrm{MLBA}]_o/[\mathrm{MLA}]_o[\mathrm{B}]_o, \tag{19}$$
$$\mathrm{MLA_o} + \mathrm{L_o} \rightleftharpoons \mathrm{ML_2A_o},$$
$$K_{\mathrm{ML_2A,o}} = K_{ex}(\mathrm{ML_2A})/K_{ex}(\mathrm{MLA}) = [\mathrm{ML_2A}]_o/[\mathrm{MLA}]_o[\mathrm{L}]_o, \tag{20}$$

where $K_{\mathrm{MLBA,o}}$ and $K_{\mathrm{ML_2A,o}}$ are the formation constants for the MLBA and the ML_2A complexes in a benzene solution respectively; they are summarized in Table 2.

TABLE 2. COMPLEX-FORMATION CONSTANTS FOR SYNERGISTIC REACTIONS IN A BENZENE SOLUTION AT 25 °C

		K^+	Rb^+	Cs^+
log $K_{\mathrm{MLBA,o}}$	15C5[3]	—	0.81	0.68
	B15C5	—	1.32	1.16
log $K_{\mathrm{ML_2A,o}}$	15C5[3]	—	2.40	1.97
	B15C5	2.37	2.17	1.72

The log $K_{\mathrm{ML_2A,o}}$ values of B15C5 for K^+ and Rb^+ are approximately identical with those in the literature[10] (K^+: 2.65 and Rb^+: 1.97 in 70 wt% CH_3OH in H_2O, K^+: 2.6 in 80 wt% CH_3OH in H_2O).

It is interesting that, in the benzene solution, both the B15C5 and 15C5 complexes with CsA accept a B molecule, while the 2-thenoyltrifluoroacetone complex with Cs^+ (Cs(TTA)) accepts two B molecules.[12] This may be largely due to that HTTA is a chelating acid, while B15C5 and 15C5 are neutral ligands.

As can be seen from Table 2, for every crown ether system, the smaller the size of the alkali metal ion is, the larger is the complex-formation constant. For the MLBA system, this may reflect the higher charge density of Rb^+ compared to Cs^+. For the ML_2A system, this is presumably attributable to both the charge density of the cation and the accommodation of the cation into the crown ether cavity.

Since B15C5 has two aromatic ether oxygen atoms, the electron density in the B15C5 cavity may be lower than that in the 15C5 cavity. Thus, the apparent charge density of the exposed part of the alkali metal ion trapped in the crown ether cavity seems higher for the case of B15C5 compared to 15C5. Consequently, this may be the reason why, in each case of Rb^+ and Cs^+, the $\log K_{MLBA,o}$ value of B15C5 is larger than that of 15C5 (Table 2). In each case of Rb^+ and Cs^+, the $\log K_{ML,A,o}$ value of B15C5 is smaller than that of 15C5. This is probably due to two aromatic ether oxygen atoms of B15C5.

The fact that the crown ether has much more donor oxygen atoms than B may be the reason why, for both B15C5 and 15C5, the $\log K_{ML,A,o}$ value of the same alkali metal ion is larger than the $\log K_{MLBA,o}$ value (Table 2).

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