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Synergistic Solvent Extraction of Alkali Metal Picrates by Crown Ethers

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The solvent extraction of rubidium and caesium picrates has been studied between benzene and water at 25 °C in the presence of tributyl phosphate (B), 12-crown-4 (12C4), 15-crown-5 (15C5), or both B and 15C5, and the complex-formation constants for the synergistic reactions in the benzene solution have been calculated. For both rubidium and caesium, the sequences of the complex-formation constants for these ligands are B<12C4<15C5, indicating that the complex-formation constant increases with an increase in the number of the donor oxygen atoms of the ligand. The complex-formation constant of rubidium is greater than that of caesium in every system.

For the rigid crown ethers such as 12-crown-4 (12C4), 15-crown-5 (15C5), and 18-crown-6, in a crown ether complex with a metal ion whose size is larger than the cavity size of the crown ether, the metal ion is located partly outside the plane of the crown ether ring. Thus, the exposed part of the metal ion can interact strongly with another crown ether or a neutral donor solvent in a solution; *e.g.*, benzo-15-crown-5 and dibenzo-18-crown-6 (DB18C6) form 2 : 1 complexes with rubidium and caesium ions.[1)]

The solvent extraction of alkali and alkaline earth metal ions with crown ethers has been widely investigated in terms of thermodynamics[1c,2)] and analytical chemistry.[3)] However, few synergistic effects for alkali and alkaline earth metal ions in the crown ether-neutral donor extractant system have been reported.

In the present study, the solvent extraction of rubidium and caesium picrates has been studied between benzene and water in the presence of 12C4, 15C5, or both tributyl phosphate (B) and 15C5, and the complex-formation constants for the synergistic reactions in the benzene solution have been calculated in order to compare the synergistic effects due to the crown ethers with those due to B.

Experimental

Materials. 12C4 and analytical-grade B were obtained from Wako-Pure Chemicals, Ltd., and 15C5 from Nisso Co., Ltd. They were 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. Benzene (analytical-grade) was washed twice with distilled water.

Apparatus and Procedure. An aqueous phase contained the alkali metal hydroxide (4.4×10^{-3}—2.0×10^{-2} M; 1 M= 1 mol dm^{-3}) and the picric acid (2.0×10^{-3}—1.0×10^{-2} M). An organic phase contained one of the extractants (B: 9.4×10^{-2}—9.9×10^{-1} M, crown ether: 4.9×10^{-2}—7.5×10^{-1} M), or both B (6.8×10^{-2}—8.0×10^{-1} M) and the crown ether (4.8×10^{-3}—5.8×10^{-2} M). The two phases in stoppered glass tubes (30 ml) 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. A portion of the aqueous phase (8 ml) was transferred into a 10-ml beaker, and the hydrogen ion concentration was determined by a Hitachi-Horiba F-5 pH meter. The extractions were conducted at pH 8.2—11.8. The picrate in the organic phase was back-extracted into 8 ml of a 0.01 M NaOH aqueous solution, and the picrate concentration was determined at 356 nm by means of a Shimadzu UV-200 spectrophotometer ($\varepsilon=1.45\times10^4$ cm^{-1} M^{-1}).

Results

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

$$K_{ex}(MB_3A) = [MB_3A]_o[H^+]/[M^+][B]_o^3[HA]_o \tag{1}$$

$$K_{ex}(ML_2A) = [ML_2A]_o[H^+]/[M^+][L]_o^2[HA]_o \tag{2}$$

$$K_{ex}(MLBA) = [MLBA]_o[H^+]/[M^+][L]_o[B]_o[HA]_o \tag{3}$$

$$K_{D,L} = [L]_o/[L] \tag{4}$$

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

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

where the subscript "o" means organic and the lack of a subscript refers to the aqueous phase. The value of $K_{ex}(HA)$ was spectrophotometrically determined to be 247. For the B system the distribution ratio of the metal may be represented by

$$D = [MB_3A]_o/[M^+]. \tag{7}$$

The substitution of Eqs. 1 and 6 into Eq. 7 gives

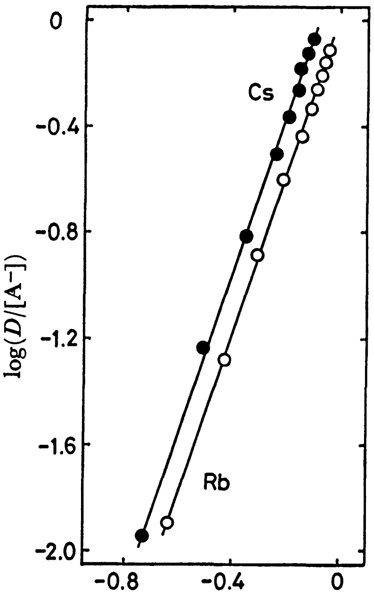

Fig. 1. Plots of log(D/[A^-]) *vs.* log[B]$_o$ for the B system.

$$D = K_{ex}(MB_3A)K_{ex}(HA)[B]_o^3[A^-]. \qquad (8)$$

The log $(D/[A^-])$ *vs.* log $[B]_o$ plot in Fig. 1 shows a straight line with a slope of 3 in each case, indicating that the $K_{ex}(MB_3A)$ in the present study can be described by Eq. 1. The value of $[B]_o$ in Eq. 8 was considered to be approximately equal to that of $[B]_t$ under the present experimental conditions and that of $[A^-]$ calculated from Eq. 9:

$$[A^-] = [HA]_t - [MB_3A]_o, \qquad (9)$$

where the subscript "t" denotes the total concentration.

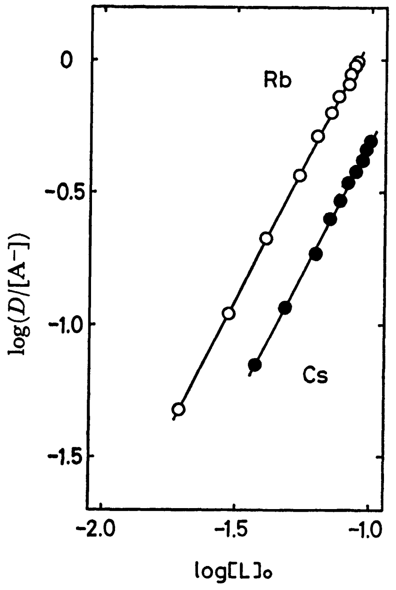

Fig. 2. Plots of $\log(D/[A^-])$ *vs.* $\log[L]_o$ for the 12C4 system.

For the 12C4 system D may be represented by

$$D = [ML_2A]_o/([M^+] + [ML^+] + [ML_2^+]). \qquad (10)$$

In the case of $[M^+] \gg [ML^+] + [ML_2^+]$, Eq. 10 becomes

$$D = K_{ex}(ML_2A)K_{ex}(HA)[L]_o^2[A^-]. \qquad (11)$$

The log $(D/[A^-])$ *vs.* log $[L]_o$ plot in Fig. 2 shows a linear relationship with a slope of 2 in each case, indicating that 12C4 forms a 2 : 1 complex with the monovalent metal ion. The values of $[L]_o$ and $[A^-]$ in Eq. 11 were calculated from Eqs. 12 and 13 respectively:

$$[L]_o = ([L]_t - 2[ML_2A]_o)/(1 + K_{D,L}^{-1}) \qquad (12)$$

($K_{D,L} = 0.15$ for 12C4[4])

$$[A^-] = [HA]_t - [ML_2A]_o. \qquad (13)$$

For the 15C5 system D may be described by Eq. 10. In the case of $[M^+] + [ML^+] \gg [ML_2^+]$, Eq. 10 becomes

$$D = K_{ex}(ML_2A)K_{ex}(HA)[L]_o^2[A^-]/$$
$$(1 + K_{ML}K_{D,L}^{-1}[L]_o). \qquad (14)$$

The log $\{D(1+K_{ML}K_{D,L}^{-1}[L]_o)/[A^-]\}$ *vs.* log $[L]_o$ plots of both Rb and Cs in Fig. 3 fall on the straight lines with a 2 slope. Thus, the extraction equilibrium can be represented by Eq. 2. The values of $[L]_o$ and $[A^-]$ in Eq. 14 were calculated from Eqs. 15 and 16 respectively:

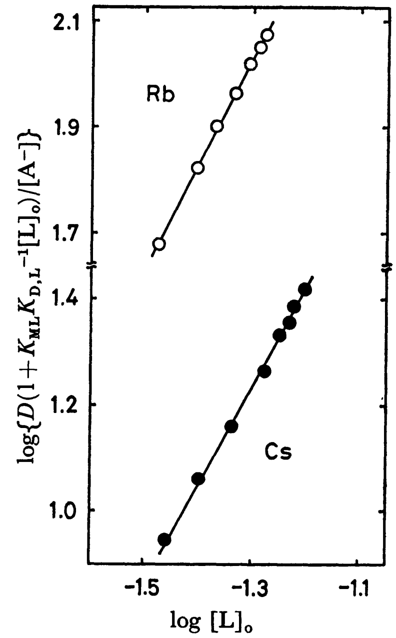

Fig. 3. Plots of $\log\{D(1+K_{ML}K_{D,L}^{-1}[L]_o)/[A^-]\}$ *vs.* $\log[L]_o$ for the 15C5 system.

$$[L]_o = ([L]_t - 2[ML_2A]_o)/$$
$$(1 + K_{D,L}^{-1} + K_{ML}K_{D,L}^{-1}[M^+]), \qquad (15)$$

($K_{D,L}=0{\cdot}15_6$ for 15C5;[2b)] $K_{ML}=4.2$ and 6.3 for Rb and Cs respectively[5)])

$$[A^-] = ([HA]_t - [ML_2A]_o)/$$
$$\{1 + (K_{HA} + K_{ex}(HA))[H^+]\}, \qquad (16)$$

where K_{HA} is the association constant of picric acid ($K_{HA}=1.9_5$[6)]).

When both 15C5 and B exist in the extraction system, D may be represented by

$$D = [MLBA]_o/([M^+]+[ML^+]). \qquad (17)$$

The substitution of Eqs. 3, 4, 5, and 6 into Eq. 17 gives

$$D = K_{ex}(MLBA)K_{ex}(HA)[L]_o[B]_o[A^-]/$$
$$(1 + K_{ML}K_{D,L}^{-1}[L]_o). \qquad (18)$$

The log $\{D(1+K_{ML}K_{D,L}^{-1}[L]_o)/[A^-]\}$ *vs.* log $[L]_o$ and log $[B]_o$ plots are illustrated in Figs. 4 and 5 respectively.

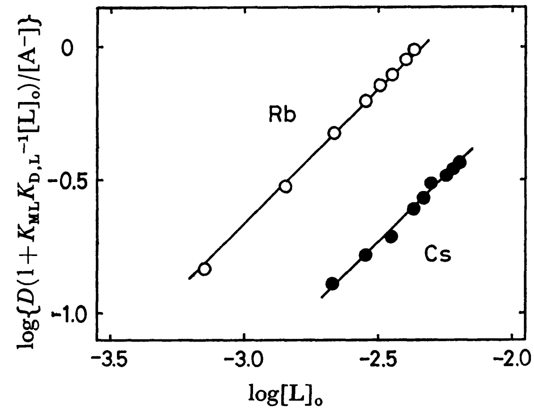

Fig. 4. Plots of $\log\{D(1+K_{ML}K_{D,L}^{-1}[L]_o)/[A^-]\}$ *vs.* $\log[L]_o$ for the 15C5–B system.

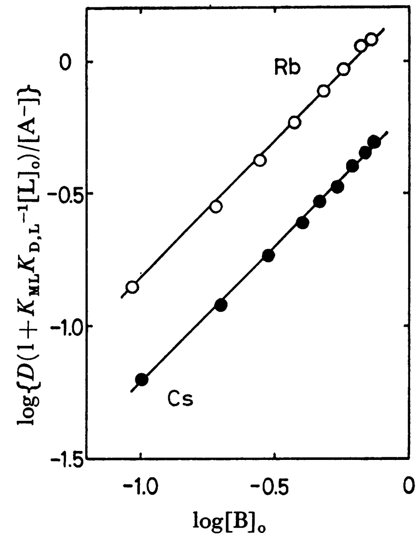

Fig. 5. Plots of $\log\{D(1+K_{ML}K_{D,L}^{-1}[L]_o)/[A^-]\}$ *vs.* $\log[B]_o$ for the 15C5–B system.

It may be noted from Figs. 4 and 5 that, in each case, the plots of both Rb and Cs have a slope of 1. Thus, the K_{ex}(MLBA) in the present study can be described by Eq. 3. The value of $[B]_o$ in Eq. 18 was considered to be nearly equal to that of $[B]_t$ under these experimental conditions, and those of $[L]_o$ and $[A^-]$ were calculated from Eqs. 19 and 20 respectively:

$$[L]_o = ([L]_t - [MLBA]_o)/(1+K_{D,L}^{-1}+K_{ML}K_{D,L}^{-1}[M^+]), \quad (19)$$

$$[A^-] = [HA]_t - [MLBA]_o. \quad (20)$$

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

TABLE 1. EXTRACTION EQUILIBRIUM CONSTANTS AT 25 °C

		Rb+	Cs+
$\log K_{ex}(MB_3A)$		−2.26	−2.14
$\log K_{ex}(MLBA)$	15C5	0.56	0.19
$\log K_{ex}(ML_2A)$	12C4	−0.29	−0.64
	15C5	2.15	1.48
	DB18C6[1c]	4.11	3.21
$\log K_{ex}(MLA)$	12C4[4]	−2.10	−2.18
	15C5[2c]	−0.25	−0.49
	DB18C6[1c]	1.36	0.68

Discussion

As can be seen from Table 1, the log $K_{ex}(MB_3A)$ value of Rb^+, which is more strongly hydrated than Cs^+, is smaller than that of Cs^+. On the contrary, for the MLA, MLBA, and ML_2A systems, Rb^+ is more extractable than Cs^+. In the cases of 12C4 and DB18C6, the extractabilities and the difference in the extractabilities of Rb^+ and Cs^+ are enhanced in going from the MLA system to the ML_2A one, and, in the case of 15C5, those increase in the system order MLA< MLBA<ML_2A.

When MLA forms MLBA and ML_2A with B and L in the organic phase, the equilibria can be written as Eqs. 21 and 22 respectively:

$$MLA_o + B_o \rightleftarrows MLBA_o$$

$$K_{MLBA,o} = K_{ex}(MLBA)/K_{ex}(MLA) = [MLBA]_o/[MLA]_o[B]_o \quad (21)$$

$$MLA_o + L_o \rightleftarrows ML_2A_o$$

$$K_{ML_2A,o} = K_{ex}(ML_2A)/K_{ex}(MLA) = [ML_2A]_o/[MLA]_o[L]_o, \quad (22)$$

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

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

		Rb+	Cs+
$\log K_{MLBA,o}$	15C5	0.81	0.68
$\log K_{ML_2A,o}$	12C4	1.81	1.54
	15C5	2.40	1.97
	DB18C6[1c]	2.7	2.5

It has been reported that in the benzene–water system at 20±2 °C the extraction of Cs^+ is enhanced by a factor of 60 with a mixture of 2-thenoyltrifluoroacetone (HTTA) and B compared with that by HTTA alone, and that the formula for the extracted species is $Cs(TTA)B_2$;[7] in the present study, the extraction is enhanced by a factor of only 4.8 with a mixture of 15C5 and B compared with that by 15C5 alone (Table 2). The large difference in the synergistic effects of the HTTA and the 15C5 systems may chiefly depend on the fact that the HTTA complex has more B than the 15C5 complex. There were no appreciable synergistic effects for the Na^+ and the K^+–15C5–B systems. Since a cation whose size exceeds the cavity size of the crown ether cannot get into the plane of the oxygen atoms of the crown ether, for the 15C5 complex, Rb^+ (crystal ionic radius: 1.48 Å[8]) and Cs^+ (crystal ionic radius: 1.69 Å[8]) may protrude from the plane of 15C5 (cavity radius: 0.85—1.1 Å[9]) much more than Na^+ (crystal ionic radius: 0.95 Å[8]) and K^+ (crystal ionic radius: 1.33 Å[8]). Consequently, the 15C5 complexes with RbA and CsA may easily accept a B molecule, while, it may be very difficult for those with NaA and KA.

It may be noted from Table 2 that the complex-formation constant of Rb^+ is greater than that of Cs^+ in every system. For the MLBA system, this may be attributed to the higher charge density of Rb^+ compared with that of Cs^+. For the ML_2A system, this may be due to the fact that Rb^+ has higher charge density than Cs^+, and moreover that Rb^+ has a more optimum size for each of the cavities of these crown ethers (cavity radius: 12C4 (0.5—0.65 Å[9]), 18C6 (1.3—1.6 Å[9])) than Cs^+.

The sequences of the number of the donor oxygen atoms for these ligands are B<12C4<15C5<DB18C6. The small number of the donor oxygen atoms of B may be the reason why, in each case of Rb^+ and Cs^+, the complex-formation constant value of MLBA is the

smallest of all the complexes (Table 2). For the crown ethers, in each case of Rb^+ and Cs^+, the accommodation of the metal ion into the crown ether cavity and the complex-formation constant value increase in the crown ether order 12C4<15C5<DB18C6 (Table 2). These results indicate that, for the same alkali metal ion, the larger the number of the donor oxygen atoms of the crown ether and the more closely the metal ion fits into the crown ether cavity, the greater is the complex-formation constant value.

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