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Stabilities and Transfer Activity Coefficients of Benzo-15-crown-5-Alkali Metal Ion Complexes in Various Solvents

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Stability constants in acetonitrile and methanol of 1:1 benzo-15-crown-5 (B15C5)-alkali metal ion complexes and the solubility of B15C5 in acetonitrile, propylene carbonate, methanol, and water were determined at 25 °C by conductometry and spectrophotometry, respectively. In general, selectivity tendency of B15C5 for the alkali metal ions except for Li^+ can be interpreted in terms of size-relationship. Stability sequences of the B15C5-alkali metal ion complex among the solvents, except for Rb^+ and Cs^+ complexes, are the reverse of solvation-ability sequences of the solvents to the corresponding alkali metal ion. By using the stability constants of the B15C5-alkali metal ion complexes, transfer activity coefficients (γ) of the B15C5 complexes were then calculated from γ values of B15C5 (obtained from solubilities of B15C5) and those of alkali metal ions. The γ value of the B15C5 complex from methanol to acetonitrile and propylene carbonate generally varies with a variety of alkali metal ions. From γ values of the B15C5 complexes, it is concluded that there exists a possible specific interaction between the alkali metal ion held in the B15C5 cavity and solvent molecules when the alkali metal ion is much smaller or larger than the B15C5 cavity.

In the previous study,[1] molar conductivities of alkali metal perchlorates were measured in propylene carbonate in the presence of benzo-15-crown-5 (B15C5), and stabilities and solvation properties of the 1:1 complexes of B15C5 with alkali metal ions were discussed from the standpoint of thermodynamics and transport phenomena, respectively. Stability sequences of the B15C5-alkali metal ion complexes in propylene carbonate are in the order $Na^+>Li^+>K^+>Rb^+>Cs^+$, which is consistent with the size-fit concept; namely, correlation between relative sizes of cation and crown ether cavity. In the cases of Na^+, K^+, Rb^+, and Cs^+, the size of the moving entity in propylene carbonate is larger for the B15C5 complex than for the corresponding alkali metal ion, whereas, in the case of Li^+, that is completely the reverse.

In the present study, in order to further investigate complexing-power tendency of B15C5 for alkali metal ions and medium effects on stabilities of the 1:1 B15C5-alkali metal ion complexes, formation constants of the B15C5 complexes in acetonitrile and methanol were conductometrically determined at 25 °C. In addition, by using the formation constants of the B15C5 complexes, transfer activity coefficients (γ) of the B15C5 complexes were then calculated from γ values of B15C5 (obtained from solubilities of B15C5) and those of alkali metal ions. From the γ values of the B15C5 complexes, properties of solute-solvent interaction of the B15C5 complexes were discussed in detail.

Experimental

Materials. The method of purification of B15C5 (Merck Japan Ltd.) was the same as that described previously.[1] Extremely pure alkali metal (Li, Na, K, Rb, Cs) chlorides were purchased from Merck Japan Ltd., and were used without further purification. Rubidium and caesium perchlorates were prepared by adding a little excess of $HClO_4$ to aqueous solutions of RbCl and CsCl, respectively. Lithium, sodium, and potassium perchlorates were commercially obtained from Merck Japan Ltd. All the perchlorates were recrystallized four times from distilled water and, prior to use, dried at 150 °C in vacuo. The method of purification of acetonitrile,[2] propylene carbonate,[3] and methanol[4] was previously reported. The conductivities of acetonitrile, propylene carbonate, methanol, and water thus purified were less than 3×10^{-7}, 5×10^{-8}, 2×10^{-7}, and 6×10^{-7} Ω^{-1} cm^{-1}, respectively. For conductometric titrations, alkali metal chlorides and perchlorates were used for methanol and acetonitrile systems, respectively.

Apparatus and Procedure. The conductance measurements were made on a Fuso conductivity apparatus, model 362 A, in a water bath thermostated at 25±0.01 °C. Two cells were used, cell constants of which were 0.059701 and 0.097765 cm^{-1}. Experimental procedures to obtain formation constants of B15C5-alkali metal ion complexes were the same as those described in a preceding paper.[3]

Solubilities of B15C5. A B15C5 suspension in a given solvent was stirred at 25±0.02 °C for 3 days, and then the solution saturated with B15C5 was filtered under nitrogen. The B15C5 concentration of the solution was determined spectrophotometrically (at 226, 222, 220, and 200 nm in acetonitrile, propylene carbonate, methanol, and water, respectively). Solubilities of B15C5 at 25 °C are 1.9, 1.2, 4.0×10^{-1}, and 1.1×10^{-1} M (1 M=1 mol dm^{-3}) in acetonitrile, propylene carbonate, methanol, and water, respectively.

Results and Discussion

The method for obtaining formation constants (K_{ML^+}) of B15C5-alkali metal ion complexes was the same as that described in a previous paper,[3] where $K_{ML^+}=[ML^+]/[M^+][L]$. M^+ and L denote an alkali metal ion and a crown ether, respectively. In this work, it is assumed that the association between a cation and an anion is negligible and that B15C5 forms a 1:1 complex with an alkali metal ion. The $\log K_{ML^+}$ values are summarized in Table 1.

Molar conductivity (Λ) vs. $[L]_t/[M]_t$ plots for

Table 1. Log(K_{ML^+}/mol^{-1} dm^3) Values of B15C5 at 25 °C and Crystal Ionic Radii of Alkali Metals (Å)

	Li^+	Na^+	K^+	Rb^+	Cs^+
Crystal ionic radius[5]	0.60	0.95	1.33	1.48	1.69
AN[a]	4.46±0.02	4.25±0.01	2.49±0.01	2.72±0.03	2.39±0.03
PC[b]	3.77±0.03[1]	4.35±0.01[1]	2.78±0.01[1]	2.38±0.03[1]	2.03±0.04[1]
H_2O	—	—	0.38[6]	—	—
CH_3OH	2.31±0.03	2.99±0.02	2.71±0.01	2.40±0.02	2.15±0.04

a) Acetonitrile. b) Propylene carbonate.

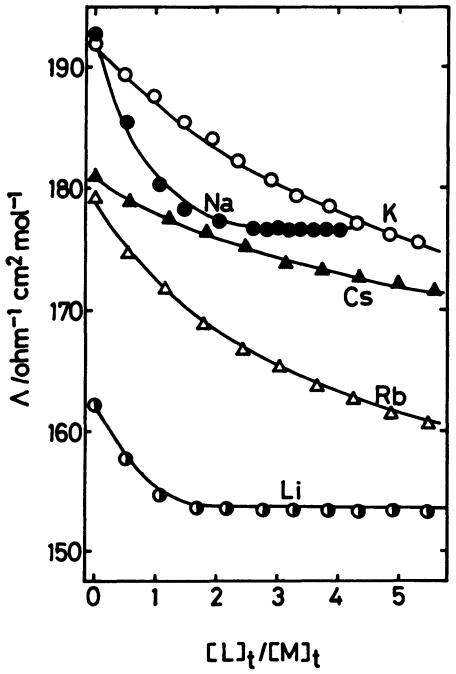

Fig. 1. Λ vs. $[L]_t/[M]_t$ curves for B15C5–alkali metal perchlorate systems in acetonitrile at 25 °C.
—— calculated curve by using K_{ML^+} value. $[M]_t$= (5.0—6.0)×10^{-4} M.

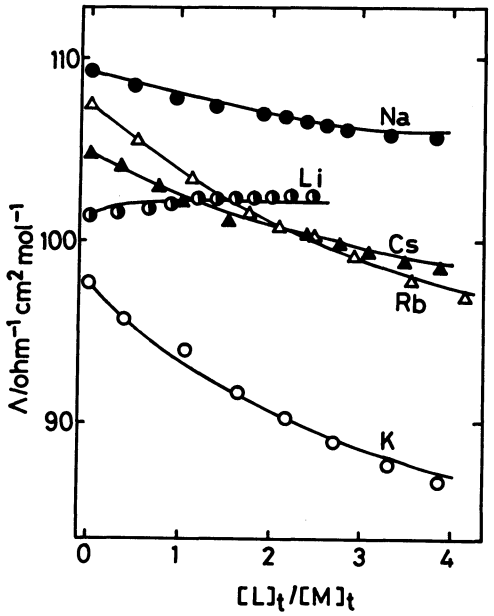

Fig. 2. Λ vs. $[L]_t/[M]_t$ curves for B15C5–alkali metal chloride systems in methanol at 25 °C.
—— calculated curve by using K_{ML^+} value. $[M]_t$= (6.0—8.0)×10^{-4} M.

acetonitrile and methanol are given in Figs. 1 and 2, $[L]_t$ and $[M]_t$ denoting total concentrations of B15C5 and the alkali metal ion, respectively. Every Λ vs. $[L]_t/[M]_t$ plot, except for the LiCl–CH_3OH system, shows a decrease in Λ with an increase in $[L]_t$, indicating that the mobility of the B15C5–alkali metal ion complex is smaller than that of the corresponding uncomplexed alkali metal ion. This can be expected on the basis of much larger size of the B15C5–alkali metal ion complex compared to the corresponding alkali metal ion. The Λ vs. $[L]_t/[M]_t$ plot of the LiCl–CH_3OH system, on the other hand, shows that moving entity of Li^+ is larger than that of the B15C5–Li^+ complex. Generally, such a phenomenon can be observed for the combination of smaller alkali metal ions (e.g., Li^+ and Na^+) and the smaller crown ethers compared to 18-crown-6 in a solvent of lower donicity (e.g., acetonitrile and propylene carbonate).[1,3] A possible explanation is as follows. In a solvent of lower donicity, a stable complex is formed even between a small alkali metal ion and a small crown ether which has a poor binding ability. On account of strong solvation of the small alkali metal ion and less solvation of its complex with the small crown ether, moving entity of the alkali metal ion is larger than that of its crown ether complex.

From Figs. 1 and 2, it is evident that a clear breaking point at $[L]_t/[M]_t$=1 is observed only in the case of the Li–acetonitrile system. It is responsible for the clear breaking point that B15C5 forms a very stable 1:1 complex with Li^+ and the complex has a lower mobility than a Li^+ ion.

Stability Constants. From Table 1, selectivity sequences of B15C5 for the alkali metal ions in acetonitrile, propylene carbonate, and methanol are as follows:

AN: $Li^+ > Na^+ \gg Rb^+ > K^+ > Cs^+$,
PC: $Na^+ > Li^+ > K^+ > Rb^+ > Cs^+$,
CH_3OH: $Na^+ > K^+ > Rb^+ > Li^+ > Cs^+$.

Table 2. Transfer Activity Coefficients at 25 °C

		s=AN[a]		s=PC[b]		s=H_2O	
log $^{CH_3OH}\gamma^s(M^+)$							
	Li^+[8]	4.47		3.15		—	
	Na^+[9]	0.9		1.54		—	
	K^+[9]	−0.4		−0.16		−1.7	
	Rb^+[9]	−0.6		−0.48		—	
	Cs^+[9]	−0.8		−0.66		—	
log $^{CH_3OH}\gamma^s(L)$		B15C5	B18C6[10]	B15C5	B18C6[10]	B15C5	B18C6
		−0.68	1.0	−0.48	0.082	0.56	—
log $^{CH_3OH}\gamma^s(ML^+)$							
	Li^+	1.64	—	1.21	—	—	—
	Na^+	−1.0	1.5	−0.29	0.8	—	—
	K^+	−0.9	1.0	−0.70	0.2	1.19	—
	Rb^+	−1.6	1.1	−0.93	0.2	—	—
	Cs^+	−1.7	0.5	−1.01	−0.08	—	—

a) Acetonitrile. b) Propylene carbonate.

Selectivity tendency of B15C5 for the alkali metal ions except for Li^+ is roughly consistent with size-relationship regardless of a variety of solvents; that is, the more closely the alkali metal ion fits into the B15C5 cavity (cavity radius 0.85 Å[7]), the more stable is the B15C5–alkali metal ion complex. For Li^+ ion, however, log K_{ML^+} value is the greatest in acetonitrile, the second largest in propylene carbonate, and the second smallest in CH_3OH among alkali metal ions. Stability of the B15C5–Li^+ complex seems to be governed largely not only by the size-relationship but also by the strength of solvation of the solvent for the free Li^+ ion. Li^+ probably undergoes the strongest solvation of all the alkali metal ions. Solvation-ability (i.e., relative solubility) sequences of the solvents for Li^+ derived from the data[8] on transfer activity coefficients are acetonitrile≪propylene carbonate≪CH_3OH, and the difference in solvation-ability of solvent[8] between Li^+ and the other alkali metal ion increases in the order acetonitrile<propylene carbonate<CH_3OH. This is responsible for the above-mentioned results of the Li^+ complex.

Stability sequences of the respective B15C5–alkali metal ion complexes for the solvents are as follows:

Li^+: AN > PC > CH_3OH,

Na^+: PC > AN > CH_3OH,

K^+: PC ≥ CH_3OH > AN ≫ H_2O,

Rb^+: AN > CH_3OH ≥ PC,

Cs^+: AN > CH_3OH > PC.

Solvation-ability sequences[8,9] of the solvents for the alkali metal ion are as follows:

Li^+: AN ≪ PC ≪ CH_3OH,

Na^+: PC < AN < CH_3OH,

K^+: CH_3OH ≤ PC < AN ≪ H_2O,

Rb^+: CH_3OH < PC ≤ AN,

Cs^+: CH_3OH < PC ≤ AN.

Stability sequences of the respective B15C5–alkali metal ion complexes in the solvents, except for the cases of Rb^+ and Cs^+ complexes in acetonitrile, are the reverse of solvation-ability sequences of the solvents for the corresponding alkali metal ion. This indicates that the B15C5–alkali metal ion complex is stable in a solvent with poor solvation-ability to the free alkali metal ion and the reverse is true. The author cannot explain the exceptional behavior of Rb^+ and Cs^+ complexes in acetonitrile at the present time.

Transfer Activity Coefficient. Logarithm of transfer activity coefficient (log $^{s_1}\gamma^{s_2}(ML^+)^\dagger$) of a B15C5–alkali metal ion complex between solvent s_1 and solvent s_2 is calculated by Eq. 1.

$$\log {}^{s_1}\gamma^{s_2}(ML^+) = (\log K_{ML^+})_{s_1} - (\log K_{ML^+})_{s_2} + \log {}^{s_1}\gamma^{s_2}(L) + \log {}^{s_1}\gamma^{s_2}(M^+), \quad (1)$$

where log $^{s_1}\gamma^{s_2}(L)^\dagger$ and log $^{s_1}\gamma^{s_2}(M^+)^\dagger$ refer to logarithm of transfer activity coefficients of B15C5 itself and a free alkali metal ion between solvent s_1 and solvent s_2, respectively, and $(\log K_{ML^+})_s$ designates log K_{ML^+} value in solvent s. By way of example, a positive log $^{s_1}\gamma^{s_2}(ML^+)$ value means that the complex, ML^+, undergoes stronger solvation in s_1 than in s_2. Transfer activity coefficient values of ML^+, M^+, and L when s_1=CH_3OH are summarized in Table 2.

From the solubility data of B15C5 determined in this study, solubility sequences of B15C5 for the solvents are in the order acetonitrile>propylene carbonate>methanol>water although there exist hydrogen bonds between ether oxygen atoms and protic solvents such as water and methanol, and, moreover, the hydrogen bonding is much stronger in water than in methanol.[11] This may be attributed to superiority of lipophilic effects of the benzo and ethylene groups over hydrogen-bonding effects of ether oxygen atoms. Benzo-18-crown-6 (B18C6) is larger in size than B15C5

† $^{s_1}\gamma^{s_2}(X)=[X]_{s_1}/[X]_{s_2}$, X denoting ML^+, L, or M^+.

by an ether oxygen atom and an ethylene group. When s=AN and PC, the log $^{CH_3OH}\gamma^{s}$(L) value changes from negative to positive in going from B15C5 to B18C6. This may be due to the additional hydrogen bonding between the added ether oxygen atom of B18C6 and methanol.

It can be seen from Table 2 that, in general, the log $^{CH_3OH}\gamma^{s}(ML^+)$ value of B15C5 varies with a variety of alkali metal ions when s=AN and PC. Positive log $^{CH_3OH}\gamma^{s}(ML^+)$ values of B15C5 are found only for the case of Li^+. They are much larger compared to those of other alkali metal ions. From Eq. 1 and Tables 1 and 2, this is attributed completely to very large and positive log $^{CH_3OH}\gamma^{s}(Li^+)$ values; namely, the fact that the B15C5-Li^+ complex undergoes much stronger solvation in methanol than in acetonitrile and propylene carbonate is due entirely to much stronger solvation of the central Li^+ in methanol than in acetonitrile and propylene carbonate.

For B15C5, the log $^{CH_3OH}\gamma^{s}$ value decreases on moving from M^+ to ML^+ when s=AN and PC, and the contrary holds for B18C6 except for the case of M^+=Na^+ and s=PC. This is owing largely to the fact that B15C5 is less solvated in methanol than in AN and PC, while B18C6 is more solvated in methanol than in AN and PC. The higher solvation of B15C5 in methanol than in H_2O is mostly responsible for the fact that the log $^{CH_3OH}\gamma^{H_2O}$ value increases in going from K^+ to B15C5-K^+ complex (Table 2).

In the cases of s=AN and PC, the log $^{CH_3OH}\gamma^{s}(ML^+)$ value increases from B15C5 to B18C6. This shows that the B18C6-alkali metal ion complex is more solvated in methanol than in AN and PC in comparison with the B15C5 complex. In each case of s=AN and PC, the difference in log $^{CH_3OH}\gamma^{s}(ML^+)$ values between B15C5 and B18C6 is roughly constant regardless of the alkali metal ions except for the system of M^+=K^+ and s=AN. As mentioned above for free B15C5 and B18C6, this may be caused primarily by the effect of the additional hydrogen bonding between the increased ether oxygen atom of B18C6 and methanol.

When L=B15C5, s=AN and PC, and M^+=Na^+ and K^+, log $^{CH_3OH}\gamma^{s}$ values for ML^+ and L are nearly the same. Log $^{PC}\gamma^{AN}$ values for B15C5-K^+ and B15C5 at 25 °C are identical (−0.2). This indicates that, generally, property of solute-solvent interaction of the B15C5-alkali metal ion complex mostly reflects that of the free B15C5 unless the alkali metal ion in the B15C5 complex is much smaller or larger than the B15C5 cavity; when log $^{s_1}\gamma^{s_2}$ values for B15C5-M^+ and B15C5 are fairly different from each other, it seems that there exists a specific interaction between the alkali metal ion in the B15C5 cavity and the solvents, where, in most cases, the alkali metal ion in the B15C5 cavity has a much smaller or larger size than that of the B15C5 cavity. A similar tendency is observed for B18C6 and its alkali metal ion complexes (Table 2 and log $^{PC}\gamma^{AN}$(B18C6)=0.92, log $^{PC}\gamma^{AN}$(M^+-B18C6)=0.7 (Na^+), 0.8 (K^+), 0.9 (Rb^+), and 0.58 (Cs^+) at 25 °C[10]).

Solvation-ability sequences of the solvents for the B15C5-alkali metal ion complex obtained from log $^{CH_3OH}\gamma^{s}(ML^+)$ values in Table 2 are as follows:

Li^+-B15C5: AN < PC ≪ CH_3OH,
Na^+-B15C5: CH_3OH < PC < AN,
K^+-B15C5: H_2O < CH_3OH < PC < AN,
Rb^+-B15C5: CH_3OH < PC < AN,
Cs^+-B15C5: CH_3OH < PC < AN.

From the solubility data of B15C5 in this study, solvation-ability sequences of the solvents for B15C5 are H_2O<CH_3OH<PC<AN; they agree completely with those for the B15C5-alkali metal ion complex except for B15C5-Li^+ complex. Solvation-ability sequences of the solvents for the B15C5-alkali metal ion complex are consistent with those for the corresponding alkali metal ion except for the cases of CH_3OH for B15C5-Na^+ complex and H_2O for B15C5-K^+ complex. Property of solute-solvent interaction of the B15C5-alkali metal ion complex is characterized by that of the corresponding free alkali metal ion and/or by that of the B15C5 itself. Whereas, property of solute-solvent interaction in AN, PC, and CH_3OH of the B18C6-alkali metal ion complex, whose ligand is larger than B15C5, is characterized by that of the B18C6 itself (solvation-ability sequences of the solvents for B18C6: AN<PC≤CH_3OH).

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