Stabilities and transfer activity coefficients from water to polar nonaqueous solvents of 1,2-bis[2-(2-methoxyethoxy)ethoxy]benzene- and benzo-18-crown-6-cation complexes

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Stabilities and transfer activity coefficients from water to polar nonaqueous solvents of 1,2-bis[2-(2-methoxyethoxy)ethoxy]benzene- and benzo-18-crown-6-cation complexes

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Formation constants (K_{ML}) for 1:1 complexes of 1,2-bis[2-(2-methoxyethoxy)ethoxy]benzene (AC·B18C6), a linear counterpart of benzo-18-crown-6 (B18C6), and B18C6 with various mono- and divalent cations were determined in water at 25°C by conductometry; the K_{ML} value for the B18C6-Li$^+$ complex was also determined in acetonitrile. By using the K_{ML} and literature values, transfer activity coefficients of the AC·B18C6- and B18C6-alkali metal ion complexes from water to polar nonaqueous solvents were calculated. The selectivity order in water of AC·B18C6 for univalent cations is different from that of B18C6, but for bivalent cations they are almost the same. For the same cation, the aqueous log K_{ML} value is lower for AC·B18C6 than for B18C6 except for size-misfitting smaller cations (H$^+$, Li$^+$, Cd^{2+}). In general, cyclization of the two binding-arms of AC·B18C6 increases the selectivity and stability for the cations in water. Although AC·B18C6 is always less hydrophilic than B18C6, the AC·B18C6-alkali metal ion complex is more hydrophilic than the corresponding B18C6 complex. It follows that the alkali metal ion in the AC·B18C6 complex is less effectively shielded and dehydration of AC·B18C6 upon complexation in water is less efficient, compared with B18C6. Hydrogen bonding between AC·B18C6 or B18C6 and water causes the unexpectedly lowest aqueous stability of the AC·B18C6- or B18C6-alkali metal ion complex among all the solvents. The same holds for the stabilities of the other metal ion complexes with AC·B18C6 or B18C6.

1. Introduction

Structures of benzo-18-crown-6 (B18C6) and its open-chain analog 1,2-bis[2-(2-methoxyethoxy)ethoxy]benzene (AC·B18C6) are shown in figure 1.

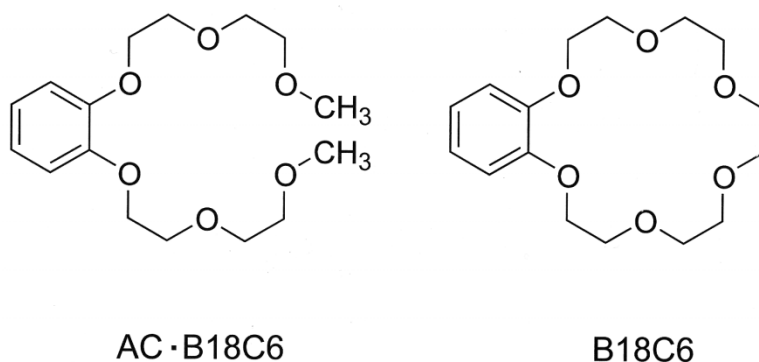*Corresponding author. E-mail: takeda@faculty.chiba-u.jp

Figure 1. Structures of AC·B18C6 and B18C6.

In a series of studies on B18C6 and AC·B18C6 complexes with metal ions, particularly alkali metal ions, in polar nonaqueous solvents, the macrocyclic effect and solute–solvent interactions for the complexes were discussed from the standpoint of equilibria and transport phenomena [1,2]. In general, the B18C6-alkali metal ion complex is more stable than the corresponding AC·B18C6 complex. Selectivity of B18C6 for alkali metal ions is greater than for AC·B18C6. The AC·B18C6-alkali metal ion complex is more mobile than the corresponding B18C6 complex; the mobility of the AC·B18C6 complex is less sensitive to a variety of alkali metal ions in the complexes than the B18C6 complex. Unexpectedly low aqueous stabilities and hydration behavior of nine B18C6-metal ion complexes [3] and two AC·B18C6 complexes [4] have also been studied on the basis of the transfer activity coefficients from water to polar nonaqueous solvents.

In this paper we report more detailed information on the macrocyclic effect and solute–solvent interactions in water for various AC·B18C6- and B18C6-cation complexes.

2. Experimental

2.1. *Materials*

AC·B18C6 was prepared by the reaction of catechol with 2-(2-methoxyethoxy)ethyl chloride in a mixture of aqueous sodium hydroxide and 1-butanol according to the literature method [5,6]. The product was purified by distillation under vacuum (bp 180.3–196.0°C/2.0–3.5 Torr) (1 Torr ≈ 133.322 Pa). B18C6 (Tokyo Chemical Industry) was recrystallized from hexane, and dried *in vacuo* prior to use (mp 42.8–43.9°C). Analytical-grade alkali metal (Li–Cs) chlorides, $LiClO_4 \cdot 3H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, $Sr(NO_3)_2$, $AgNO_3$, $TlNO_3$ and $HClO_4$, were purchased from Merck Japan Ltd; analytical-grade $Cd(NO_3)_2 \cdot 4H_2O$, $Pb(NO_3)_2$ and nitric acid were from Wako Pure Chemicals Ltd; all were used without further purification. The purification method for acetonitrile (AN) was reported previously [5]. The conductivities of the final products of AN and water were less than 7.5×10^{-8} and $9.0 \times 10^{-7}\, S\, cm^{-1}$, respectively. Lithium perchlorate was used for the AN system and the other metal salts for the water system.

2.2. *Apparatus and procedure for conductometry*

Conductivity measurements were carried out on a Fuso Model 362A or 362B instrument at $25.00 \pm 0.02°C$. Three cells with cell constants of 0.21199, 0.19627, and $0.18768 \, cm^{-1}$ were used. The experimental procedure for obtaining formation constants of crown ether complexes with cations was similar to that described previously [6]. Conductivity measurements for Ag^+, Cd^{2+} and Pb^{2+} were performed at pH 2.8–3.9 to prevent hydrolysis of the metal ions. The concentration ranges of the metal salts and perchloric acid were $(1.0–5.7) \times 10^{-3} \, M$.

3. Results and discussion

Plots of molar conductivity (Λ) in water *vs* $[L]_t/[HClO_4]_t$ are shown in figure 2; $[L]_t$ and $[HClO_4]_t$ are the total concentrations of $AC \cdot B18C6$ or B18C6 and perchloric acid, respectively. Plots of Λ *vs* $[L]_t/[M]_t$ for the other systems are similar and have been omitted; $[M]_t$ denotes the total metal-salt concentration. Analysis of the conductometric data to obtain formation constants (K_{ML}) of crown ether–cation 1:1 complexes has been described elsewhere [6], where $K_{ML} = [ML^{m+}]/[M^{m+}][L]$; M^{m+} and L denote a cation and a crown ether, respectively. The association between a cation and an anion and corrections for viscosity changes due to solute were neglected. The respective aqueous K_{ML} values for $AC \cdot B18C6-Ag^+$, $-Cd^{2+}$, $-Pb^{2+}$ and $B18C6-Ag^+$ complexes were measured at different pH values. The K_{ML} values for the same complex are nearly equal regardless of the pH value. The $\log K_{ML}$ value in water for the $AC \cdot B18C6-Ag^+$, $-Cd^{2+}$, $-Pb^{2+}$ or $B18C6-Ag^+$ complex shown in table 1 is the average of the $\log K_{ML}$ values determined at different pH values. In propylene carbonate (PC) and CH_3OH, very little change in Λ occurred despite an increase in the B18C6 concentration for Li^+. It was impossible to determine the K_{ML} value of the
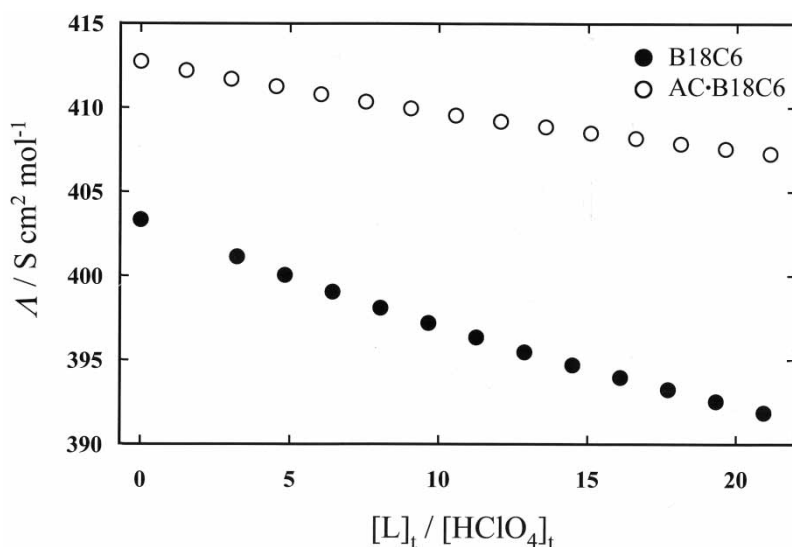

Figure 2. Plots of Λ *vs* $[L]_t/[HClO_4]_t$ for $AC \cdot B18C6$ and B18C6 in water at 25°C.

Table 1.　$\log(K_{ML}/\text{mol}^{-1}\,\text{dm}^3)$ values for AC·B18C6 and B18C6 at 25°C.

Cation	H$_2$O		AN		PC		CH$_3$OH	
	AC·B18C6	B18C6	AC·B18C6	B18C6	AC·B18C6	B18C6	AC·B18C6	B18C6
H$^+$	0.17 ± 0.08	−0.60 ± 0.10						
Li$^+$	0.48 ± 0.05	0.47 ± 0.15		4.68 ± 0.05	1.93[f]			
Na$^+$	0.68 ± 0.06[a]	0.81[b]	2.85[f]	4.9[g]	3.07[f]	5.3[g]	1.44[h]	4.5[g]
K$^+$	0.38 ± 0.07[a]	1.744[c]	2.619[f]	5.3[g]	2.544[f]	5.4[g]	2.25[f]	5.7[g]
		1.664[d]						
Rb$^+$	0.02 ± 0.08	1.15[c]	2.403[f]	4.4[g]	2.12[f]	4.5[g]	2.116[f]	5.1[g]
Cs$^+$	0.18 ± 0.03	0.64 ± 0.14	1.75[f]	3.8[g]	1.82[f]	3.6[g]	1.83[f]	4.1[g]
Ag$^+$	0.89 ± 0.07	1.23 ± 0.03						
Tl$^+$	0.20 ± 0.05	1.68[c]						
Ca^{2+}	1.12 ± 0.01	1.22 ± 0.05						
Sr^{2+}	0.81 ± 0.02	2.41[c]						
Ba^{2+}	0.98 ± 0.04	2.90[c]						
Cd^{2+}	0.54 ± 0.06	0.11[e]						
Pb^{2+}	1.0 ± 0.1	3.19[c]						

[a]Ref. [4]; [b]Ref. [7]; [c]Ref. [3]; [d]Ref. [8]; [e]Ref. [9]; [f]Ref. [2]; [g]Ref. [1]; [h]Ref. [10].

B18C6-Li$^+$ complex in PC and CH$_3$OH. The order of decreasing aqueous K_{ML}-values for AC·B18C6 for uni- and divalent cations are Ag$^+$ > Na$^+$ > Li$^+$ ≥ K$^+$ > Tl$^+$ ≥ Cs$^+$ ≈ H$^+$ ≥ Rb$^+$ and Ca^{2+} > Pb^{2+} ≈ Ba^{2+} > Sr^{2+} > Cd^{2+}, respectively; those of B18C6 are K$^+$ ≥ Tl$^+$ > Ag$^+$ ≥ Rb$^+$ > Na$^+$ ≥ Cs$^+$ ≥ Li$^+$ > H$^+$ and Pb^{2+} > Ba^{2+} > Sr^{2+} > Ca^{2+} > Cd^{2+}, respectively. The selectivity orders of AC·B18C6 and B18C6 for univalent cations are different; those for divalent cations are the same except for Ca^{2+}. For alkali metal ions, the differences between the largest and the smallest $\log K_{ML}$ values in water are 0.66 for AC·B18C6 and 1.27 for B18C6; for alkaline earth metal ions, those values are 0.31 for AC·B18C6 and 1.68 for B18C6. The selectivity for the neighboring alkali metal ions in the periodic table is lower for AC·B18C6 than for B18C6 (figure 3). The same holds for the alkaline earth metal ions (figure 4). For the same cation, the aqueous $\log K_{ML}$ value is always lower for AC·B18C6 than for B18C6, except for H$^+$, Li$^+$ and Cd^{2+}, which are size-misfitting smaller cations. On moving from the size-fitting cation to the smaller size-mismatched cation, the $\log K_{M(B18C6)} - \log K_{M(AC \cdot B18C6)}$ value in water for the same cation decreases with a decrease in cation size. It follows from this that the size-misfitting smaller cation attracts the donor oxygen atoms of AC·B18C6 more strongly because of its two flexible arms, resulting in a more stable complex with AC·B18C6 compared with B18C6. Generally, cyclization of the two flexible binding arms of AC·B18C6 increases the selectivity and the stability for the cation in water.

The logarithm of the transfer activity coefficient of a crown ether–alkali metal ion complex between solvent s$_1$ and solvent s$_2$ [$\log {}^{s_1}\gamma^{s_2}(\text{ML}^+)$] is calculated by equation (1):

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

where $(\log K_{ML})_s$ and ${}^{s_1}\gamma^{s_2}(\text{M}^+)$ denote the $\log K_{ML}$ in solvent s and the transfer activity coefficient of an alkali metal ion between s$_1$ and s$_2$, respectively; ${}^{s_1}\gamma^{s_2}(\text{X}) = [\text{X}]_{s_1}/[\text{X}]_{s_2}$. The $\log {}^s\gamma^{H_2O}$ values at 25°C for M$^+$, L and ML$^+$ are compiled in table 2. For both AC·B18C6 and B18C6, the $\log {}^s\gamma^{H_2O}(\text{ML}^+)$ value for a given solvent varies
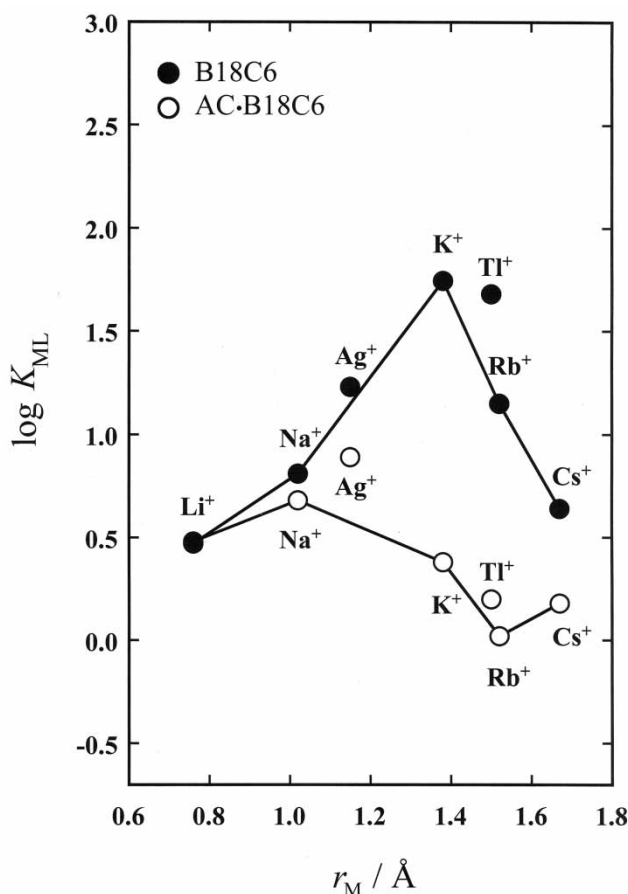
Figure 3. Plots of $\log K_{ML}$ *vs* effective ionic radii (r_M) of univalent cations.

with the alkali metal ion. The interaction of the ML^+ complex with solvents is affected by the trapped alkali metal ion. For $AC \cdot B18C6$ or $B18C6$, the largest $|\log{}^s\gamma^{H_2O}(M_2L^+) - \log{}^s\gamma^{H_2O}(M_1L^+)|$ value is observed for $M_1^+ = Li^+$ and $M_2^+ = Na^+$ or $M_1^+ = Na^+$ and $M_2^+ = K^+$ in a given solvent except for the $B18C6/CH_3OH$ system, where M_1^+ and M_2^+ denote neighboring alkali metal ions in the periodic table, and the M_1^+ ion is smaller than the M_2^+ ion; the $|\log{}^s\gamma^{H_2O}(M_2L^+) - \log{}^s\gamma^{H_2O}(M_1L^+)|$ value for $M_1^+ = K^+$ and $M_2^+ = Rb^+$ is roughly equal to that for $M_1^+ = Rb^+$ and $M_2^+ = Cs^+$. The interaction of the ML^+ complex with solvents is more strongly influenced by the size-mismatched smaller cation in the cavity. The $|\log{}^s\gamma^{H_2O}(M_2L^+) - \log{}^s\gamma^{H_2O}(M_1L^+)|$ value for $AC \cdot B18C6$ is greater than or equal to the corresponding one for $B18C6$. $AC \cdot B18C6$ screens the alkali metal ion in the complex less effectively than $B18C6$.

Every $\log{}^s\gamma^{H_2O}(ML^+) - \log{}^s\gamma^{H_2O}(M^+)$ value for the same alkali metal ion is positive. This shows that the alkali metal ion, which is more strongly solvated in water than in the nonaqueous solvent, enhances its lipophilicity on complexation because of the greater desolvation effect of the alkali metal ion in water compared with the nonaqueous solvents. Although $AC \cdot B18C6$ is always less hydrophilic than $B18C6$,
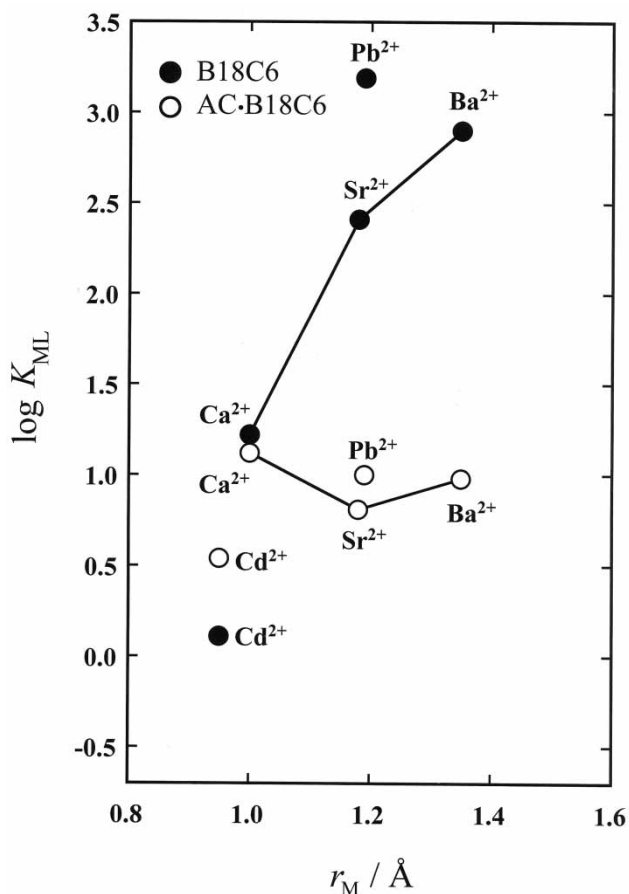
Figure 4. Plots of log K_{ML} *vs* effective ionic radii (r_M) of bivalent cations.

the AC·B18C6–alkali metal ion complex is more hydrophilic than the corresponding B18C6 complex. It thus appears that the alkali metal ion in the AC·B18C6 complex is less effectively shielded and dehydration of AC·B18C6 upon complexation in water is less efficient, compared with B18C6.

The $\log {}^s\gamma^{H_2O}(ML^+) - \log {}^s\gamma^{H_2O}(L)$ value for AC·B18C6 is positive or nearly zero except for Li^+ and Na^+; that for B18C6 is positive except for Li^+. Although the alkali metal ion undergoes stronger solvation in water than in AN, PC or CH_3OH, the complex with AC·B18C6 or B18C6 is more soluble in the nonaqueous solvent than in water, compared with the crown ether itself. This is attributable to an enforcement of the aqueous hydrogen-bonded structure for the bulky complex ion caused by the much reduced hydrogen bonding between ether oxygen atoms and water on complexation. The Li^+ and Na^+ ions are much more strongly solvated by water than by AN or PC compared with the other alkali metal ions. For AC·B18C6, the effect of the possible strong interaction with water of the Li^+ or Na^+ ion in the complex surpasses that of the greatly decreased hydrogen bonding, resulting in the negative $\log {}^s\gamma^{H_2O}(ML^+) - \log {}^s\gamma^{H_2O}(L)$ value when s = AN or PC. The Na^+ ion undergoes less solvation in water than in CH_3OH compared with the other heavier alkali metal

Table 2. Transfer activity coefficients at 25°C.

S=	AN		PC		CH$_3$OH	
log $^s\gamma^{H_2O}(M^+)$[a]						
Li$^+$	-4.3[b]		-4.2[c]		$-$	
Na$^+$	-2.3		-2.9_4		-1.4	
K$^+$	-1.3		-1.5_4		-1.7	
Rb$^+$	-1.1		-1.2_2		-1.7	
Cs$^+$	-0.8		-0.9_4		-1.6	
	AC·B18C6	B18C6	AC·B18C6	B18C6	AC·B18C6	B18C6
log $^s\gamma^{H_2O}(L)$[d]	1.56	1.10	1.35	0.96	1.09	0.57
log $^s\gamma^{H_2O}(ML^+)$						
Li$^+$	$-$	1.0	-1.4		$-$	$-$
Na$^+$	1.4[d]	2.9[e]	0.8$_0$[d]	2.5[e]	0.5[d]	2.9[e]
K$^+$	2.5[d]	3.4[e]	1.9$_7$[d]	3.1[e]	1.3[d]	2.8[e]
Rb$^+$	2.8	3.3[e]	2.2$_3$	3.1[e]	1.5	2.8[e]
Cs$^+$	2.3	3.5	2.0$_5$	3.0	1.1	2.4

[a]Ref. [11]; [b]Ref. [12]; [c]Ref. [13]; [d]Ref. [4]; [e]Recalculated using the data of Refs. [3] and [4].

ions. The log $^{CH_3OH}\gamma^{H_2O}(NaL^+)$ – log $^{CH_3OH}\gamma^{H_2O}$ (L) value for AC·B18C6, however, is negative. This is attributed to the less effective dehydration of Na$^+$ and AC·B18C6 themselves upon complexation compared with K$^+$, Rb$^+$ and Cs$^+$. For B18C6, the negative log $^s\gamma^{H_2O}(ML^+)$ – log $^s\gamma^{H_2O}(L)$ value is found only when M$^+$ = Li$^+$ and s = AN. The log $^s\gamma^{H_2O}(ML^+)$ – log $^s\gamma^{H_2O}(L)$ value for AC·B18C6 is always smaller than the corresponding B18C6 value. It can be concluded that dehydration of the alkali metal ion and the crown ether on complexation is more efficient for the cyclic crown ether B18C6 than for the acyclic AC·B18C6. The less effective dehydration of AC·B18C6 and the size-misfitted smaller cation on complexation leads to the much higher hydrophilicity of the AC·B18C6 complex compared with B18C6. This also contributes to the fact that, on moving from K$^+$ to Li$^+$, the aqueous log K_{ML} values of AC·B18C6 and B18C6 for the same ion become similar. The above discussion shows that hydrogen bonding between AC·B18C6 or B18C6 and water causes the unexpectedly lowest aqueous stability of the AC·B18C6– or B18C6–alkali metal ion complex among all the solvents. It follows from this that the same holds for the stabilities of the other metal ion complexes with AC·B18C6 or B18C6 (table 1).

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