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Stabilities in Water and Transfer Activity Coefficients from Water to Nonaqueous Solvents of Benzo-18-crown-6–Metal Ion Complexes

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Formation constants in water of 1 : 1 benzo-18-crown-6 (B18C6)–metal ion complexes and the B18C6 solubility in water were determined at 25 °C by conductometry or potentiometry with ion-selective electrodes and spectrophotometry, respectively. The selectivity sequences of B18C6 for metal ions in water are $Pb^{2+}>Ba^{2+}>Sr^{2+}>Ag^{+}>K^{+}>Tl^{+}>Na^{+}>Rb^{+}$. In each case of alkali and alkaline earth metal ions, the more closely a metal ion fits into the B18C6 cavity, the more stable is the B18C6–metal ion complex. Although the solvation power of water for an alkali metal ion is not the largest of all solvents, the formation constant of a given B18C6–alkali metal ion complex in water is by far the smallest of all solvents. The transfer activity coefficients (γ) from water to nonaqueous solvents of the B18C6–metal ion complexes were then calculated from the formation constants of the B18C6 complexes, γ values of B18C6 (obtained from solubilities of B18C6), and γ values of the uncomplexed metal ions. The γ value of B18C6 is larger than those of B18C6–alkali metal ion complexes. This shows that when B18C6 forms a complex with an alkali metal ion, the B18C6 complex becomes more soluble in nonaqueous solvents than in water, compared with uncomplexed B18C6.

The formation constants in water and transfer activity coefficients from water to nonaqueous solvents of crown ether–metal ion complexes provide valuable information on effects of water on the stabilities and aspects of hydration of crown ether complexes, respectively, where the transfer activity coefficients of the crown ether complexes are calculated by using the formation constants of the crown ether complexes. The formation constants[1] in water and the transfer activity coefficients[2–4] from water to nonaqueous solvents of 18-crown-6 (18C6)- and dibenzo-18-crown-6 (DB18C6)–metal ion complexes have been reported. However, no data on the stabilities of benzo-18-crown-6 (B18C6)–metal ion complexes in water[1] have been reported.

In this study, the formation constants in water and the transfer activity coefficients from water to nonaqueous solvents of B18C6–metal ion complexes were determined at 25 °C. Effects on the stabilities in water and the aspects of hydration of the B18C6–metal ion complexes are discussed in detail.

Experimental

Materials. Benzo-18-crown-6 was prepared according to a method of Pedersen.[5] The product was recrystallized four times from hexane and dried in a vacuum oven at room temperature. Its purity was checked by melting point (mp 44—45 °C), elemental analysis, NMR, and conductometry.

Extremely pure NaCl, KCl, RbCl, CsCl, $Sr(NO_3)_2$, $Ba(NO_3)_2$, and analytical grade $TlNO_3$ were obtained from Merck Japan Ltd. They were used without further purification. Analytical grade $AgNO_3$ and $Pb(NO_3)_2$ were purchased from Wako Pure Chemicals Ltd. The purities of $AgNO_3$ and $Pb(NO_3)_2$ were determined by means of KCl and EDTA titration, respectively. The conductivity of water was less than $4\times10^{-7}\ \Omega^{-1}\ cm^{-1}$.

Apparatus and Procedure. The conductance measurements were made on a Fuso conductivity apparatus (model 362B) in a water bath thermostated at 25±0.005 °C. Two cells with cell constants of 0.05823 and 0.08135 cm^{-1} were used. The experimental procedure to obtain the formation constants of B18C6–metal ion complexes was almost the same as that described in a previous paper.[6]

The emf measurements were carried out with a Denki Kagaku Keiki ion meter apparatus (model IOC-10) in a water bath thermostated at 25±0.05 °C. For Na^+ and K^+, a Horiba 1512A-06T Na^+-selective electrode and a Toko Kagaku 1200 K^+-selective electrode were used, respectively. The Denki Kagaku Keiki 7080 Ag^+-selective electrode and the 7180 Pb^{2+}-selective electrode were used for Ag^+ and Pb^{2+}, respectively. Horiba 2535A-06T (Ag|AgCl electrode) and Denki Kagaku Keiki 4083 (Ag|AgCl electrode) were used as references for Na^+, K^+ measurements, and for Ag^+, Pb^{2+} measurements, respectively. Experiments for obtaining the formation constants of B18C6–metal ion complexes were performed according to the method of Frensdorff.[7]

Solubility of B18C6. A B18C6 suspension in water was stirred at 25±0.02 °C for 3 days; then, the solution saturated with B18C6 was filtered under nitrogen. The B18C6 concentration of the aqueous solution was determined spectrophotometrically (at 273 nm). The solubility of B18C6 in water (average of seven measurements) at 25 °C was 0.94±0.02 M (1 M=1 mol dm^{-3}).

Results and Discussion

The analysis of conductometric data for obtaining the formation constants (K_{ML}) of complexes of B18C6 with K^+, Rb^+, Tl^+, Sr^{2+}, and Ba^{2+} was the same as that described elsewhere.[6] Here, $K_{ML}=[ML^{m+}]/[M^{m+}][L]$; M^{m+} and L are a metal ion and a crown ether, respectively. The analysis of potentiometric data for obtaining K_{ML} values of complexes of B18C6 with Na^+, K^+, Ag^+, and Pb^{2+} was the same as that described by Frensdorff.[7] In this study, it is assumed that the association between a cation and an anion is negligible and that B18C6 forms a 1 : 1 complex with a metal ion. The log K_{ML} values are compiled in Table 1.

Stability Constants. It can be seen from Table 1 that the selectivity sequence of B18C6 for alkali metal ions

Table 1. $\log(K_{ML}/\mathrm{mol^{-1}\,dm^3})$ Values at 25 °C

	Ionic radius (Å)$^{a)}$	18C6	B18C6						DB18C6
		H_2O	AN$^{b)}$	PC$^{c)}$	CH_3OH	H_2O	DMF	DMSO	H_2O
Na^+	1.02	$0.8_0^{d)}$ $0.8_2^{e,f)}$	$4.9^{k)}$	$5.3^{k)}$	$4.5^{k)}$ $4.0_3^{l)}$ $4.35^{m)}$	$1.38\pm0.02^{n)}$	$2.5^{k)}$	—	$1.1_6^{q)}$ $1.1^{r)}$
K^+	1.38	$2.0_3^{d)}$ $2.04_7^{e)}$ $2.0_6^{g)}$ $2.03_4^{h)}$	$5.3^{k)}$	$5.4^{k)}$	$5.7^{k)}$ $5.2_7^{l)}$ $5.05^{m)}$	$1.744\pm0.004^{o)}$ $1.79\pm0.02^{n)}$	$3.6^{k)}$	$2.8^{k)}$	$1.6_7^{q)}$ $1.6^{r)}$
Rb^+	1.49	$1.5_6^{d)}$	$4.4^{k)}$	$4.5^{k)}$	$5.1^{k)}$ $4.6_2^{l)}$	$1.15\pm0.02^{o)}$	$3.2^{k)}$	$2.6^{k)}$	$1.0_8^{q)}$
Cs^+	1.70	$0.9_9^{d)}$ $0.9_8^{e)}$ $0.8^{g)}$	$3.8^{k)}$	$3.6^{k)}$	$4.1^{k)}$ $3.6_6^{l)}$	$(0.88)^{p)}$	$2.8^{k)}$	$2.4^{k)}$	$0.8_3^{q)}$
Ag^+	1.15	$1.5_0^{d)}$ $1.6^{g)}$	—	—	—	$1.83\pm0.02^{n)}$	—	—	$1.4_1^{q)}$ $1.5^{r)}$
Tl^+	1.50	$2.2_7^{d)}$ $2.2^{i)}$	—	—	—	$1.68\pm0.01^{o)}$	—	—	$1.5_0^{q)}$ $1.5^{r)}$
Sr^{2+}	1.13	$2.7_2^{d)}$ $2.8^{j)}$	—	—	$4.92^{l)}$	$2.41\pm0.01^{o)}$	—	—	$1.0_0^{q)}$
Ba^{2+}	1.36	$3.8_7^{d)}$	—	—	$5.35^{l)}$	$2.90\pm0.02^{o)}$	—	—	$\sim1.9_5^{q)}$
Pb^{2+}	1.19	$4.2_7^{d)}$ $4.4^{i)}$	—	—	—	$3.19\pm0.02^{n)}$	—	—	$1.8_8^{q)}$

a) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B,* **25**, 925 (1969). b) Acetonitrile. c) Propylene carbonate. d) Ref. 8, calorimetry. e) Ref. 9, ion exchange membrane. f) Ref. 10, NMR. g) Ref. 7, potentiometry. h) Ref. 11, conductometry. i) Ref. 12, potentiometry. j) Ref. 13, potentiometry. k) Ref. 14, conductometry. l) Ref. 15, spectrophotometry. m) Ref. 16, potentiometry. n) This study, ion selective electrode. o) This study, conductometry. p) Estimated value from $\log K_{ML}$ values of 18C6 and DB18C6 complexes in H_2O; $\{(0.99+0.98+0.8)/3+0.83\}/2\simeq0.88$. q) Ref. 17, spectrophotometry. r) Ref. 2, solubility.

in H_2O is $K^+>Na^+>Rb^+$ $(>Cs^+)$. The selectivity tendency in H_2O of B18C6 for alkali metal ions other than Na^+ agrees completely with those of 18-crown-6 (18C6) and dibenzo-18-crown-6 (DB18C6); namely, the more closely the metal ion fits into the B18C6 cavity (18C6 cavity radius: 1.38 Å$^{18)}$), the more stable is the B18C6-metal ion complex (size-fit concept). A similar selectivity trend of 18C6, B18C6, and DB18C6 for K^+, Rb^+, and Cs^+ was observed in nonaqueous solvents.$^{14)}$ The sodium ion-selective tendency of B18C6 in H_2O is consistent with that of DB18C6, but is different from that of 18C6. This may be attributed largely to the higher ligand-ring rigidity of B18C6 caused by the benzo group, compared with 18C6. It has been reported that a complexation reaction of Na^+ with a flexible crown ether causes a large ligand-ring conformational change, resulting in a great entropy-destabilization of the Na^+ complex.$^{14)}$ The $K_{ML}(K^+)/K_{ML}(Na^+)$ ratio of B18C6 varies somewhat with the solvent, in comparison with DB18C6; however, the $K_{ML}(K^+)/K_{ML}(Na^+)$ ratio of 18C6 varies greatly. Kolthoff and Chantooni, Jr.$^{2)}$ reported that, from the $K_{ML}(K^+)/K_{ML}(Na^+)$ ratios of 18C6 and DB18C6, the conformation of L in ML^+ seemed to be more affected by the solvent when L is 18C6 than when it is DB18C6. It, thus, appears from this that the conformation of B18C6 in ML^+ is somewhat greater, and is less affected by the solvent, compared with DB18C6 and 18C6, respectively.

A K^+ ion fits most nicely into the B18C6 cavity, whereas the size of a Ag^+ ion is smaller than that of the B18C6 cavity; though the Gibbs-free energy of hydration ($\Delta G_h{}^\circ$) of Ag^+ is smaller than that of K^+ (Table 3), the B18C6 forms a slightly more stable complex with Ag^+ than K^+ in water (Table 1). Although the ionic sizes of Tl^+ and Rb^+ are almost the same and $\Delta G_h{}^\circ$ of Tl^+ is slightly smaller than that of Rb^+, the Tl^+-B18C6 complex is more stable than the Rb^+-B18C6 complex in water.

From Table 1, the $\log K_{ML}$ value of a B18C6-Ba^{2+} complex in water is larger than that of a B18C6-Sr^{2+} complex; this tendency is entirely consistent with the size-fit concept. The same is true for the cases of 18C6 and DB18C6. A Pb^{2+} ion has a less suitable size for the B18C6 cavity than does a Ba^{2+} ion; though $\Delta G_h{}^\circ$ of Ba^{2+} is larger than that of Pb^{2+} (Table 3), the Pb^{2+}-B18C6 complex is somewhat more stable than the Ba^{2+}-B18C6 complex in water. The unexpected behavior of B18C6 complexes with Ag^+, Tl^+, and Pb^{2+} may be ascribed to different binding forms of Ag^+, Tl^+, and Pb^{2+} with ether oxygen atoms of B18C6 from those of s-block metal ions.

Ba^{2+} and K^+ are nearly identical in size; though $\Delta G_h{}^\circ$ of Ba^{2+} is very much smaller than that of K^+ (Table 3), Ba^{2+} forms a more stable complex with B18C6 than K^+ in water. The ionic radii of Sr^{2+} and Pb^{2+} are approximately equal to that of Ag^+; though $\Delta G_h°$ of Sr^{2+} and Pb^{2+} are very much smaller than that of Ag^+, Sr^{2+}- and Pb^{2+}-B18C6 complexes are more stable than a Ag^+-B18C6 complex in water. The same trend is found for 18C6 and DB18C6, except for the cases of Sr^{2+}- and Ag^+-DB18C6 complexes (Table 1).

On account of the higher basicity of an aliphatic ether oxygen atom compared with an aromatic ether oxygen atom, it can be expected that the stabilities of the complexes of a given metal ion with the three crown ethers in water decrease in the order 18C6> B18C6> DB18C6. The data on water given in Table 1 are consistent with this expectation, except for the cases of Na^+ and Ag^+. For each case of Na^+ and Ag^+, the B18C6 complex is more stable than the DB18C6 complex in water, which is in accord with the expectation; however, the stability sequence of the 18C6 complex among these three crown ether complexes is unexpected. On account of the smaller size of the metal ion compared with the 18C6 cavity-size and the higher ligand-ring flexibility of 18C6, the metal ion with higher charge density may cause a large conformational change upon complexation. Thus, the 18C6 complex is entropy-destabilized, resulting in the unexpected stability sequence.

Although the solvation power of water for an alkali metal ion (i.e., relative solubility of the alkali metal ion), which is derived from the data on transfer activity coefficients of the alkali metal ion,[2] is the third largest of all the solvents listed in Table 1, the $\log K_{ML}$ value of a given B18C6-alkali metal ion complex in water is by far the smallest of all the solvents. The same tendency was observed for the cases of 18C6- and DB18C6-alkali metal-ion systems.[14] It appears from this finding that the hydrogen bonds between ether oxygen atoms of the crown ether and water molecules cause the much lower stability of the crown ether-alkali metal ion complex in water than all the other solvents.

Benzo-18-crown-6 forms much more unstable complexes with Sr^{2+} and Ba^{2+} in water than in methanol (Table 1). The much stronger solvation of Ba^{2+} in water than in methanol[20] is probably responsible for the much lower stability of the Ba^{2+} complex in water than in methanol.

Transfer Activity Coefficient. The logarithm of the transfer activity coefficient ($\log {}^{s_1}\gamma^{s_2}(ML^{m+})$[21]) of a B18C6-metal ion complex between solvent s_1 and solvent s_2 is calculated as follows:

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

where ${}^{s_1}\gamma^{s_2}(L)$[21] and ${}^{s_1}\gamma^{s_2}(M^{m+})$[21] refer to the transfer activity coefficients of B18C6 and a metal ion between solvent s_1 and solvent s_2, respectively. Further, $(\log K_{ML})_s$ denotes the $\log K_{ML}$ value in solvent s. When $\log {}^{s_1}\gamma^{s_2}(ML^{m+})$ is positive, it can be considered that the complex, ML^{m+}, undergoes stronger solvation in s_1 than in s_2. The transfer activity coefficient values of ML^{m+}, M^{m+}, and L when $s_1=H_2O$ are compiled in Table 2.

$\log {}^{H_2O}\gamma^s(L)$ values of benzo-15-crown-5 (B15C5) at 25 °C are −1.24, −1.04, and −0.56, when $s=CH_3CN$ (AN), propylene carbonate (PC), and methanol, respectively.[26] In each case of s=AN and PC, the $\log {}^{H_2O}\gamma^s(L)$ value of B18C6 is larger than that of B15C5; the $\log {}^{H_2O}\gamma^{CH_3OH}(L)$ value of B18C6 is slightly greater than that of B15C5. This shows that, from B15C5 to B18C6, the crown ether is more soluble in water than in the nonaqueous solvents. The size of B18C6 is larger than that of B15C5 by an ether oxygen atom and an ethylene group. Thus, the additional hydrogen bonding between the added ether oxygen atom of B18C6 and water may be responsible for the higher $\log {}^{H_2O}\gamma^s(L)$ values of B18C6 compared with B15C5. The $\log {}^{H_2O}\gamma^s(L)$ value of B18C6 is larger than the corresponding $\log {}^{H_2O}\gamma^s(L)$ value of DB18C6; $\log {}^{H_2O}\gamma^{CH_3OH}$ (18C6) is greater than $\log {}^{H_2O}\gamma^{CH_3OH}$(B18C6) (Table 2). This reveals that with more benzo groups, the crown ether is more soluble in nonaqueous sol-

Table 2. Transfer Activity Coefficients at 25 °C

s=	CH_3CN		Propylene carbonate		CH_3OH			DMF		DMSO	
$\log {}^{H_2O}\gamma^s(M^{m+})$											
Na^+[2]	2.3		2.9_4		1.4			−1.7		−2.5	
K^+[2]	1.3		1.5_4		1.7			−1.8		−2.2	
Rb^+[2]	1.1		1.2_2		1.7			−1.9		−2.0	
Cs^+[2]	0.8		0.9_4		1.6			−1.7		−2.3	
Ba^{2+}[22]	—		—		3.2			—		—	
$\log {}^{H_2O}\gamma^s(L)$	B18C6	DB18C6[2]	B18C6	DB18C6[2]	18C6[3]	B18C6	DB18C6	B18C6	DB18C6[2]	B18C6	DB18C6[2]
	0.53	−3.5	−0.41	-2.9_1	1.6_6	−0.49	-1.8_5[2]	−0.50	-3.4_5	−0.47	-3.3_9
$\log {}^{H_2O}\gamma^s(ML^{m+})$											
Na^+	−0.7	-5.0_5	−1.4	-4.0_5	-0.4_4	−2.2	-3.7_5[2]	−3.3	-6.8_5	−3.3[23]	-6.6_5
K^+	−1.7	-5.4_5	−2.5	-4.9_0	-0.6_4	−2.7	-3.5_5[2]	−4.2	—	−3.7	-6.4_5
Rb^+	−1.6	—	−2.5	—	—	−2.7	—	−4.5	—	−3.9	—
Cs^+	−1.6	—	−2.2	—	—	−2.1	—	−4.1	—	−4.3	—
Ba^{2+}	—	—	—	—	1.7_6	0.2_6[24]	-0.9_5[3]	—	—	—	—

vents than in water. This is due to the lipophilicity of the benzo group.

Generally, $\log{}^{\mathrm{H_2O}}\gamma^{\mathrm{s}}$ values of B18C6-$\mathrm{K^+}$ and -$\mathrm{Rb^+}$ complexes for a given solvent s are approximately equal; but, $\log{}^{\mathrm{H_2O}}\gamma^{\mathrm{s}}$ values of B18C6-$\mathrm{K^+}$ and -$\mathrm{Rb^+}$ complexes are somewhat different from those of B18C6-$\mathrm{Na^+}$ and -$\mathrm{Cs^+}$ complexes. This indicates that the nature of solute-solvent interactions of the B18C6-$\mathrm{K^+}$ and -$\mathrm{Rb^+}$ complexes is almost the same; however, this is different from the nature of the solute-solvent interactions of the B18C6-$\mathrm{Na^+}$ and -$\mathrm{Cs^+}$ complexes. This reflects the fact that both $\mathrm{K^+}$ and $\mathrm{Rb^+}$ have more suitable sizes for the B18C6 cavity than do $\mathrm{Na^+}$ and $\mathrm{Cs^+}$.

The $\log{}^{\mathrm{H_2O}}\gamma^{\mathrm{s}}(\mathrm{M}^{m+})$ value is larger than the corresponding $\log{}^{\mathrm{H_2O}}\gamma^{\mathrm{s}}(\mathrm{ML}^{m+})$ value of B18C6. This shows that when a M^{m+} ion forms a complex with B18C6, the M^{m+} ion complexed with B18C6 becomes less soluble in water than in nonaqueous solvents, compared with the free M^{m+} ion; namely, B18C6 plays a role in enhancing the lipophilicity of the M^{m+} ion. When s=AN, PC, DMF, and DMSO, $\log{}^{\mathrm{H_2O}}\gamma^{\mathrm{s}}(\mathrm{ML^+})$ value of a given alkali metal ion decreases in the order B18C6>DB18C6 (3.7—4.4, 2.4—2.7, 3.6, and 2.7—3.4 units, respectively); the $\log{}^{\mathrm{H_2O}}\gamma^{\mathrm{CH_3OH}}(\mathrm{ML}^{m+})$ value sequence of a given metal ion is 18C6>B18C6>DB18C6 (the differences: 1.5—2.1 and 0.8—1.6 units, respectively). Similar differences are observed for the cases of free 18C6, B18C6, and DB18C6. It can be concluded from this finding that the more the number of benzo groups is, the more hydrophobic (lipophilic) the crown ether-M^{m+} complex is, regardless of a variety of the metal ions. This may be ascribed largely to the hydrophobic entropy effect[3)] caused by the enforcement of a hydrogen-bonded structure of water against the benzo group.

For a given solvent s, $\log{}^{\mathrm{H_2O}}\gamma^{\mathrm{s}}(\mathrm{B18C6})$ is larger than $\log{}^{\mathrm{H_2O}}\gamma^{\mathrm{s}}$ of B18C6-alkali metal-ion complexes; the same is true for the cases of 18C6 and DB18C6. This shows that when B18C6 forms a complex with an alkali metal ion, the B18C6 complex becomes more soluble in nonaqueous solvents than in water, compared with uncomplexed B18C6. Chantooni, Jr. and Kolthoff[3)] have reported that upon the complexation of a crown ether with a M^{m+} ion, hydrogen bonding to the ether oxygen atoms is greatly decreased as a result of ionic M^{m+}-O bonding. The considerably reduced strength of hydrogen bonding between ether oxygen atoms and water may cause an enforcement of the hydrogen-bonded structure of water for a bulky crown ether complex, resulting in a higher hydrophobicity of the complex, compared with an uncomplexed crown ether. The solvation power of DMF and DMSO for an alkali metal ion is greater than that of water.[27)] When s=DMF and DMSO, both the effect of the reduced strength of hydrogen bonding and the stronger interaction between the complexed alkali metal ion and solvents may be responsible for the result, $\log{}^{\mathrm{H_2O}}\gamma^{\mathrm{s}}(\mathrm{L})>\log{}^{\mathrm{H_2O}}\gamma^{\mathrm{s}}(\mathrm{ML^+})$. Although water has a stronger solvation power for an alkali metal ion than do acetonitrile, propylene carbonate, and methanol,[27)] $\log{}^{\mathrm{H_2O}}\gamma^{\mathrm{s}}(\mathrm{L})$ is larger than the corresponding $\log{}^{\mathrm{H_2O}}\gamma^{\mathrm{s}}(\mathrm{ML^+})$. The solvation power of water for an alkali metal ion is not so large as that of DMF or DMSO.[27)] Thus, the superiority of the effect of reduced strength of hydrogen bonding between ether oxygen atoms and water over the effect of the stronger solvation power of water may result in $\log{}^{\mathrm{H_2O}}\gamma^{\mathrm{s}}(\mathrm{L})>\log{}^{\mathrm{H_2O}}\gamma^{\mathrm{s}}(\mathrm{ML^+})$. The above discussion is supported by a large difference in $\log{}^{\mathrm{H_2O}}\gamma^{\mathrm{s}}(\mathrm{L})-\log{}^{\mathrm{H_2O}}\gamma^{\mathrm{s}}(\mathrm{ML^+})$ for the same alkali metal ion and crown ether between a group of AN, PC, $\mathrm{CH_3OH}$ and that of DMF, DMSO.

$\log{}^{\mathrm{H_2O}}\gamma^{\mathrm{CH_3OH}}$ of a B18C6-$\mathrm{Ba^{2+}}$ complex is larger than that of a free B18C6. The same is true for the cases of 18C6 and DB18C6. This is different from the cases of alkali metal ions, which is due to a difference in the charge density between $\mathrm{Ba^{2+}}$ and $\mathrm{M^+}$. Since $\mathrm{Ba^{2+}}$ is much more strongly solvated in water than in methanol, compared with an alkali metal ion ($\log{}^{\mathrm{H_2O}}\gamma^{\mathrm{CH_3OH}}(\mathrm{Ba^{2+}})=3.2$ in Table 2), the effect of a very much stronger interaction with water of the $\mathrm{Ba^{2+}}$ ion in the crown ether complex than with methanol probably surpasses the effect of the reduced strength of hydrogen bonding between ether oxygen atoms and water, resulting in $\log{}^{\mathrm{H_2O}}\gamma^{\mathrm{CH_3OH}}(\mathrm{BaL^{2+}})>\log{}^{\mathrm{H_2O}}\gamma^{\mathrm{CH_3OH}}(\mathrm{L})$.

These data on the transfer activity coefficients strongly support the conclusion in the preceding section that the unexpected lowest stability of the crown ether-metal ion complex in water of all the solvents can be attributed to the very strong hydrogen bonding between the ether oxygen atoms of the uncomplexed crown ether and water molecules.

Although the solvation power of water for an alkali metal ion is the third largest of all the solvents listed in Table 2,[27)] that of water for a B18C6-alkali metal ion complex is the smallest. The same tendency is found for 18C6- and DB18C6-alkali metal ion complexes. This can probably be ascribed to the above-mentioned effect produced by the greatly reduced strength of hydrogen bonding between ether oxygen atoms and water on a bulky crown ether-alkali metal ion complex.

From Table 2, a B18C6-$\mathrm{Ba^{2+}}$ complex is slightly more soluble in water than in methanol; the reverse is

Table 3. Gibbs Free Energy of Hydration ($\Delta G_{\mathrm{h}}^{\circ}$) of Metal Ions at 25 °C[19)]

Ion	$-\Delta G_{\mathrm{h}}^{\circ}/\mathrm{kJ\ mol^{-1}}$
$\mathrm{Na^+}$	411.3
$\mathrm{K^+}$	338
$\mathrm{Rb^+}$	320
$\mathrm{Cs^+}$	297
$\mathrm{Ag^+}$	479.1
$\mathrm{Tl^+}$	343
$\mathrm{Sr^{2+}}$	1447
$\mathrm{Ba^{2+}}$	1318
$\mathrm{Pb^{2+}}$	1497

true for the B18C6–alkali metal ion complexes. The very much stronger interaction of Ba^{2+} with water than with methanol, compared with the cases of alkali metal ions, may be responsible for the slightly higher solubility of the B18C6–Ba^{2+} complex in water than in methanol.

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