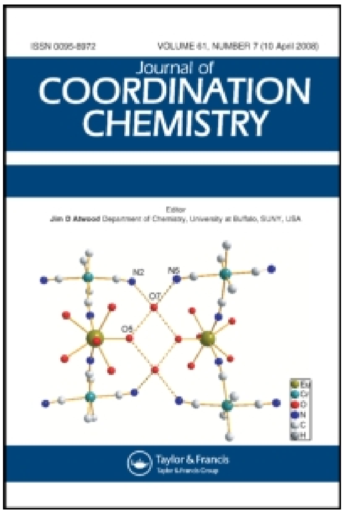

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Stabilities and Transfer Activity Coefficients from Water to Polar Nonaqueous Solvents of Benzo-15-Crown-5- and 15-Crown-5-Alkali Metal Ion Complexes

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To cite this Article Takeda, Yasuyuki , Tanaka, Munehiro , Yamada, Hiroaki and Katsuta, Shoichi(2002) 'Stabilities and Transfer Activity Coefficients from Water to Polar Nonaqueous Solvents of Benzo-15-Crown-5- and 15-Crown-5-Alkali Metal Ion Complexes', Journal of Coordination Chemistry, 55: 4, 459 — 468

To link to this Article: DOI: 10.1080/00958970211903

URL: http://dx.doi.org/10.1080/00958970211903

J. Coord. Chem., 2002, Vol. 55(4), pp. 459–468

STABILITIES AND TRANSFER ACTIVITY COEFFICIENTS FROM WATER TO POLAR NONAQUEOUS SOLVENTS OF BENZO-15-CROWN-5- AND 15-CROWN-5-ALKALI METAL ION COMPLEXES

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(Received 11 September 2000; In final form 23 March 2001)

Stability constants (K_{ML}) of 1:1 benzo-15-crown-5 (B15C5) complexes with alkali metal ions were conductometrically measured in water at 25°C. Transfer activity coefficients of B15C5 and 15-crown-5 (15C5) from water to polar nonaqueous solvents were determined at 25°C. By using these data and the literature values, transfer activity coefficients of the B15C5 and 15C5 complexes with alkali metal ions from water to the polar nonaqueous solvents were calculated to study the solute-solvent interaction of the crown ether complexes. The stability of the B15C5 complex is lower in water than in any other nonaqueous solvent. The K_{ML} value for B15C5 is always smaller than the corresponding K_{ML} value for 15C5. The interaction of the B15C5 or the 15C5 complex with the solvents depends on the alkali metal ion in the crown cavity. All the B15C5 and 15C5 complexes undergo hydrophobic hydration, which is particularly stronger for the B15C5 complexes with Na^+ and K^+. The unexpectedly lowest stability of the B15C5- or the 15C5-alkali metal ion complex in water among all the solvents is caused by the hydrogen bonding between ether oxygen atoms of uncomplexed B15C5 or 15C5 and water.

Keywords: Stability constants; Transfer activity coefficients from water; Benzo-15-crown-5; 15-crown-5; Alkali metal ions; Polar nonaqueous solvents

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ISSN: 0095-8972 © 2002 Taylor & Francis Ltd DOI: 10.1080/00958970290005529

INTRODUCTION

Generally, a crown ether selectively forms a stable complex with the cation whose size best matches the cavity. The selectivity and the stability are influenced by solvent properties. For example, benzo-15-crown-5 (B15C5, Fig. 1) and 15-crown-5 (15C5, Fig. 1) show higher selectivity for Na^+ over K^+, Rb^+, and Cs^+ in acetonitrile than in methanol [1]. In water, little selectivity of 15C5 for the alkali metal ions is observed [2]. Unexpectedly the stability of crown ether-metal ion complexes is much lower for water than for polar nonaqueous solvents [3].

In this work, complex-formation constants of B15C5 with alkali metal ions were measured in water by conductometry at 25°C; transfer activity coefficients of B15C5 and 15C5 from water to polar nonaqueous solvents were determined at 25°C. By using these data and the literature values, the transfer activity coefficients of the B15C5- and the 15C5-alkali metal ion complexes from water to the polar nonaqueous solvents were obtained to study the solute-solvent interaction of the crown ether complexes. The unexpectedly much lower stability of the B15C5 and the 15C5 complexes in water was elucidated.

EXPERIMENTAL

Materials

Benzo-15-crown-5 (Merck Japan Ltd.) was dissolved in heptane, filtered while hot, and then recrystallized from heptane twice. It was dried at 40°C in a vacuum prior to use. 15-Crown-5 (Nisso Co., Ltd.) was purified by distillation under vacuum. Analytical-grade $LiCl \cdot H_2O$ and NaCl were purchased from Merck Japan Ltd. They were used without further purification. The purification methods of DMF [4] and DMSO [5] were

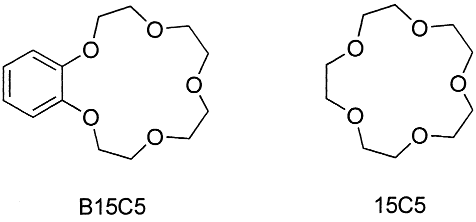

FIGURE 1 Structures of B15C5 and 15C5.

described elsewhere. Analytical-grade tetradecane (TD) from Wako Pure Chemicals Ltd. was used without further purification. The conductivity of water was less than $6 \times 10^{-7}\,\mathrm{S\,cm^{-1}}$.

Apparatus and Procedure for Conductometry

The conductivity measurements were performed with a Fuso conductivity apparatus, Model 362B, at 25 ± 0.02°C. Two cells were used, with cell constants of 0.1962 and $0.1876\,\mathrm{cm^{-1}}$.

The experimental procedure to obtain formation constants of B15C5 complexes with alkali metal ions in water was almost the same as that described in a previous paper [6]. The concentration range of the alkali metal chlorides was $(1.4-4.2) \times 10^{-3}\,\mathrm{M}$.

Distribution Coefficients of B15C5 and 15C5

A 12 mL portion of an aqueous ($5.3 \times 10^{-4} - 3.7 \times 10^{-3}\,\mathrm{M}$), a DMF ($2.6 \times 10^{-3} - 2.1 \times 10^{-2}\,\mathrm{M}$), or a DMSO solution ($3.1 \times 10^{-3} - 2.6 \times 10^{-2}\,\mathrm{M}$) of B15C5 and an equal volume of tetradecane in a stoppered glass tube (volume 30 mL) were shaken in a thermostated water bath at 25 ± 0.2°C for more than 2 h and centrifuged. The B15C5 in the TD phase was extracted into water. The B15C5 concentration in the aqueous phase was spectrophotometrically determined at 273 nm ($\varepsilon = 2.51 \times 10^3\,\mathrm{cm^{-1}\,M^{-1}}$). The experimental procedure for determining the distribution constants of 15C5 was much the same as that described previously [7]. The initial concentration of 15C5 was from 2.8×10^{-4} to $6.3 \times 10^{-2}\,\mathrm{M}$. The experiments were performed at 25 ± 0.2°C. The distribution constants ($K_{\mathrm{D,L}}$) of B15C5 and 15C5 are listed in Table I.

TABLE I Distribution constants of 15C5 and B15C5 at 25°C

Crown ether	*System*	$K_{D,L}$	$\log K_{D,L}$
15C5	TD/H_2O	$(2.66 \pm 0.03) \times 10^{-3}$	−2.575
	TD/DMF	$(3.95 \pm 0.06) \times 10^{-2}$	−1.403
	TD/DMSO	$(4.70 \pm 0.09) \times 10^{-2}$	−1.328
B15C5	TD/H_2O	$(1.66 \pm 0.02) \times 10^{-1}$	−0.780
	TD/DMF	$(1.61 \pm 0.06) \times 10^{-2}$	−1.793
	TD/DMSO	$(1.47 \pm 0.04) \times 10^{-2}$	−1.833

$K_{\mathrm{D,L}} = [\mathrm{L}]_{s_1}/[\mathrm{L}]_{s_2}$, s_1 and s_2 denoting solvents s_1 and s_2, respectively. Each distribution constant value is the average of 8–14 measurements. The uncertainties are the standard deviations.

RESULTS AND DISCUSSION

The molar conductivity (Λ) *vs.* $[L]_t/[M]_t$ plots for the B15C5-Li^+ and -Na^+ systems in water are given in Figure 2, $[L]_t$ and $[M]_t$ designating total concentrations of a crown ether and an alkali metal ion, respectively.

The analysis of the conductometric data for obtaining the formation constants (K_{ML}) of B15C5 1 : 1 complexes with Li^+ and Na^+ was the same as that described elsewhere [6], where $K_{ML} = [ML^+]/[M^+][L]$; M^+ and L denote an alkali metal ion and a crown ether, respectively. It is assumed that the association between a cation and an anion is negligible in water. Corrections for viscosity changes due to solute were neglected. The $\log K_{ML}$ values together with literature ones are summarized in Table II.

The logarithm of the transfer activity coefficient of a crown ether-alkali metal ion complex between solvent s_1 and solvent s_2 ($\log {}^{s_1}\gamma^{s_2}(ML^+)$) is calculated as follows:

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

where ${}^{s_1}\gamma^{s_2}(M^+)$ designates the transfer activity coefficient of an alkali metal ion between solvent s_1 and solvent s_2; $(\log K_{ML})_s$ denotes the $\log K_{ML}$ value in solvent s; ${}^{s_1}\gamma^{s_2}(X) = [X]_{s_1}/[X]_{s_2}$. A positive $\log {}^{s_1}\gamma^{s_2}(X)$ value means that

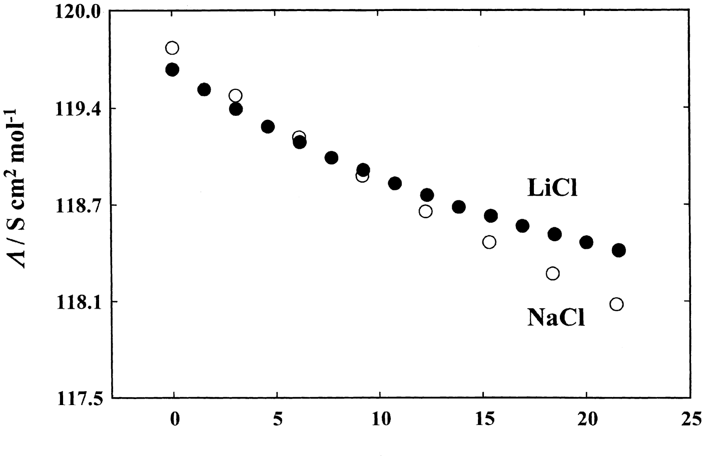

FIGURE 2 Λ *vs.* $[L]_t/[M]_t$ plots for B15C5-Li^+ and -Na^+ systems in water at 25°C. $[Li]_t = 1.7 \times 10^{-3}$ M; $[Na]_t = 1.0 \times 10^{-3}$ M.

TABLE II Log(K_{ML}/mol^{-1}dm^3) values of B15C5 and 15C5 at 25°C

Alkali metal ion	*AN*		*PC*		*H_2O*		*CH_3OH*		*DMF*		*DMSO*	
	*B*15*C*5[a]	15*C*5[b]	*B*15*C*5[c]	15*C*5[d]	*B*15*C*5	15*C*5[h]	*B*15*C*5[a]	15*C*5	*B*15*C*5	15*C*5	*B*15*C*5	15*C*5
Li^+	4.46	5.34	3.77	4.26	0.76 ± 0.13[f]	–	2.31	–	–	–	–	–
Na^+	4.25	5.38	4.35	4.70 ± 0.09[e]	0.45 ± 0.23[f]	0.70	2.99	3.28[i]	1.6[j]	1.97[j]	1.1[j]	1.31[j]
K^+	2.49	3.98	2.78	3.41	0.38[g]	0.74	2.71	3.3[b]	–	–	–	–

[a] Ref. [1].
[b] Ref. [8].
[c] Ref. [9].
[d] Ref. [6].
[e] The K_{ML} value of a 15C5-Na^+ complex in PC at 25°C was recalculated from the conductivity data concerning Ref. [6] in order to confirm the K_{ML} value reported in Ref. [6].
[f] Each log K_{ML} value of B15C5 in water is the average of 5–7 measurements. The uncertainties are the standard deviations.
[g] Ref. [10].
[h] Ref. [2].
[i] Ref. [7].
[j] Ref. [11].

the chemical species X undergoes stronger solvation in s_1 than in s_2. The reverse holds for the negative $\log {}^{s_1}\gamma^{s_2}(X)$ value. The $\log {}^{s}\gamma^{H_2O}$ values at 25°C of ML^+, L, and M^+ are listed in Table III.

For the same ML^+, the stability of ML^+ is always lower in water than in any other solvent (Tab. II). This can be explained by using Eq. (2) derived from Eq. (1).

$$(\log K_{ML})_s - (\log K_{ML})_{H_2O} = \log {}^{s}\gamma^{H_2O}(ML^+) - \log {}^{s}\gamma^{H_2O}(M^+) - \log {}^{s}\gamma^{H_2O}(L). \quad (2)$$

B15C5 is more strongly solvated in the nonaqueous solvents than in water ($\log {}^{s}\gamma^{H_2O}(B15C5) > 0$). This causes the lower stability of $M(B15C5)^+$ in the nonaqueous solvents than in water. However, for AN, PC, and CH_3OH, $\log {}^{s}\gamma^{H_2O}(M^+) < 0$ and $\log {}^{s}\gamma^{H_2O}(ML^+) > 0$ except for $Li(B15C5)^+$ in PC result in $(\log K_{ML})_s > (\log K_{ML})_{H_2O}$; in DMF and DMSO, the $Na(B15C5)^+$ complex is much more strongly solvated than in water, leading to $(\log K_{ML})_s > (\log K_{ML})_{H_2O}$ despite $\log {}^{s}\gamma^{H_2O}(Na^+) > 0$. Contrary to B15C5, 15C5 is more strongly solvated in water than in the nonaqueous solvents ($\log {}^{s}\gamma^{H_2O}(15C5) < 0$). This is one of the factors determining the lower stability of $M(15C5)^+$ in water than in the nonaqueous solvents. Moreover, for AN and PC, both $\log {}^{s}\gamma^{H_2O}(M^+) < 0$ and $\log {}^{s}\gamma^{H_2O}(M(15C5)^+) > 0$ contribute to $(\log K_{ML})_s > (\log K_{ML})_{H_2O}$; for CH_3OH, $\log {}^{s}\gamma^{H_2O}(M^+) < 0$ favors the higher stability of $M(15C5)^+$ in CH_3OH than in water despite $\log {}^{CH_3OH}\gamma^{H_2O}(ML^+) < 0$; for DMF and DMSO, $\log {}^{s}\gamma^{H_2O}(Na(15C5)^+) > 0$ makes a contribution to $(\log K_{ML})_s > (\log K_{ML})_{H_2O}$ in spite of $\log {}^{s}\gamma^{H_2O}(Na^+) > 0$.

The Born-Haber cycle for the 1 : 1 complexation of M^+ with L in a solvent s is shown below:

$$\begin{tikzcd}
M^+_{(g)} \arrow[d, "{{}^{s}\gamma^{g}(M^+)}"] & + & L_{(g)} \arrow[r, "(K_{ML})_g"'] \arrow[d, "{{}^{s}\gamma^{g}(L)}"] & ML^+_{(g)} \arrow[d, "{{}^{s}\gamma^{g}(ML^+)}"] \\
M^+_{(s)} & + & L_{(s)} \arrow[r, "(K_{ML})_s"'] & ML^+_{(s)}
\end{tikzcd}$$

where g denotes gas. The $\log K_{ML}$ value of B15C5 is always smaller than the corresponding $\log K_{ML}$ value of 15C5 (Tab. II). Because B15C5 has two aromatic ether oxygen atoms, the $(K_{ML})_g$ value is expected to be larger for 15C5 than for B15C5. This favors the greater $(K_{ML})_s$ value of 15C5 compared with B15C5. It follows from the $\log {}^{s}\gamma^{H_2O}(L)$ and

TABLE III Transfer activity coefficients at 25°C

$s =$	*AN*		*PC*		*CH_3OH*		*DMF*		*DMSO*	
$\log {}^{s}\gamma^{H_2O}(M^+)$ [a]										
Li^+	-4.3^b		-4.2^c		-0.7^c		1.7^c		2.6^c	
Na^+	-2.3		-2.9_4		-1.4		1.7		2.5	
K^+	-1.3		-1.5_4		-1.7		1.8		2.2	
	B15C5	15C5	B15C5	15C5	B15C5	15C5	B15C5	15C5	B15C5	15C5
$\log {}^{s}\gamma^{H_2O}(L)$	1.24^d	-0.98^e	1.04^d	-0.23^e	0.56^d	-1.29^e	1.01	-1.17	1.05	-1.25
$\log {}^{s}\gamma^{H_2O}(ML^+)$										
Li^+	0.6	–	-0.2	–	1.4	–	–	–	–	–
Na^+	2.7	1.4^e	2.0_0	0.8_3	1.7	-0.1^e	3.9	1.8	4.2	1.9
K^+	2.1	1.0^e	1.9_0	$0.9_0{}^e$	1.2	-0.4^e	–	–	–	–

[a] I. M. Kolthoff and M. K. Chantooni, Jr., *Anal Chem.*, **52**, 1039 (1980).

[b] M. K. Chantooni, Jr. and I. M. Kolthoff, *J. Chem. Eng. Data*, **25**, 208 (1980).

[c] B. G. Cox, G. R. Hedwig, A. J. Parker and D. W. Watts, *Aust. J. Chem.*, **27**, 477 (1974).

[d] Ref. [1].

[e] Ref. [7].

$\log {}^{s}\gamma^{H_2O}$ (ML^+) values of B15C5 and 15C5 that $\log {}^{H_2O}\gamma^{g}(B15C5) <$ $\log {}^{H_2O}\gamma^{g}(15C5)$ and $\log {}^{H_2O}\gamma^{g}(M(B15C5)^+) < \log {}^{H_2O}\gamma^{g}(M(15C5)^+)$. For $s = H_2O$, the greater $\log {}^{H_2O}\gamma^{g}(ML^+)$ and $\log {}^{H_2O}\gamma^{g}(L)$ values of 15C5 make more and less favorable contributions, respectively, to the larger K_{ML} value of 15C5, compared with B15C5.

The $\log {}^{s}\gamma^{H_2O}(ML^+)$ of B15C5 for a given solvent varies with the alkali metal ion. The same holds for 15C5 (Tab. III) [7]. The interaction of the ML^+ complex with solvents depends on the alkali metal ion in the crown cavity. Although the $\log {}^{s}\gamma^{H_2O}(M^+)$ value of Na^+ is smaller than that of K^+ for s = AN and PC and that of Li^+ for $s = CH_3OH$, for the same crown ether and solvent, the NaL^+ complex shows the highest lipophilicity among all the alkali metal ions, except for the 15C5/PC system where the $\log {}^{s}\gamma^{H_2O}(ML^+)$ values of Na^+ and K^+ are nearly equal. The solvation power for the M^+ ion is greater for water than for AN, PC, and CH_3OH (Tab. III). It thus appears that, among all the alkali metal ions, the size-fitted Na^+ ion is most effectively dehydrated and shielded by B15C5 and 15C5 and the NaL^+ complex undergoes the strongest hydrophobic hydration. This is supported by the fact that the $\log {}^{s}\gamma^{H_2O}(ML^+) -$ $\log {}^{s}\gamma^{H_2O}(M^+)$ value of Na^+ is the largest for the same system. The $\log {}^{s}\gamma^{PC}(M^+)$ value decreases in the order $Na^+ > K^+ > Li^+$ for s = AN and $Li^+ > Na^+ > K^+$ for $s = CH_3OH$. When s = AN and CH_3OH, the $\log {}^{s}\gamma^{PC}(ML^+)$ value of B15C5 decreases in the order $Li^+ \geq Na^+ > K^+$ and $Li^+ > Na^+ > K^+$, respectively; that of 15C5 in the order $Na^+ >$ K^+. The order of the $\log {}^{s}\gamma^{PC}(ML^+)$ value is consistent with that of the corresponding $\log {}^{s}\gamma^{PC}(M^+)$ one, except for the $\log {}^{AN}\gamma^{PC}(Li(B15C5)^+)$ value. Generally, a similar tendency is observed for the order of the $\log {}^{CH_3OH}\gamma^{AN}(ML^+)$ value of B15C5 or 15C5 for the alkali metal ions and that of the $\log {}^{CH_3OH}\gamma^{AN}(M^+)$ value. When both s_1 and s_2 are polar nonaqueous solvents, the order of the $\log {}^{s_1}\gamma^{s_2}(ML^+)$ value of B15C5 or 15C5 among the alkali metal ions is governed largely by that of the difference in the solvation power for the alkali metal ion M^+ between s_1 and s_2. The above-mentioned transfer phenomena for ML^+ and M^+ between polar nonaqueous solvents also show that, among all the alkali metal ions, the largest $\log {}^{s}\gamma^{H_2O}(ML^+)$ value of Na^+ is largely attributed to the strongest enforcement of hydrogen-bonded structure of water for the NaL^+ complex.

The $\log {}^{s}\gamma^{H_2O}(Na(B15C5)^+) - \log {}^{s}\gamma^{H_2O}(Na(15C5)^+)$ value is equal or nearly equal to the corresponding $\log {}^{s}\gamma^{H_2O}(B15C5) - \log {}^{s}\gamma^{H_2O}(15C5)$ value, except for s = AN. Since the additivity of the functional group contribution is valid [12], these differences correspond to the value of

$\Pi_{C_6H_4} - \Pi_{CH_2} \times 2$, where $\Pi_{C_6H_4}$ and Π_{CH_2} denote the contributions of a benzo group and a methylene group to the $\log {}^{s}\gamma^{H_2O}(L)$ value, respectively. This shows that the Na^+ ion equally interacts with every oxygen atom of B15C5 and 15C5, and that it is effectively screened in a similar manner by B15C5 and 15C5; the difference in the solvation power for the Na^+ ion in the B15C5 cavity between s and water is nearly equal to that in the 15C5 cavity between s and water. No explanation for the case of $s =$ AN can be offered at the present stage. The $\log {}^{s}\gamma^{H_2O}(K(B15C5)^+) - \log {}^{s}\gamma^{H_2O}(K(15C5)^+)$ value is slightly lower than the corresponding $\log {}^{s}\gamma^{H_2O}(Na(B15C5)^+) - \log {}^{s}\gamma^{H_2O}(Na(15C5)^+)$ value, indicating that the difference in the solvation power for the size-misfitted K^+ ion in the B15C5 cavity between s and water differs from that in the 15C5 cavity between s and water, because it can be considered that the K^+ ion interacts with every oxygen atom of B15C5 and 15C5.

From Table III, the solvation power for ML^+ and M^+ increases as follows:

$Li(B15C5)^+$ $PC < H_2O < AN < CH_3OH$,
$Na(B15C5)^+$ $H_2O \ll CH_3OH < PC < AN < DMF < DMSO$,
$K(B15C5)^+$ $H_2O < CH_3OH < PC < AN$,
$Na(15C5)^+$ $CH_3OH \leq H_2O < PC < AN < DMF \leq DMSO$,
$K(15C5)^+$ $CH_3OH < H_2O < PC \leq AN$,
Li^+ $AN \leq PC \ll CH_3OH < H_2O$,
Na^+ $PC < AN < CH_3OH < H_2O \ll DMF < DMSO$,
K^+ $CH_3OH < PC < AN < H_2O$.

The solvation ability for B15C5 and 15C5 increases in the order as follows:

B15C5 $H_2O < CH_3OH < DMF \approx PC \approx DMSO < AN$,
15C5 $CH_3OH \approx DMSO \approx DMF < AN < PC < H_2O$.

From the above data, in general, the order of the solvation ability for the ML^+ complex is governed by that for the M^+ ion, except for the cases of CH_3OH for NaL^+ and water. The interaction of the alkali metal ion in the complex with solvents partially remains after complexation. The solvation ability of water for the M^+ ion is the highest except for DMF and DMSO, but that for $Na(B15C5)^+$ and $K(B15C5)^+$ the lowest and for the other ML^+ complexes the second lowest. All the ML^+ complexes undergo hydrophobic hydration, which is particularly stronger for the B15C5 complexes with Na^+ and K^+ owing to the benzo group.

For $s =$ AN, PC, and CH_3OH, the $\log {}^{s}\gamma^{H_2O}(ML^+)$ value is larger than the corresponding $\log {}^{s}\gamma^{H_2O}(L)$ value except for the cases of $Li(B15C5)^+$

when s = AN and PC. The alkali metal ion is more strongly solvated by water than by AN, PC, or CH_3OH. However, when B15C5 or 15C5 forms a complex with the alkali metal ion, the complex ion becomes more soluble in the nonaqueous solvent than in water, compared with the free crown ether. This is attributable to hydrophobic hydration of the bulky complex ion caused by the drastically decreased hydrogen bonding between the ether oxygen atoms and water and the greatly reduced hydration of the alkali metal ion upon complexation. The Li^+ ion is much more strongly solvated by water than by AN or PC compared with the other alkali metal ions. The negative value of $\log {}^{s}\gamma^{H_2O}(Li(B15C5)^+) - \log {}^{s}\gamma^{H_2O}(B15C5)$ when s = AN and PC is due to the strong interaction of the Li^+ ion with water in the B15C5 complex. For s = DMF and DMSO, the $\log {}^{s}\gamma^{H_2O}(NaL^+)$ value is also greater than the corresponding $\log {}^{s}\gamma^{H_2O}(L)$ value. The $\log {}^{s}\gamma^{H_2O}(NaL^+) - \log {}^{s}\gamma^{H_2O}(L)$ value of DMF or DMSO is larger than that of AN, PC, or CH_3OH. This is caused by the stronger interaction of the Na^+ ion in the crown ether complex with DMF or DMSO because the Na^+ ion is much more strongly solvated by DMF and DMSO than by water compared with AN, PC, and CH_3OH. It can be concluded from the above discussion that the hydrogen bonding between ether oxygen atoms of B15C5 or 15C5 and water is responsible for the unexpectedly lowest stability of the B15C5- or the 15C5-alkali metal ion complex in water among all the solvents.

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