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Behavior of Benzo-18-crown-6 Complexes with Alkali Metal Ions in Various Nonaqueous Solvents

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The formation constants for 1 : 1 complexes of benzo-18-crown-6 (B18C6) with alkali metal ions and the solubility of B18C6 in various solvents were determined at 25 °C by conductometry and spectrophotometry, respectively. In general, the selectivity of B18C6 for alkali metal ions is governed primarily by the size relationship between cations and the B18C6 cavity. For a given alkali metal ion, the solvation ability of the solvent plays the most important role in determining stability sequences of the B18C6 complex in the solvents. Transfer activity coefficients of B18C6-alkali metal ion complexes were calculated. The transfer activity coefficient of the B18C6 complex from methanol to aprotic solvents somewhat varies with alkali metal ions in the B18C6 cavity. The magnitudes of the transfer activity coefficients of the B18C6 complex from acetonitrile and propylene carbonate to DMF and DMSO are determined mainly by the relative strength of the solvation ability of the former group and the latter group for the alkali metal ion in the B18C6 cavity. In methanol, due to the hydrogen bonds between ether oxygen atoms of B18C6 and methanol, the B18C6 complex is more strongly solvated than the corresponding alkali metal ion, compared to the case of the aprotic solvents.

In a previous paper,[1] various factors, which affect stabilities of 18-crown-6 (18C6) and dibenzo-18-crown-6 (DB18C6) complexes with alkali metal ions in several protic and aprotic solvents, were systematically investigated from a thermodynamic point of view. These factors are (1) the relative sizes of the alkali metal ions and the crown ether cavity, (2) the solvation ability of a solvent for the alkali metal ions, (3) the electron density of the crown ether cavity, and (4) the ligand-ring flexibility.

The behavior of 18C6 and DB18C6 complexes with alkali metal ions in a variety of solvents was studied by conductometry.[1-3] In each case of propylene carbonate[3] and *N,N*-dimethylformamide (DMF),[1] the mobilities of 18C6 complexes with alkali metal ions (Na^+, K^+, Rb^+, Cs^+) were nearly equal. Although the sizes of the 18C6-K^+ complex and $(n\text{-}C_4H_9)_4N^+$ are almost identical, the 18C6 complex in H_2O and CH_3OH does not enforce the hydrogen-bonded structure around the complexed ion as $(n\text{-}C_4H_9)_4N^+$ does.[2] It was proved from Walden products that the behavior of the 18C6-K^+ complex regarding transport phenomena is much the same in protic and aprotic solvents, as is the DB18C6-K^+ complex.[2] In order to obtain information about solute-solvent interactions with regard to 18C6[4,5] and DB18C6[6] complexes with univalent metal ions dissolved in various solvents, transfer activity coefficients of the complexes were determined. The solvation properties of the complexes are discussed in detail.

The structure of benzo-18-crown-6 (B18C6) is intermediate between 18C6 and DB18C6. In analytical chemistry, B18C6 is widely used as a moiety of bis(crown ether)s,[7] a pendant of polymers,[8] and colorimetric extraction-reagents[9] in order to achieve high selectivity for a given metal ion. Only a few thermodynamic studies have, however, been reported on B18C6 complexes with metal ions in solutions.[10-12]

In the present work, formation constants for 1:1 complexes of B18C6 with alkali metal ions and the solubility of B18C6 in protic and aprotic solvents were determined at 25°C by conductometry and spectrophotometry, respectively. The transfer activity coefficients of the B18C6 complexes with alkali metal ions were calculated from these data and values found in the literature regarding the transfer activity coefficients of alkali metal ions. The stabilities and solvation behavior of the B18C6 complexes in solutions are discussed.

Experimental

Materials. Benzo-18-crown-6 was prepared according to Pedersen.[13] The product was recrystallized three times from heptane and dried at 40°C in a vacuum oven before use. Its purity was checked by melting point, elemental analysis, NMR, and conductometry.

Extremely pure sodium, potassium, rubidium, and caesium chlorides were obtained from Merck Japan Ltd., and were used without further purification. Rubidium and caesium perchlorates were prepared by adding a little excess of perchloric acid to aqueous solutions of rubidium and caesium chlorides, respectively. Sodium and potassium perchlorates were purchased from Merck Japan Ltd. All the perchlorates were recrystallized four times from distilled water and, prior to use, dried at 150°C in a vacuum oven.

The method of purification of acetonitrile,[2] propylene carbonate,[3] methanol,[14] DMF,[1] and dimethyl sulfoxide (DMSO)[2] was previously described. For these five solvents, the middle 70% of the distillate was used. The conductivities of these final products of acetonitrile, propylene carbonate, methanol, DMF, and DMSO were less than 3×10^{-7}, 6×10^{-8}, 2×10^{-7}, 3×10^{-7}, and 7×10^{-8} $\Omega^{-1}cm^{-1}$, respectively.

Alkali metal chlorides were employed for the methanol system and alkali metal perchlorates for the other solvent systems.

Apparatus and Procedure. The conductance measurements were made on a Fuso conductivity apparatus, model 362A, in a water bath thermostated at 25±0.005 °C. Three cells were used with cell constants of 0.059705, 0.093939, and 0.097761 cm^{-1}. The experimental procedure to obtain formation constants of B18C6 complexes with alkali metal ions was almost the same as that described in a previous paper.[3]

Solubilities of B18C6. Solubilities of B18C6 in acetonitrile (275 nm), propylene carbonate (275 nm), methanol (225 nm), DMF (278 nm), and DMSO (276 nm) were determined spectrophotometrically at 25±0.02 °C. They are 2.8×10^{-1}, 2.4, 2.9, 3.0, and 2.8 M (1 M=1 mol dm^{-3}) for acetonitrile, propylene carbonate, methanol, DMF, and DMSO, respectively.

Results and Discussion

The procedure for obtaining formation constants (K_{ML^+}) of B18C6 complexes with alkali metal ions was the same as that described in a previous work,[3] where $K_{\mathrm{ML}^+}=[\mathrm{ML}^+]/[\mathrm{M}^+][\mathrm{L}]$. M^+ and L designate an alkali metal ion and a crown ether, respectively. In the present study, it is assumed that the association between a cation and an anion is negligible under the highly dilute experimental conditions (total concentration of an alkali metal ion$\approx 5 \times 10^{-4}$ M) and that B18C6 forms a 1 : 1 complex with an alkali metal ion. Since the B18C6 concentration was kept below 2.5×10^{-3} M during the experiments, corrections for viscosity changes were neglected. The log K_{ML^+} values are listed in Table 1, together with the literature values.

The molar conductivity (Λ) *vs.* $[\mathrm{L}]_t/[\mathrm{M}]_t$ plots for propylene carbonate and DMF systems at 25 °C are illustrated in Figs. 1 and 2, where $[\mathrm{L}]_t$ and $[\mathrm{M}]_t$ denote total concentrations of B18C6 and the alkali metal ion, respectively. Since the Λ *vs.* $[\mathrm{L}]_t/[\mathrm{M}]_t$ curves for the other solvent systems are similar, they have been omitted. Every plot of Λ *vs.* $[\mathrm{L}]_t/[\mathrm{M}]_t$, except for the $\mathrm{NaClO_4}$–DMSO system, shows a decrease in Λ with an increase in the B18C6 concentration. This indicates that the alkali metal ion complexed by B18C6 is less mobile than the corresponding free alkali metal ion. For the $\mathrm{NaClO_4}$–DMSO system, the change in Λ was so small in spite of an increase in the B18C6 concentration that the complex-formation constant could not be determined conductometrically. It can be seen from Fig. 1 that, in the cases of Na^+, K^+, and Rb^+, the slope of each curve changes sharply at $[\mathrm{L}]_t/[\mathrm{M}]_t=1$. The same

TABLE 1. Log ($K_{\mathrm{ML}^+}/\mathrm{mol}^{-1}\,\mathrm{dm}^3$) VALUES AT 25 °C AND CRYSTAL IONIC RADII OF ALKALI METALS (Å)

		Na^+	K^+	Rb^+	Cs^+
Crystal ionic radius[15]		0.95	1.33	1.48	1.69
AN[a]	18C6	4.5_5[6]	5.7_0[6] 5.7_1[2]	—	>4[16]
	B18C6	4.9	5.3	4.4	3.8
	DB18C6	4.8_5[6] 5.0_0[17] 5.0[18]	4.8_1[6] 4.7_0[17] 4.8[18] 4.7_9[2]	3.7_0[17]	3.5_9[6] 3.5_0[17]
PC[b]	18C6	5.6_8[3] 5.2_5[6]	6.2_4[3] 6.3_2[6]	5.3_2[3]	4.4_8[3] 4.5_2[6] 4.2[16]
	B18C6	5.3	5.4	4.5	3.6
	DB18C6	5.2_0[6]	5.1_3[6]	3.9_1[6]	3.3_1[6]
$\mathrm{CH_3OH}$	18C6	4.3_2[19] 4.3_6[20,21]	6.1[19] 6.0_6[20] 6.0_7[2] 6.1_6[21]	5.3[20]	4.6_2[19] 4.7_9[20]
	B18C6	4.5 4.0_3[10] 4.35[11]	5.7 5.2_7[10] 5.05[11]	5.1 4.6_2[10]	4.1 3.6_6[10]
	DB18C6	4.3_6[19] 4.4[6] 4.5[22]	5.0_0[19] 5.0_5[6] 5.1[22] 4.6_0[17] 4.6[18] 5.0_7[2]	4.2_3[6]	3.5_5[19]
DMF	18C6	2.4[1]	4.3_1[1]	3.9_8[1]	3.6_7[1] 3.9[16]
	B18C6	2.5	3.6	3.2	2.8
	DB18C6	2.4[6] 2.8_0[23]	2.8[6]	2.1[6]	1.5[16]
DMSO	18C6	1.4_3[6]	3.2_1[6] 3.2_7[2]	—	3.0[16]
	B18C6	—	2.8	2.6	2.4
	DB18C6	1.9_3[6]	2.4_6[6] 2.5[24] 2.5_1[2]	1.9[6]	1.3[16]

a) Acetonitrile. b) Propylene carbonate.

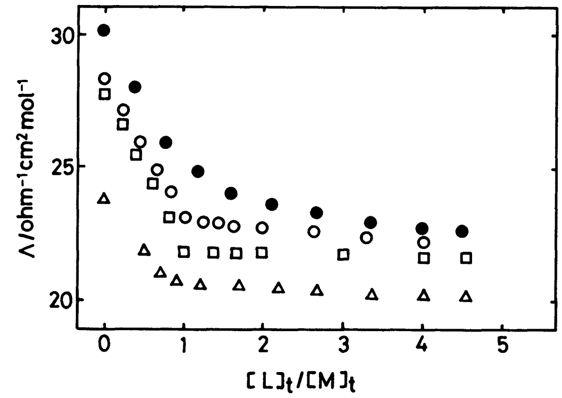

Fig. 1. Λ vs. $[\mathrm{L}]_t/[\mathrm{M}]_t$ curves for B18C6-alkali metal perchlorate systems in propylene carbonate at 25 °C.
△: Na^+, □: K^+, ○: Rb^+, ●: Cs^+, $[\mathrm{M}]_t=5\times10^{-4}$ M.

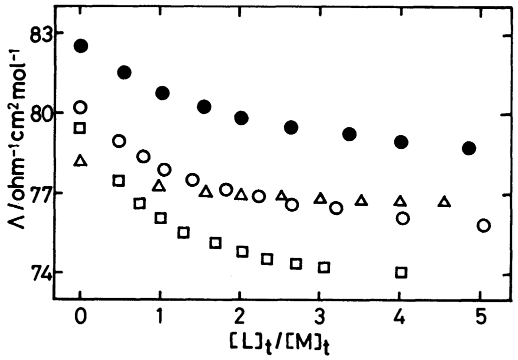

Fig. 2. Λ vs. $[\mathrm{L}]_t/[\mathrm{M}]_t$ curves for B18C6-alkali metal perchlorate systems in DMF at 25 °C.
△: Na^+, □: K^+, ○: Rb^+, ●: Cs^+, $[\mathrm{M}]_t=5\times10^{-4}$ M.

tendency was observed for the Na^+-, K^+- acetonitrile, and the Na^+-, K^+-, Rb^+-methanol systems. For the other systems, no such clear breaking point was observed. These data indicate that the following three factors play an important role in causing the clear breaking point. (1) Benzo-18-crown-6 forms a stable complex with an alkali metal ion (log $K_{ML^+}\geqq4.5$). (2) The difference in mobility between the B18C6-alkali metal ion complex and the corresponding free alkali metal ion is large. (3) A higher-order B18C6 complex such as a 1:2 sandwich complex of an alkali metal ion with B18C6 is not formed.

Stability Constants. It can be seen from Table 1 that the log K_{ML^+}-value sequences of B18C6 complexes with K^+, Rb^+, and Cs^+ for the same solvent are $K^+>Rb^+>Cs^+$. This indicates that the selectivity tendency of B18C6 (18C6 cavity radius: 1.34—1.43 Å[20]) agrees well with the size-fit concept. Among all the B18C6 complexes with alkali metal ions (Na^+, K^+, Rb^+, Cs^+), the log K_{ML^+} value of the Na^+-B18C6 complex is the second largest for acetonitrile and propylene carbonate, the third largest for methanol, and the smallest for DMF and DMSO. This reflects the fact that in every one of these solvents Na^+ is the most strongly solvated of all the alkali metal ions (Na^+, K^+, Rb^+, Cs^+), and that the differences in the free energies of the solvation of Na^+ and K^+, Na^+ and Rb^+, and Na^+ and Cs^+ are much smaller for acetonitrile and propylene carbonate than for the other solvents.[1] A similar tendency to that described above was observed for the stabilities of 18C6 and DB18C6 complexes with alkali metal ions in various solvents.[1]

Since an aliphatic ether oxygen atom is more basic than an aromatic ether oxygen atom, the interaction of an alkali metal ion with the former is stronger than that with the latter. Benzo-18-crown-6 and DB18C6 have two and four aromatic ether oxygen atoms, respectively. Thus, it can be expected that the stabilities of the complexes of these three crown ethers with the same alkali metal ion in a given solvent decrease in the order 18C6>B18C6>DB18C6. The data in Table 1 are in good accord with this expectation except for the Na^+-acetonitrile, methanol, DMF, and DMSO systems. For propylene carbonate, however, the difference in the log K_{ML^+} values of Na^+ between 18C6 and B18C6 (0.4), and that between B18C6 and DB18C6 (0.1) are both small compared to the other alkali metal ions (K^+, Rb^+, Cs^+). Since Na^+ is smaller than the 18C6 cavity and has the greatest charge density of all the alkali metal ions (Na^+, K^+, Rb^+, Cs^+), Na^+ held in the cavity may attract the donor oxygen atoms of the crown ether much more strongly than the other alkali metal ions. It follows from this that the complexation reaction of Na^+ with a flexible crown ether causes the largest ligand-ring conformational change among all the alkali metal ions. Consequently, the more flexible is a crown ether, the more destabilized is the Na^+ complex with the crown ether on account of entropy contribution. It thus appears from Table 1 that the stability sequences of Na^+ complexes with 18C6, B18C6, and DB18C6 for the same solvent largely depend on competition between the ligand-ring flexibility and the electron density of the crown ether cavity.

For acetonitrile and propylene carbonate, the log K_{ML^+} value of Na^+ with DB18C6 is the largest; while, those with B18C6 and 18C6 are the second largest. For methanol, the log K_{ML^+} values of Na^+ with DB18C6, B18C6, and 18C6 are the second largest, the second smallest, and the smallest, respectively. For DMF and DMSO, the log K_{ML^+} value of Na^+ with DB18C6 is the second largest; while, those with B18C6 and 18C6 are the smallest. For the same solvent, the difference in the log K_{ML^+} values of the same crown ether between Na^+ and the other alkali metal ion, which forms a more stable complex with the crown ether compared to Na^+, increases in the order DB18C6<B18C6<18C6; that between Na^+ and the other alkali metal ion, which forms a less stable complex with the crown ether compared to Na^+, decreases in the order DB18C6>B18C6>18C6. These results indicate that, on moving from DB18C6 to 18C6, the Na^+ complex is much more destabilized than the other alkali metal ion complexes on account of entropy contribution because the ligand-ring flexibility increases in the order DB18C6<B18C6<18C6.

Solvation-ability sequences of the solvents for the same alkali metal ion are as follows:

Na^+: $PC < AN < CH_3OH \ll DMF < DMSO$,
K^+ : $CH_3OH < PC < AN \ll DMF < DMSO$,
Rb^+: $CH_3OH < PC \leqq AN \ll DMF \leqq DMSO$,
Cs^+ : $CH_3OH < PC \leqq AN \ll DMF < DMSO$.[1)]

Log K_{ML^+}-value sequences of the B18C6 complex with the same alkali metal ion for the solvents are as follows:

Na^+: $PC > AN > CH_3OH \gg DMF$,
K^+ : $CH_3OH > PC \geqq AN \gg DMF > DMSO$,
Rb^+: $CH_3OH > PC \geqq AN \gg DMF > DMSO$,
Cs^+ : $CH_3OH > AN > PC \gg DMF > DMSO$,

where PC and AN denote propylene carbonate and acetonitrile respectively (Table 1). This shows that, for the same alkali metal ion, the log K_{ML^+}-value sequences of B18C6 for the solvents are completely the reverse of the solvation-ability sequences of the solvents except for the log K_{ML^+}-value sequence of Cs^+ for acetonitrile and propylene carbonate. For the solvents used in this work, there exists a very large difference in the solvation ability for the same alkali metal ion between the group of methanol, propylene carbonate, and acetonitrile, and that of DMF and DMSO,[1)] and also a large difference in the log K_{ML^+} values of B18C6 about the same alkali metal ion. From the above discussion, it can be concluded that, for the same alkali metal ion, the solvation ability of a solvent plays the most important role in determining the stability sequences of the B18C6 complex for the solvents. A similar conclusion to that mentioned above was obtained for 18C6 and DB18C6.[1)]

Transfer Activity Coefficient. The transfer activity coefficient ($\log^{s_1}\gamma^{s_2}(ML^+)$) of a B18C6-alkali metal ion complex between the solvent S_1 and the solvent S_2 is calculated by Eq. 1.

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

These values are listed in Table 2.

It is noted that, although ether oxygen atoms of B18C6 form hydrogen bonds with methanol, the solubility of B18C6 for methanol is approximately equal to those for the aprotic solvents other than acetonitrile. The $\log^{CH_3OH}\gamma^s(L)$ value of B18C6 is much larger than the corresponding $\log^{CH_3OH}\gamma^s(L)$ value of DB18C6, indicating that B18C6 is much more soluble in methanol than in the aprotic solvents, as compared to DB18C6. This is ascribed to the fact that, since DB18C6 has one more benzo group than B18C6, enforcement of a hydrogen-bonded structure of methanol for the hydrophobic benzo group more decreases the solubility of DB18C6 in methanol than that of B18C6. From Table 2, when s=PC, DMF, and DMSO, $\log^{CH_3OH}\gamma^s(B18C6) - \log^{CH_3OH}\gamma^s(DB18C6)$ is of the order of 1, whereas, only for acetonitrile, that is of the order of 2.

In general, in the case of B18C6, $\log^{CH_3OH}\gamma^s(ML^+)$ values for the same aprotic solvent of K^+ and Rb^+ are nearly equal to each other; however, they are somewhat different from those of Na^+ and Cs^+. These results reflect the following fact. The sizes of K^+ and Rb^+ are nearly identical with that of the B18C6 cavity; Cs^+ is larger than the B18C6 cavity. Since Na^+ is smaller than the B18C6 cavity, it shifts up and down in the direction perpendicular to the plane of oxygen atoms of B18C6. Thus, the surface charge of K^+ and Rb^+ held in the B18C6 cavity is more effectively screened by the B18C6 from surrounding solvent molecules than that of Na^+ and Cs^+. Consequently, both B18C6 complexes with K^+ and Rb^+ exhibit apparently similar chemical nature; however, the Na^+ and the Cs^+ complexes show somewhat different chemical nature from the others.

From $\log^{CH_3OH}\gamma^s(ML^+)$ values in Table 2, solvation-ability sequences of the solvents for the same B18C6-alkali metal ion complex are as follows:

Na^+-B18C6: $AN < PC < CH_3OH < DMF$,
K^+-B18C6 : $AN < PC < CH_3OH < DMSO < DMF$,
Rb^+-B18C6: $AN < PC < CH_3OH < DMSO < DMF$,
Cs^+-B18C6 : $AN < CH_3OH \approx PC \ll DMF < DMSO$.

For the aprotic solvents, the solvation ability of DMF and DMSO for the same B18C6-alkali metal ion

Table 2. Transfer activity coefficients at 25 °C

		s=AN[a)]		s=PC[b)]		s=DMF		s=DMSO	
$\log^{CH_3OH}\gamma^s(M^+)$[6)]									
	Na^+	0.9		1.5_4		−3.1		−3.9	
	K^+	−0.4		-0.1_6		−3.5		−3.9	
	Rb^+	−0.6		-0.4_8		−3.6		−3.7	
	Cs^+	−0.8		-0.6_6		−3.3		−3.9	
		B18C6	DB18C6[6)]	B18C6	DB18C6[6)]	B18C6	DB18C6[6)]	B18C6	DB18C6[6)]
$\log^{CH_3OH}\gamma^s(L)$		1.0	-1.6_5	0.082	-1.0_6	−0.015	-1.6_0	0.015	-1.5_4
$\log^{CH_3OH}\gamma^s(ML^+)$									
	Na^+	1.5	−1.3	0.8	−0.3	−1.1	−3.1	—	−2.9
	K^+	1.0	−1.9	0.2	-1.3_5	−1.4	—	−1.0	−2.9
	Rb^+	1.1	−1.8	0.2	-1.2_2	−1.7	—	−1.2	—
	Cs^+	0.5	−2.5	−0.08	-1.4_8	−2.0	−2.9	−2.2	−3.1

a) Acetonitrile. b) Propylene carbonate.

complex is relatively larger than that of AN and PC; similarly, that of DMF and DMSO with respect to the same alkali metal ion is much greater than that of PC and AN. When s_1=AN and PC and s_2=DMF and DMSO, $\log {}^{s_1}\gamma^{s_2}$(M$^+$-B18C6) is much smaller than $\log {}^{s_1}\gamma^{s_2}$(B18C6). This indicates that, in DMF and DMSO, a B18C6-alkali metal ion complex much more strongly undergoes solvation than a free B18C6, in comparison with the cases of AN and PC. From the above data, it can be concluded that there is an appreciable interaction between the alkali metal ion held in the B18C6 cavity and solvent molecules, and, furthermore, that, when s_1=AN and PC and s_2=DMF and DMSO, the magnitude of the $\log {}^{s_1}\gamma^{s_2}$(ML$^+$) value is determined mainly by the relative strength of solvation ability of s_1 and s_2 for the alkali metal ion in the B18C6 cavity. $\mathrm{Log}\,{}^{\mathrm{PC}}\gamma^{\mathrm{AN}}$(ML$^+$)$-\log {}^{\mathrm{PC}}\gamma^{\mathrm{AN}}$(L) values of B18C6 for Na$^+$, K$^+$, and Cs$^+$ are negative, and that for Rb$^+$ is nearly equal to zero. Although an alkali metal ion is more strongly solvated in acetonitrile than in propylene carbonate, the reverse is true for a B18C6-alkali metal ion complex. This may be attributed to the fact that B18C6 itself is comparatively more soluble in propylene carbonate than in acetonitrile ($\log {}^{\mathrm{PC}}\gamma^{\mathrm{AN}}$(B18C6)=0.93).

The solvation ability of methanol for K$^+$, Rb$^+$, and Cs$^+$ is the lowest of all the solvents used in this work; however, that for the B18C6 complexes with K$^+$, Rb$^+$, and Cs$^+$ is the third largest. $\mathrm{Log}\,{}^{\mathrm{CH_3OH}}\gamma^{s}$(ML$^+$)$-\log {}^{\mathrm{CH_3OH}}\gamma^{s}$(M$^+$) values for B18C6 are positive except the Na$^+$–PC system. These results reflect the fact that, in methanol, on account of hydrogen bonds between ether oxygen atoms of B18C6 and methanol molecules, a B18C6-alkali metal ion complex is more strongly solvated than the corresponding alkali metal ion, compared to the case of the aprotic solvent.

Values of $\log {}^{\mathrm{CH_3OH}}\gamma^{s}$(M$^+$-B18C6)$-\log {}^{\mathrm{CH_3OH}}\gamma^{s}$(M$^+$-DB18C6) are 2.8—3.0, 1.1—1.6, 0.9—2.0, and 0.9—1.9 for s=AN, PC, DMF, and DMSO, respectively (Table 2). Generally, these values are nearly equal to the corresponding values of $\log {}^{\mathrm{CH_3OH}}\gamma^{s}$(B18C6)$-\log {}^{\mathrm{CH_3OH}}\gamma^{s}$(DB18C6). Since s is an aprotic solvent, this may be largely due to the entropy effect[4] caused by the enforcement of a hydrogen-bonded structure of methanol for the benzo group, as is mentioned above.

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