



Stabilities in Polar Nonaqueous Solvents and Transfer Activity Coefficients from Water to Nonaqueous Solvents of 19-Crown-6-Alkali Metal Ion Complexes

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Abstract. Formation constants of 1 : 1 19-crown-6 (19C6) complexes with alkali metal ions were determined conductometrically at 25 °C in acetonitrile (AN), propylene carbonate (PC), methanol, DMF, and DMSO. 19C6 always forms the most stable complex with K^+ . The selectivity order of 19C6 for heavy alkali metal ions is $K^+ > Rb^+ > Cs^+$. The selectivity for Na^+ varies with the solvent; that for Li^+ is the second lowest (AN, DMSO) or the lowest (PC). Transfer activity coefficients ($S_{\gamma}^{H_2O}$) of 19C6 from water to the nonaqueous solvents (S) were measured at 25 °C. The contributions of a methylene group and an ether oxygen atom to the $\log S_{\gamma}^{H_2O}$ value of a crown ether were obtained. The $S_{\gamma}^{H_2O}$ values of the 19C6–alkali metal ion complexes ($S_{\gamma}^{H_2O}(ML^+)$) were calculated, M^+ and L denoting an alkali metal ion and a crown ether, respectively. For AN, PC, and CH_3OH , although the M^+ ion is more strongly solvated by water than by AN, PC, or CH_3OH , the $\log S_{\gamma}^{H_2O}(ML^+)$ is larger than the corresponding $\log S_{\gamma}^{H_2O}(L)$ expect for the case of $M^+ = Li^+$. The higher lipophilicity of the 19C6 complex ion is attributed to an enforcement of the hydrogen-bonded structure of water for the complex ion caused by the greatly decreased hydrogen bonding between ether oxygen atoms and water upon complexation. For DMF and DMSO, the $\log S_{\gamma}^{H_2O}(ML^+)$ is also greater than the corresponding $\log S_{\gamma}^{H_2O}(L)$. It was concluded from this finding that the unexpectedly lowest stability of the 19C6 complex ion in water is due to the hydrogen bonding between 19C6 and water. The stabilities and the $\log S_{\gamma}^{H_2O}$ of 19C6–alkali metal ion complexes were compared with those of 18C6 complexes.

Key words: stability constants, transfer activity coefficients from water, additivity, functional group contributions, 19-crown-6, 18-crown-6, alkali metal ions, complexes, polar nonaqueous solvents, conductometry.

1. Introduction

19-Crown-6 (19C6) has the same number of donor oxygen atoms as 18-crown-6 (18C6). 19C6 is however less symmetrical than 18C6 owing to the extra methylene group. The formation constants in water of 1 : 1 19C6 complexes with alkali

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metal ions at 25 °C have been reported [1]. The selectivity orders of 19C6 and 18C6 for the alkali metal ions are different from each other. The selectivity for the neighboring alkali metal ions in the periodic table is lower for 19C6 than for 18C6 except for the case of Rb⁺ and Cs⁺. For Na⁺ and the ion which is smaller in size than Na⁺, the complex stability is higher for 19C6 than for 18C6, but the contrary holds for all the other ions of larger size than Na⁺. The lower stabilities of 19C6 complexes with size-fitting and size-misfitting larger metal ions are due to an unfavorable conformation of 19C6 for complexation with the metal ions caused by the less symmetrical arrangement of donor oxygen atoms compared with 18C6.

In this work, in order to systematically study solvent effects on stabilities of 1 : 1 19C6 complexes with alkali metal ions, formation constants of the 19C6 complexes were conductometrically determined in various polar nonaqueous solvents at 25 °C. Moreover, transfer activity coefficients of 19C6 from water to the nonaqueous solvents were measured at 25 °C. By using the values, transfer activity coefficients of the 19C6 complexes with alkali metal ions from water to the nonaqueous solvents were obtained to study in detail the solute-solvent interaction of the 19C6 complexes. The formation constants and the transfer activity coefficients of the 19C6 complexes were compared with those of the 18C6 complexes with alkali metal ions.

2. Experimental

2.1. MATERIALS

19C6 was synthesized by the method of Ouchi *et al.* [2]. Alkali metal chlorides purchased from Merck Japan Ltd. were analytical grade reagents, and were used without further purification. Lithium, sodium, and potassium perchlorates were obtained from Merck Japan Ltd. Rubidium and caesium perchlorates were prepared by adding a small excess of perchloric acid to aqueous solutions of rubidium and caesium chlorides, respectively. All the perchlorates were recrystallized three times from deionized water and, prior to use, dried at 150 °C in vacuo. The purification methods of acetonitrile (AN) [3], propylene carbonate (PC) [4], methanol [5], DMF [6], and DMSO [3] are described elsewhere. For each solvent, the middle 70% of the distillate was used. The conductivities of the final products of AN, PC, methanol, DMF, and DMSO were less than 1.1×10^{-7} , 2.9×10^{-8} , 9.3×10^{-8} , 3.1×10^{-7} , and 3.1×10^{-8} S cm⁻¹, respectively. Alkali metal chlorides were used for the methanol system and alkali metal perchlorates for the other solvent systems.

2.2. APPARATUS AND PROCEDURE

The conductivity measurements were made on a Fuso conductivity apparatus (model 362A or 362B) in a water bath thermostated at 25 ± 0.02 °C. Two cells with cell constants of 0.08621 and 0.1880 cm⁻¹ were used. The experimental procedure to obtain formation constants of 19C6 complexes with alkali metal ions was as

Table I. Distribution constants of 19C6 at 25 °C

System	19C6
TD/H ₂ O	$(3.78 \pm 0.10) \times 10^{-3}$
TD/AN	$(1.66 \pm 0.06) \times 10^{-2}$
TD/PC	$(3.63 \pm 0.08) \times 10^{-2}$
TD/CH ₃ OH	$(4.61 \pm 0.10) \times 10^{-2}$
TD/DMF	$(3.96 \pm 0.06) \times 10^{-2}$
TD/DMSO	$(4.84 \pm 0.04) \times 10^{-2}$

TD designates tetradecane. Each distribution constant is the average of 11–17 measurements. The uncertainties are the standard deviations.

follows. 200 mL of a solution of an alkali metal salt ($(1.0\text{--}1.9) \times 10^{-3}$ mol dm⁻³) was placed in the cell (volume 350 mL) and its resistance measured. A step-by-step increase in the 19C6 concentration was effected by a rapid transfer from the 19C6 solution (4.5×10^{-3} – 5.6×10^{-2} mol dm⁻³) to the cell under a nitrogen atmosphere, until the total concentration of 19C6 was from 1.6 to 13 times as large as that of the alkali metal salt. The resistance of the solution in the cell was remeasured after each transfer.

2.3. DISTRIBUTION MEASUREMENTS OF 19C6

The experimental procedure for obtaining the distribution constants of 19C6 was much the same as that described previously [7]. The initial concentration of 19C6 was from 4.6×10^{-5} to 7.3×10^{-2} mol dm⁻³. The experiments were conducted at 25 ± 0.02 °C. In this work, CH₂Cl₂ was used to totally extract 19C6 from the aqueous solution as a 1:1:1 19C6-potassium picrate complex. The distribution constants of 19C6 are summarized in Table I.

3. Results and Discussion

The molar conductivity Λ vs. $[L]_t/[M]_t$ plots of 19C6 for PC, CH₃OH, and DMSO are shown in Figures 1, 2, and 3, respectively, where $[L]_t$ and $[M]_t$ denote total concentrations of 19C6 and an alkali metal, respectively. The plots for AN and DMF are similar, and so they have been omitted. Despite an increase in the 19C6 concentration, negligible changes in Λ are found for Li/CH₃OH, Li and Na/DMF, and Na/DMSO systems. It was impossible to determine the complex-formation constants of 19C6 with Li⁺ in CH₃OH and DMF and with Na⁺ in DMF and DMSO.

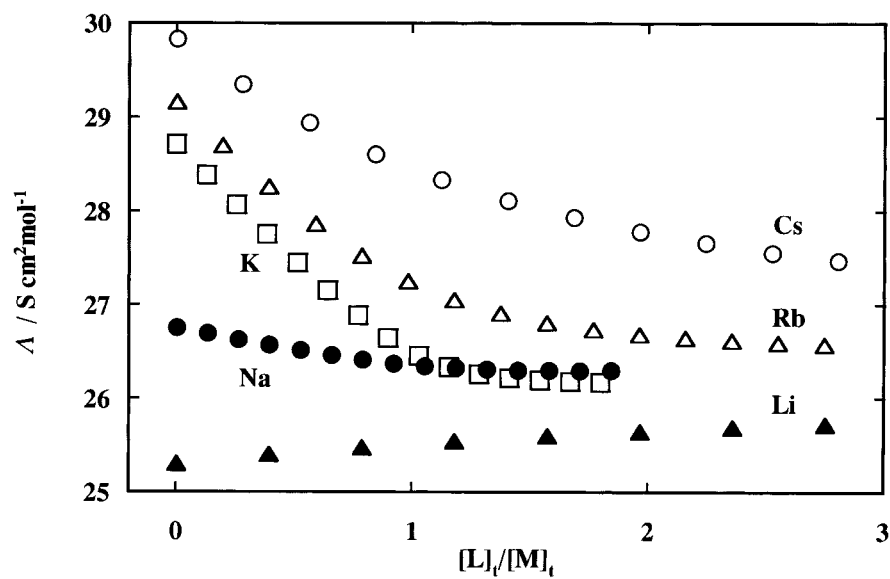


Figure 1. Δ vs. $[L]_t/[M]_t$ curves for 19C6-alkali metal perchlorate systems in PC at 25 °C.

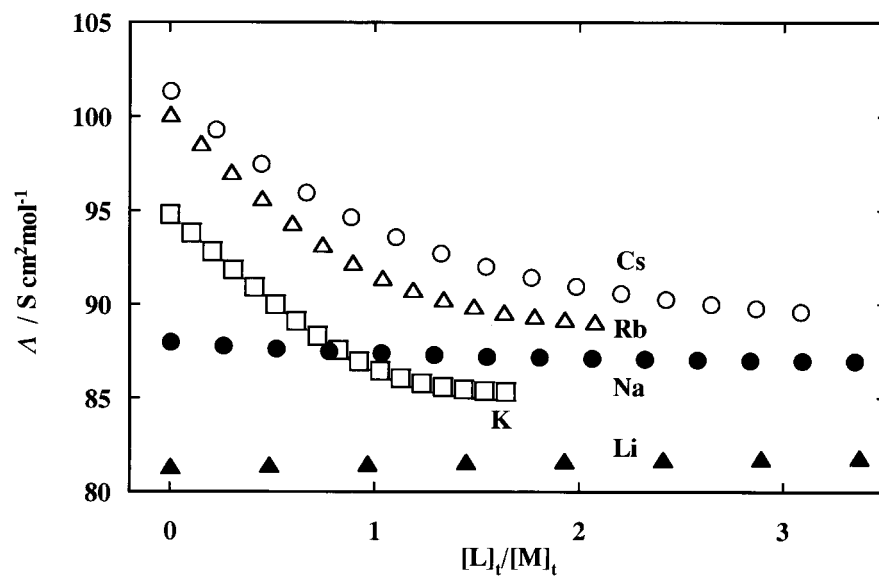


Figure 2. Δ vs. $[L]_t/[M]_t$ curves for 19C6-alkali metal perchlorate systems in CH₃OH at 25 °C.

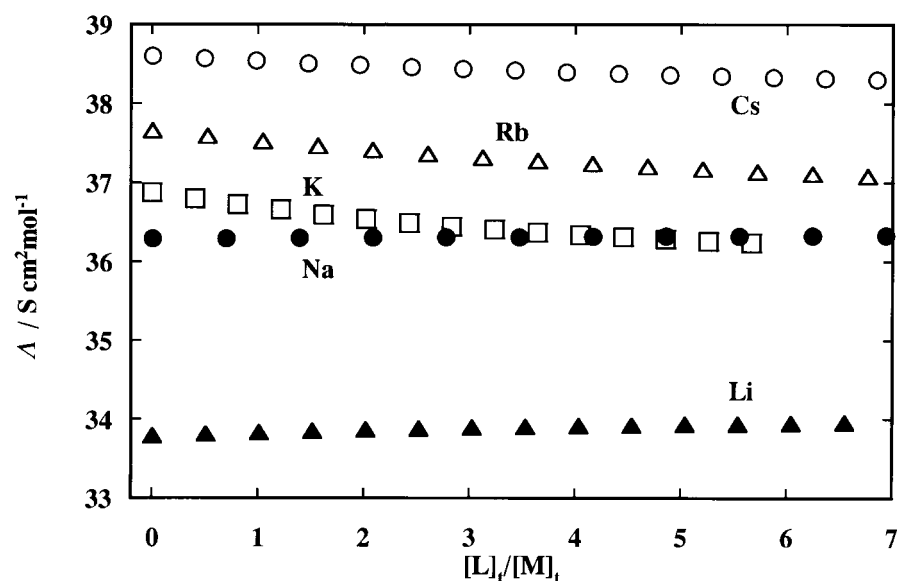
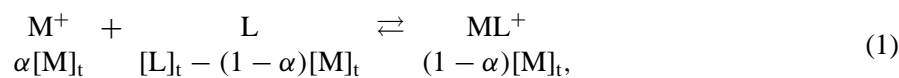


Figure 3. Λ vs. $[L]_t/[M]_t$ curves for 19C6-alkali metal perchlorate systems in DMSO at 25 °C.

When a crown ether (L) forms a 1 : 1 complex with an alkali metal ion (M^+), the equilibrium equation is written as



α being the fraction of free alkali metal ion. The complex-formation constant K_{ML} is defined by

$$\begin{aligned} K_{ML} &= [ML^+]/[M^+][L] \\ &= (1 - \alpha)/\alpha[L]. \end{aligned} \quad (2)$$

The observed conductivity κ is given by

$$\kappa = \kappa_{MA} + \kappa_{MLA}, \quad (3)$$

where A^- is an anion, and κ_{MA} and κ_{MLA} designate the conductivities of the alkali metal salt and the alkali metal crown ether salt, respectively. The molar conductivities are written as

$$\Lambda_{MA} = \kappa_{MA}/[M^+] = \kappa_{MA}/\alpha[M]_t, \quad (4)$$

$$\Lambda_{MLA} = \kappa_{MLA}/[ML^+] = \kappa_{MLA}/(1 - \alpha)[M]_t, \quad (5)$$

Λ_{MA} and Λ_{MLA} denoting the molar conductivities of the alkali salt and alkali metal crown ether salt, respectively. As a consequence of Equations (4) and (5), Equation (3) is transformed into

$$\begin{aligned}\Lambda &= \kappa/[M]_t \\ &= \alpha\Lambda_{MA} + (1 - \alpha)\Lambda_{MLA}.\end{aligned}\quad (6)$$

Equation (2) is transformed via Equation (6) to give

$$K_{ML} = (\Lambda_{MA} - \Lambda)/(\Lambda - \Lambda_{MLA})[L], \quad (7)$$

where $[L] = [L]_t - [M]_t(\Lambda_{MA} - \Lambda)/(\Lambda_{MA} - \Lambda_{MLA})$. The Λ_{MLA} is estimated from the Λ values at the points of large $[L]_t$ to $[M]_t$ ratios. The K_{ML} of Equation (7) is calculated from this Λ_{MLA} . The actual K_{ML} and Λ_{MLA} values were obtained by a successive approximation method. The $\log K_{ML}$ values for 19C6 are compiled in Table II, together with the literature values for 18C6.

3.1. STABILITY OF 19C6 COMPLEXES

The K^+ complex is the most stable among all the 19C6-alkali metal ion complexes except for the Rb^+ complex in water. The selectivity order of 19C6 for the heavy alkali metal ions are the same, $K^+ > Rb^+ > Cs^+$, regardless of solvent except for the case of K^+ and Rb^+ complexes in water. The same tendency is found for 18C6. Figures 4–6 show that the lines K^+ - Rb^+ and Rb^+ - Cs^+ for 19C6 run parallel with the corresponding ones for 18C6 except for the lines K^+ - Rb^+ for water; for the size-fitting and -misfitting larger heavy alkali metal ions (K^+ , Rb^+ , Cs^+), the selection ability of 19C6 for the neighboring cations in the periodic table is almost the same as that of 18C6. For each heavy alkali metal ion in a given solvent, the extra methylene group decreases the $\log K_{ML}$ value from 18C6 to 19C6. This is attributable to an unfavorable orientation of the donor oxygen atoms of 19C6 to the cation because of the unsymmetrical structure and the higher flexibility of 19C6 compared with 18C6. The selectivity of 19C6 for Li^+ which undergoes the strongest solvation is the second lowest (AN, DMSO) or the lowest (PC, H_2O). The selectivity of 19C6 for Na^+ varies with the solvent. Of all the alkali metal ion-19C6 complexes, the stability of the Na^+ complex is the highest for PC and the second for AN, but that is the lowest for CH_3OH and the next lowest for water. A similar trend for Li^+ and Na^+ is observed for 18C6. For AN, PC, and CH_3OH , the $\log K_{ML}$ value of the 19C6 complex with the light alkali metal ion (Li^+ , Na^+) is lower than that of the corresponding 18C6 complex except for the Li^+ complexes in AN. This is caused by an unfavorable orientation of the donor oxygen atoms of 19C6 to the size-misfitting smaller cation due to the unsymmetrical structure and the higher flexibility of 19C6. The difference in $\log K_{ML}$ between 18C6 and 19C6 in a given solvent decreases in the order the heavy alkali metal ions $> Na^+ > Li^+$. For K^+ , Na^+ , and Li^+ , the selection ability for the neighboring cations in the periodic table

Table II. $\log K_{ML}$ values of 19C6 and 18C6 with metal ions in various solvents at 25 °C

Metal ion	Ionic radius (Å) [8]	H ₂ O		AN		PC	
		19C6 [1]	18C6	19C6	18C6	19C6	18C6
Li ⁺	0.74	0.76	0.31 ± 0.01 ^a	3.73 ± 0.05	3.73 [11]	2.29 ± 0.02	2.78 [15]
Na ⁺	1.02	0.93	0.73 [1]	4.31 ± 0.05	4.55 [12]	4.49 ± 0.07	5.68 [4]
K ⁺	1.38	1.27	2.03 [9, 10]	4.62 ± 0.05	5.72 [3]	4.49 ± 0.01	6.24 [4]
Rb ⁺	1.49	1.33	1.56 [10]	4.06 ± 0.03	5.24 [13]	3.72 ± 0.00	5.32 [4]
Cs ⁺	1.70	0.71	0.99 [10]	3.29 ± 0.05	4.36 [14]	2.92 ± 0.01	4.48 [4]
		CH ₃ OH		DMF		DMSO	
		19C6	18C6	19C6	18C6 [6]	19C6	18C6
Li ⁺		–	–	–	–	1.72 ± 0.19	–
Na ⁺		2.83 ± 0.03	4.36 [16]	–	2.4	–	1.43 [12]
K ⁺		4.21 ± 0.06	6.08 [3]	2.60 ± 0.01	4.31	2.01 ± 0.05	3.28 [3]
Rb ⁺		3.76 ± 0.01	5.32 [16]	2.25 ± 0.03	3.98	1.73 ± 0.06	3.16 ^b
Cs ⁺		3.00 ± 0.01	4.79 [16]	1.89 ± 0.05	3.67	1.54 ± 0.08	3.04 [18]

^a Determined by conductometry using LiCl at 25 ± 0.02 °C. This study.

^b Calculated from $\log {}^{PC}\gamma^{DMSO}(ML^+) = -0.80$ [17] by Equation (8), using $\log K_{ML} = 5.32$ in PC [4].

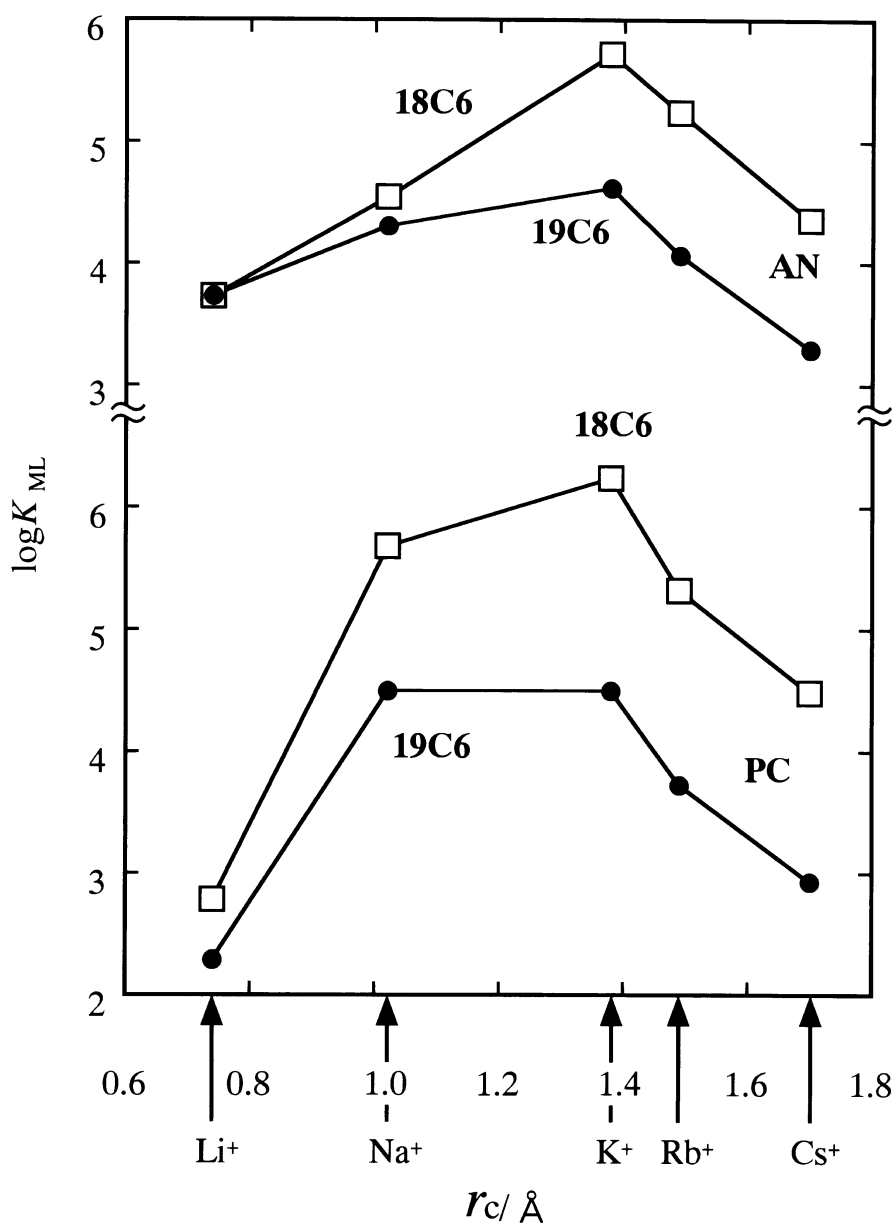


Figure 4. Plots of $\log K_{ML}$ vs. crystal radii of alkali metal ions for AN and PC.

is lower for 19C6 than for 18C6 (Figures 4–6). For the same alkali metal ion, the difference in $\log K_{ML}$ between 18C6 and 19C6 in the nonaqueous solvent is greater than the corresponding one in water. This is attributed to the fact that 19C6 is more lipophilic than 18C6, but the reverse holds for the ML^+ complexes of the same cation (Table V).

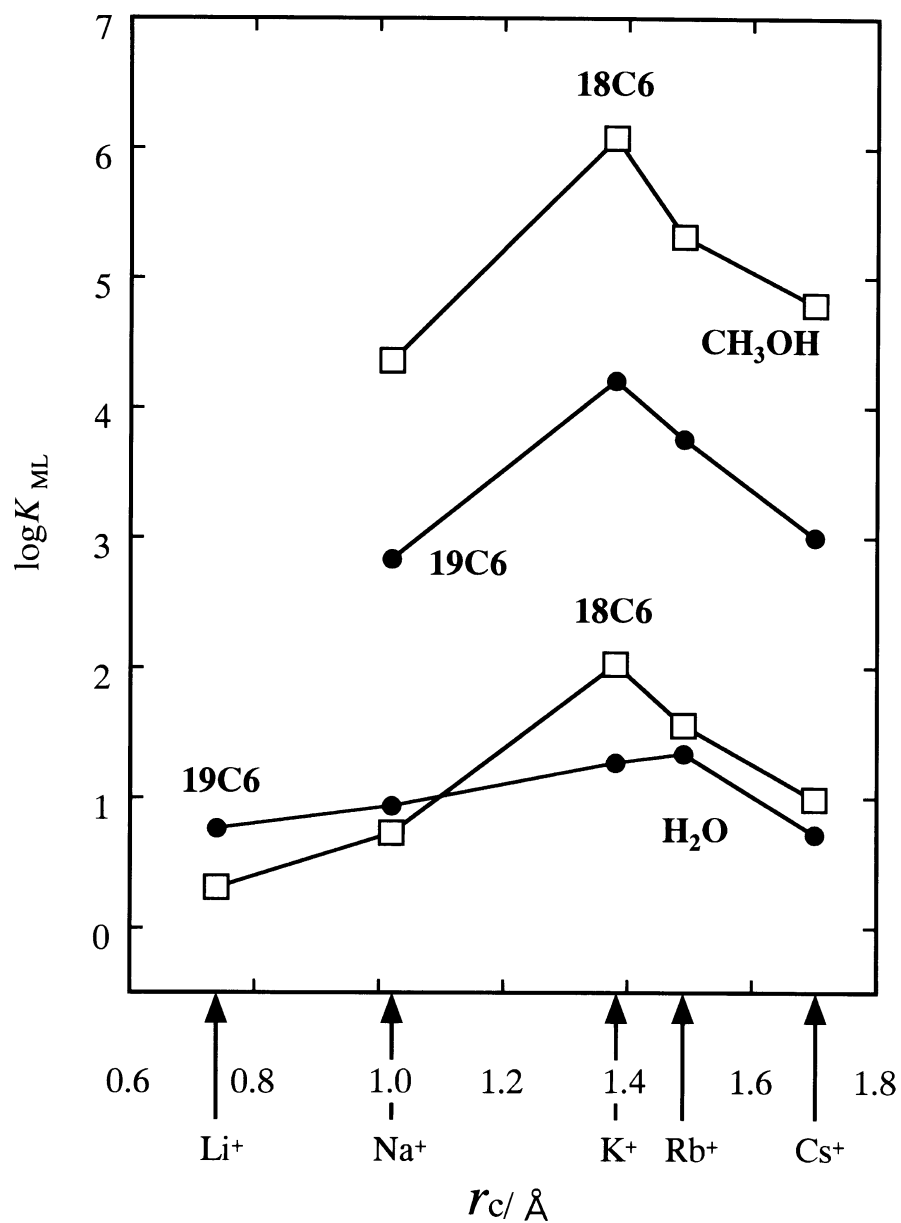


Figure 5. Plots of $\log K_{ML}$ vs. crystal radii of alkali metal ions for CH_3OH and H_2O .

Table V shows that an alkali metal ion is much more strongly solvated by DMF and DMSO than by water. But the stability of the 19C6-alkali metal ion complex in water is lower than in DMF and DMSO; the same tendency is also found for 18C6. Hydrogen bonding between ether oxygen atoms of the crown ether and water is

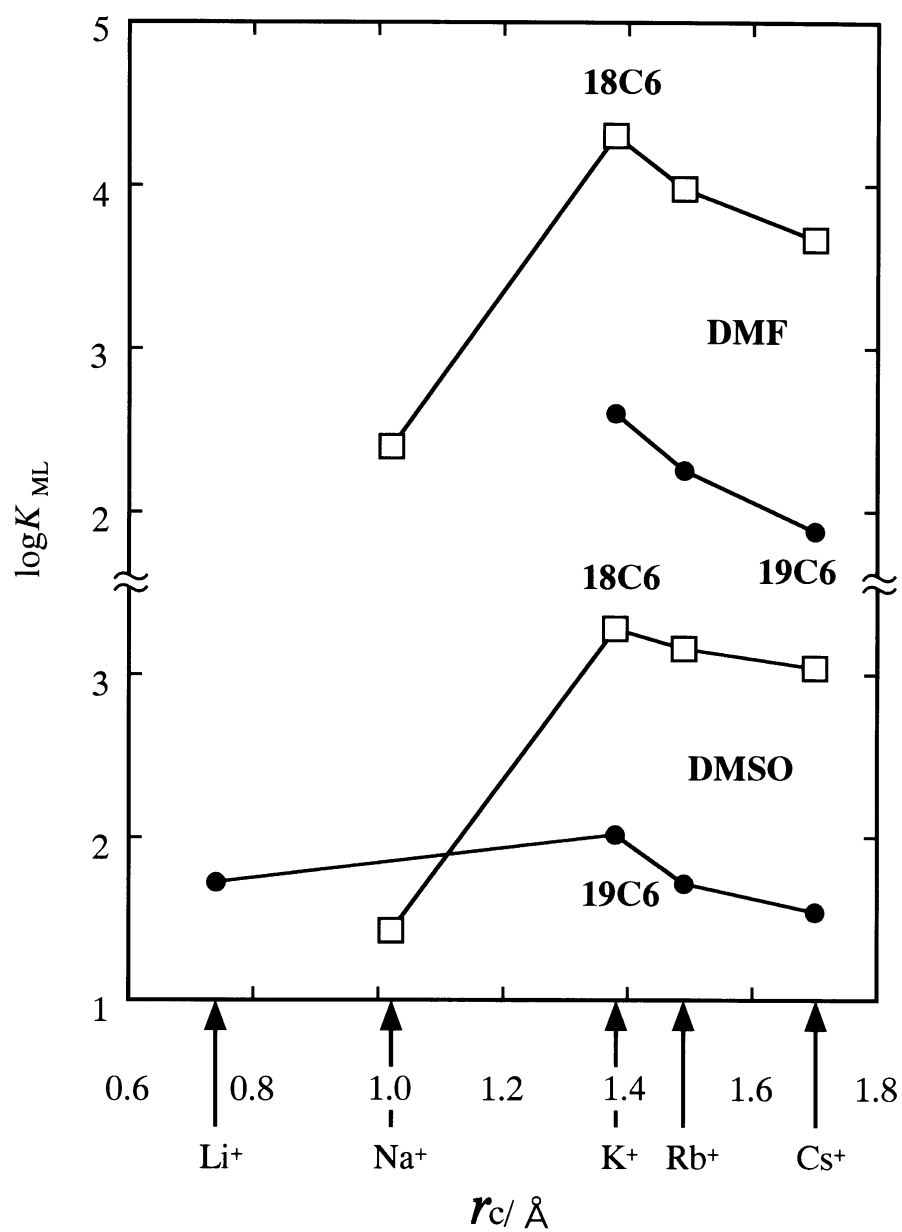


Figure 6. Plots of $\log K_{ML}$ vs. crystal radii of alkali metal ions for DMF and DMSO.

Table III. $K_{ML}(M_1)/K_{ML}(M_2)$ values at 25 °C

M ₁	M ₂	L	AN	PC	CH ₃ OH	H ₂ O	DMF	DMSO
Na	Li	19C6	4	159	–	2	–	–
		18C6	7	794	–	3	–	–
K	Na	19C6	2	1	24	2	–	–
		18C6	15	4	53	20	81	71
K	Rb	19C6	4	6	3	1	2	2
		18C6	3	8	6	3	2	1
Rb	Cs	19C6	6	6	6	4	2	2
		18C6	8	7	3	4	2	1

one of the dominant factors in causing the unexpectedly low stability of the crown ether complex in water.

Table III shows that the $K_{ML}(M_1)/K_{ML}(M_2)$ ratio of 19C6 or 18C6 varies greatly with the solvent in the cases of $M_1 = \text{Na}$, $M_2 = \text{Li}$ and $M_1 = \text{K}$, $M_2 = \text{Na}$, where the $r_c(M_1)/r_c(M_2)$ ratio is far larger than unity (Na/Li 1.38 and K/Na 1.35), r_c being the crystal ionic radius. But the $K_{ML}(M_1)/K_{ML}(M_2)$ ratio of the crown ether varies only slightly with the solvent in the cases of $M_1 = \text{K}$, $M_2 = \text{Rb}$ and $M_1 = \text{Rb}$, $M_2 = \text{Cs}$, where the $r_c(M_2)/r_c(M_1)$ ratio is close to unity (Rb/K 1.08 and Cs/Rb 1.14). This is caused by the difference between the difference in solvation energy between M_1^+ and M_2^+ and that between M_1L^+ and M_2L^+ ($M_1^+ + M_2L^+ \rightleftharpoons M_2^+ + M_1L^+$), and by the difference in complexation energy of ML^+ at gaseous state between M_1^+ and M_2^+ .

3.2. TRANSFER ACTIVITY COEFFICIENTS OF CROWN ETHERS

The transfer activity coefficients (${}^{S_1}\gamma^{S_2}(L)$) of a crown ether between solvents S_1 and S_2 is defined as follows,

$${}^{S_1}\gamma^{S_2}(L) = [L]_{S_1}/[L]_{S_2}.$$

The contributions of a methylene group (π_{CH_2}), and an ether oxygen atom (π_{O}), to $\log {}^{S_1}\gamma^{S_2}(L)$ between S_1 and S_2 at 25 °C can be estimated from $\log {}^{S_1}\gamma^{S_2}(L)$ of 19C6 and 18C6; $\pi_{\text{CH}_2} = \log {}^{S_1}\gamma^{S_2}(19\text{C6}) - \log {}^{S_1}\gamma^{S_2}(18\text{C6})$ and $\pi_{\text{O}} = (\log {}^{S_1}\gamma^{S_2}(L) - \pi_{\text{CH}_2} \times a) \div b$, a and b denoting the numbers of methylene groups and ether oxygen atoms, respectively. The contribution of a benzo group ($\pi_{\text{C}_6\text{H}_4}$) to $\log {}^{S_1}\gamma^{S_2}(L)$ between S_1 and S_2 at 25 °C can be evaluated from $\log {}^{S_1}\gamma^{S_2}(L)$ of benzo-crown ethers by using the π_{CH_2} and π_{O} values; $\pi_{\text{C}_6\text{H}_4} = \log {}^{S_1}\gamma^{S_2}(L) - \pi_{\text{CH}_2} \times a - \pi_{\text{O}} \times b$. The π_{CH_2} , π_{O} , and $\pi_{\text{C}_6\text{H}_4}$ values are compiled in Table IV, together with the π_{CH_2}

and π_{O} values estimated from $\log^{S_1} \gamma^{S_2}(\text{L})$ of 15-crown-5 (15C5) and 16-crown-5 (16C5), and experimental $\log^{S_1} \gamma^{S_2}(\text{L})$ values of crown ethers at 25 °C and those calculated from the empirical parameters, where DB18C6, DB21C7, DB24C8, and DB30C10 designate dibenzo-18-crown-6, dibenzo-21-crown-7, dibenzo-24-crown-8, and dibenzo-30-crown-10, respectively. Except for the PC/H₂O system, the π_{CH_2} , π_{O} , and $\pi_{\text{C}_6\text{H}_4}$ values calculated from the combination of 19C6 and 18C6 are in relatively good agreement with those of 16C5 and 15C5; experimental and calculated $\log^{S_1} \gamma^{S_2}(\text{L})$ values of a given crown ether ($S_1 = \text{AN}$ or CH_3OH) are nearly equal except for the case of DB18C6 for the $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ system. The structural effect on the π_{CH_2} values is not observed. For the PC/H₂O system, the π_{CH_2} , π_{O} , and $\pi_{\text{C}_6\text{H}_4}$ values evaluated from the combination of 19C6 and 18C6 are different from those of 16C5 and 15C5. Experimental and calculated $\log^{\text{PC}} \gamma^{\text{H}_2\text{O}}(\text{L})$ values of 15C5, 16C5, 18C6, or 19C6 are different. For each dibenzo-crown ether, the $\log^{\text{PC}} \gamma^{\text{H}_2\text{O}}(\text{L})$ value calculated from the combination of 19C6 and 18C6 is more consistent with the experimental one than that of 16C5 and 15C5. The $\log^{\text{PC}} \gamma^{\text{H}_2\text{O}}(\text{L})$ values of 15C5 and 16C5 were determined by directly measuring the distribution of 15C5 and 16C5 between PC and water without tetradecane [7]. The high mutual-solubility of PC and H₂O causes the larger inconsistency between experimental and calculated $\log^{\text{PC}} \gamma^{\text{H}_2\text{O}}(\text{L})$ values from the combination of 16C5 and 15C5 and the great difference between experimental $\log^{\text{PC}} \gamma^{\text{H}_2\text{O}}(\text{L})$ values of 15C5 and 16C5 and those calculated from the combination of 19C6 and 18C6.

The orders of increasing solubility of a methylene group, an ether oxygen atom, and a benzo group are $\text{H}_2\text{O} < \text{AN} \approx \text{PC} < \text{CH}_3\text{OH} < \text{DMF} < \text{DMSO}$, $\text{DMSO} \ll \text{DMF} < \text{CH}_3\text{OH} < \text{PC} \leq \text{AN} < \text{H}_2\text{O}$, and $\text{H}_2\text{O} \ll \text{AN} < \text{PC} < \text{CH}_3\text{OH} < \text{DMF} \ll \text{DMSO}$, respectively. The solubility sequences for the solvents of the methylene and benzo groups are the same and completely the reverse of that of the ether oxygen atom. The ether oxygen atom is hydrophilic, but methylene and benzo groups are hydrophobic. The benzo group is much more lipophilic than the methylene group. The ether oxygen atom is the most soluble in water which has the greatest acceptor number [25] among all these solvents. For the other cases, however, there is no relation between the acceptor number of the solvent and the solubility of the methylene group, the ether oxygen atom, or the benzo group. It is interesting that, except for water, the order of solubility of the ether oxygen atom is completely the reverse of that of the donor number of the solvents (AN 14.1, PC 15.1, H₂O 18.0, CH₃OH 19, DMF 26.6, DMSO 29.8 [25]). When $S_1 = \text{DMF}$ or DMSO , the much larger experimental $\log^{S_1} \gamma^{\text{H}_2\text{O}}(\text{L})$ value compared with the corresponding calculated value is found for DB21C7, DB24C8, and DB30C10 except for the DB24C8-DMSO/H₂O system; the difference between the experimental and calculated $\log^{S_1} \gamma^{\text{H}_2\text{O}}(\text{L})$ values increases from DB18C6 to DB30C10 with an increase in the flexibility of the dibenzo crown ether ring. The difference between the interaction of the ether oxygen atom with water and that with the nonaqueous solvent S_1 is much greater for the DMF/ and DMSO/H₂O systems than for the others. It follows from this that the interaction of the ether oxygen atom with water

Table IV. π_{CH_2} , π_{O} , $\pi_{\text{C}_6\text{H}_4}$, and $\log S_1 \gamma^{\text{S}_2}(\text{L})$ values at 25 °C

S_1/S_2	π_{CH_2}	π_{O}	$\pi_{\text{C}_6\text{H}_4}$	$\log S_1 \gamma^{\text{H}_2\text{O}}(\text{L})$							
				15C5		16C5		18C6		19C6	
				Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
AN/H ₂ O	0.33 ^a 0.34 ^b	-0.82 ^a -0.87 ^b	2.71 ^{a,c} 2.90 ^{b,c}	-0.98 ^e	-0.80 ^a	-0.64 ^e	-0.47 ^a	-0.97 ^{f,g}	-1.14 ^b	-0.64	-0.80 ^b
PC/H ₂ O	0.34 ^a 0.12 ^b	-0.90 ^a -0.29 ^b	2.89 ^{a,c} 1.52 ^{b,c}	-0.23 ^e	-1.10 ^a	-0.11 ^e	-0.76 ^a	-1.32 ^{f,g}	-0.30 ^b	-0.98	-0.18 ^b
CH ₃ OH/H ₂ O	0.57 ^a 0.41 ^b	-1.42 ^a -1.09 ^b	3.25 ^{a,c} 2.87 ^{b,c}	-1.29 ^e	-1.40 ^a	-0.88 ^e	-0.83 ^a	-1.66 ^g	-1.62 ^b	-1.09	-1.21 ^b
DMF/H ₂ O	0.78 ^m	-1.86 ^m	3.99 ⁿ	-	-1.50 ^m	-	-0.72 ^m	-1.80	-	-1.02	-
DMSO/H ₂ O	1.47 ^a	-3.37 ^a	5.99 ^{a,d}	-	-2.15 ^a	-	-0.68 ^a	-2.58 ^{f,g}	-	-1.11	-

S_1/S_2	$\log S_1 \gamma^{\text{H}_2\text{O}}(\text{L})$							
	DB18C6		DB21C7		DB24C8		DB30C10	
	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
AN/H ₂ O	3.50 ^h	3.14 ^{a,c} 3.30 ^{b,c}	3.37 ^j	2.98 ^{a,c} 3.11 ^{b,c}	3.06 ^{j,k}	2.82 ^{a,c} 2.92 ^{b,c}	2.90 ^j	2.50 ^{a,c} 2.54 ^{b,c}
PC/H ₂ O	2.89 ^h	3.10 ^{a,c} 2.26 ^{b,c}	3.02 ^j	2.88 ^{a,c} 2.21 ^{b,c}	2.72 ^{j,k}	2.66 ^{a,c} 2.16 ^{b,c}	2.34 ^j	2.22 ^{a,c} 2.06 ^{b,c}
CH ₃ OH/H ₂ O	1.84 ^h	2.54 ^{a,c} 2.48 ^{b,c}	2.04 ^j	2.26 ^{a,c} 2.21 ^{b,c}	1.88 ^{j,k}	1.98 ^{a,c} 1.94 ^{b,c}	1.49 ^j	1.42 ^{a,c} 1.40 ^{b,c}
DMF/H ₂ O	3.45 ^{h,i}	3.06 ⁿ	3.44 ^j	2.76 ⁿ	3.10 ^j	2.46 ⁿ	2.82 ^j	1.86 ⁿ
DMSO/H ₂ O	3.38 ^{h,i}	3.52 ^{a,d}	-	3.09 ^{a,d}	2.94 ^j	2.66 ^{a,d}	2.62 ^j	1.80 ^{a,d} 2.66 ^{j,l}

^a Calculated from $\log S_1 \gamma^{\text{H}_2\text{O}}(\text{L})$ of 19C6 and 18C6 [17,19]. ^b Calculated from $\log S_1 \gamma^{\text{H}_2\text{O}}(\text{L})$ of 16C5 and 15C5 [7]. ^c The average of $\pi_{\text{C}_6\text{H}_4}$ calculated from $\log S_1 \gamma^{\text{H}_2\text{O}}(\text{L})$ of B15C5 [20] and B18C6 [21]. ^d Calculated from $\log S_1 \gamma^{\text{H}_2\text{O}}(\text{L})$ of B18C6 [21]. ^e Ref. [7]. ^f Ref. [17]. ^g Ref. [19]. ^h Ref. [12]. ⁱ Ref. [22]. ^j Ref. [17]. ^k Ref. [23]. ^l Ref. [24]. ^m Calculated from $\log S_1 \gamma^{\text{H}_2\text{O}}(\text{L})$ of 19C6 and 18C6 determined in this study. ⁿ Calculated from $\log S_1 \gamma^{\text{H}_2\text{O}}(\text{L})$ of 19C6, 18C6, and B18C6 determined in this study.

is more effectively decreased in the DMF/ and DMSO/H₂O systems than in the others owing to the increasing flexibility of the dibenzo crown ether ring. This is responsible for the fact that the difference between experimental and calculated $\log {}^{S_1}\gamma^{\text{H}_2\text{O}}(\text{L})$ values increases from DB18C6 to DB30C10 when $S_1 = \text{DMF}$ and DMSO.

3.3. TRANSFER ACTIVITY COEFFICIENTS OF CROWN ETHER-METAL ION COMPLEXES

The $\log {}^{S_1}\gamma^{S_2}(\text{ML}^+)$ value is calculated by Equation (8).

$$\log {}^{S_1}\gamma^{S_2}(\text{ML}^+) = (\log K_{\text{ML}})_{S_1} - (\log K_{\text{ML}})_{S_2} + \log {}^{S_1}\gamma^{S_2}(\text{L}) + \log {}^{S_1}\gamma^{S_2}(\text{M}^+), \quad (8)$$

where ${}^{S_1}\gamma^{S_2}(\text{ML}^+)$ and ${}^{S_1}\gamma^{S_2}(\text{M}^+)$ designate transfer activity coefficients of a crown ether-monovalent metal ion complex and a monovalent metal ion between S_1 and S_2 , respectively; $(\log K_{\text{ML}})_S$ denotes $\log K_{\text{ML}}$ in a solvent S . The $\log {}^S\gamma^{\text{H}_2\text{O}}(\text{ML}^+)$ and $\log {}^S\gamma^{\text{H}_2\text{O}}(\text{M}^+)$ values at 25 °C are compiled in Table V.

The $\log {}^S\gamma^{\text{H}_2\text{O}}(\text{ML}^+)$ of 19C6 for a given solvent varies with the alkali metal ion. The same is true of 18C6. This shows the interaction of the ML^+ complex with solvents depends on the alkali metal ion held in the cavity. It is interesting that, for 19C6 or 18C6, much the greatest $|\log {}^S\gamma^{\text{H}_2\text{O}}(\text{M}_b\text{L}^+) - \log {}^S\gamma^{\text{H}_2\text{O}}(\text{M}_a\text{L}^+)|$ value is found for the case of $\text{M}_a = \text{Li}$ and $\text{M}_b = \text{Na}$ in a given solvent, although the $r_c(\text{Na})/r_c(\text{Li})$ ratio is nearly equal to the $r_c(\text{K})/r_c(\text{Na})$ ratio, where M_a and M_b denote neighboring alkali metals in the periodic table, and the M_b^+ ion is larger in size than the M_a^+ ion. The interaction of the ML^+ complex with solvents is more strongly affected by the smaller cation held in the cavity. The $|\log {}^S\gamma^{\text{H}_2\text{O}}(\text{M}_b\text{L}^+) - \log {}^S\gamma^{\text{H}_2\text{O}}(\text{M}_a\text{L}^+)|$ of 19C6 is larger than or nearly equal to the corresponding one of 18C6, except for the case of $\text{M}_a = \text{Li}$, $\text{M}_b = \text{Na}$, and $S = \text{PC}$. 19C6 shields the alkali metal ion in the complex less effectively than does 18C6.

The $\log {}^S\gamma^{\text{H}_2\text{O}}(\text{ML}^+) - \log {}^S\gamma^{\text{H}_2\text{O}}(\text{M}^+)$ value of a given alkali metal ion for 19C6 decreases in the order $\text{AN} > \text{PC} > \text{CH}_3\text{OH} > \text{DMF} > \text{DMSO}$. A similar tendency is found for 18C6. This shows that the alkali metal ion which is more strongly solvated in water than in the nonaqueous solvent increases its lipophilicity upon complexation with 19C6 or 18C6, and that the contrary holds. When $S = \text{AN}$, PC , and CH_3OH , because the alkali metal ion is more strongly solvated in water than in AN , PC , and CH_3OH , the $\log {}^S\gamma^{\text{H}_2\text{O}}(\text{ML}^+) - \log {}^S\gamma^{\text{H}_2\text{O}}(\text{M}^+)$ value is positive owing to the greater desolvation effect of the ion in water upon complexation compared with AN , PC , and CH_3OH . The alkali metal ion in DMSO undergoes much stronger solvation than in water, resulting in the negative $\log {}^{\text{DMSO}}\gamma^{\text{H}_2\text{O}}(\text{ML}^+) - \log {}^{\text{DMSO}}\gamma^{\text{H}_2\text{O}}(\text{M}^+)$ value because of the greater desolvation effect of the ion in DMSO upon complexation compared with water.

Table V. Transfer activity coefficients at 25 °C

S =	AN		PC		CH ₃ OH		DMF		DMSO	
$\log S_{\gamma}^{\text{H}_2\text{O}}(\text{M}^+)^{\text{a}}$										
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	
Rb ⁺	-1.1		-1.2 ₂		-1.7		1.9		2.0	
Cs ⁺	-0.8		-0.9 ₄		-1.6		1.7		2.3	
$\log S_{\gamma}^{\text{H}_2\text{O}}(\text{L})$	19C6	18C6	19C6	18C6	19C6	18C6	19C6	18C6	19C6	18C6
	-0.64	-0.97 ^{d,e}	-0.98	-1.32 ^{d,e}	-1.09	-1.66 ^d	-1.02	-1.80 ^f	-1.11	-2.58 ^{d,e}
$\log S_{\gamma}^{\text{H}_2\text{O}}(\text{ML}^+)$										
Li ⁺	-2.0	-1.9	-3.7	-3.1	-	-	-	-	2.5	-
Na ⁺	0.4	0.6	-0.3 ₆	0.6 ₉	-0.6	0.6	-	1.6	-	0.6
K ⁺	1.4	1.4	0.7 ₀	1.3 ₅	0.2	0.7	2.1	2.3	1.8	0.9
Rb ⁺	1.0	1.6	0.1 ₉	1.2 ₂	-0.4	0.4	1.8	2.5	1.3	1.0
Cs ⁺	1.1	1.6	0.2 ₉	1.2 ₃	-0.4	0.5	1.9	2.6	2.0	1.8

^a Ref. [12]. ^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. [19]. ^e Ref. [17]. ^f This study.

Although 19C6 is always more lipophilic than 18C6, the 19C6-alkali metal ion complex is more hydrophilic than the corresponding 18C6 complex except for the case of $S = \text{DMSO}$. It follows from this that 19C6 screens the alkali metal ion in the complex from solvents less effectively than does 18C6, and that dehydration of 19C6 on complexation with the alkali metal ion in water is less efficient than that of 18C6, owing to the less symmetric arrangement of the donor oxygen atoms of 19C6 for the alkali metal ion. When $S = \text{DMSO}$, the effect of the interaction with DMSO of the alkali metal ion in the 19C6 complex surpasses the dehydration effect because of the greatest solvation ability of DMSO, resulting in the higher lipophilicity of the 19C6 complex ion compared with the corresponding 18C6 one. It has been reported that 16C5 is more lipophilic than 15C5, and that, even when $S = \text{AN}$, PC, and CH_3OH , the 16C5 complex with the alkali metal ion is also more lipophilic than the corresponding 15C5 one [7]. The higher lipophilicity of the 16C5 complex ion is attributable to the favorable arrangement of the donor oxygen atoms of 16C5 for the alkali metal ion despite the extra methylene group.

When $S = \text{AN}$, PC, and CH_3OH , the $\log {}^S\gamma^{\text{H}_2\text{O}}(\text{ML}^+)$ value is larger than the corresponding $\log {}^S\gamma^{\text{H}_2\text{O}}(\text{L})$ value except for the case of $\text{M}^+ = \text{Li}^+$. Although the alkali metal ion is more strongly solvated by water than by AN, PC, or CH_3OH , when 19C6 or 18C6 forms a complex with the alkali metal ion, the complex ion becomes more soluble in the nonaqueous solvents than in water, compared with the crown ether itself. The higher lipophilicity of the complex ion compared with the uncomplexed crown ether is due to an enforcement of the hydrogen-bonded structure of water for the bulky complex ion caused by the greatly decreased hydrogen bonding between ether oxygen atoms and water upon complexation. The Li^+ ion is much more strongly solvated by water than by AN or PC compared with the other alkali metal ions. Thus, the effect of the possible strong interaction with water of the Li^+ ion in the crown ether complex exceeds that of the greatly reduced hydrogen bonding, leading to the smaller $\log {}^S\gamma^{\text{H}_2\text{O}}(\text{ML}^+)$ of Li^+ than the corresponding $\log {}^S\gamma^{\text{H}_2\text{O}}(\text{L})$ for $S = \text{AN}$ and PC. For DMF and DMSO, the $\log {}^S\gamma^{\text{H}_2\text{O}}(\text{ML}^+)$ value is larger than the corresponding $\log {}^S\gamma^{\text{H}_2\text{O}}(\text{L})$ value. The $\log {}^S\gamma^{\text{H}_2\text{O}}(\text{ML}^+) - \log {}^S\gamma^{\text{H}_2\text{O}}(\text{L})$ value of DMF or DMSO for a given alkali metal ion is much greater than that of AN, PC, or CH_3OH . This is ascribed to the possible stronger interaction with DMF or DMSO of the alkali metal ion in the crown ether complex because the alkali metal ion is much more strongly solvated by DMF and DMSO than by water compared with AN, PC, and CH_3OH . The above discussion strongly supports the foregoing conclusion that the hydrogen bonding between ether oxygen atoms of 19C6 or 18C6 and water causes the unexpectedly lowest stability of the 19C6- or 18C6-alkali metal ion complex in water among all the solvents. The $\log {}^S\gamma^{\text{H}_2\text{O}}(\text{ML}^+) - \log {}^S\gamma^{\text{H}_2\text{O}}(\text{L})$ value of 19C6 is always smaller than the corresponding 18C6 value. This shows that dehydration of 19C6 on complexation with the alkali metal ion in water is less efficient than that of 18C6.

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