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Stabilities in Water and Transfer Activity Coefficients between Nonaqueous Solvents and Water of 1 : 1 Complexes of 15,15-Dimethyl-16-crown-5 with Metal Ions

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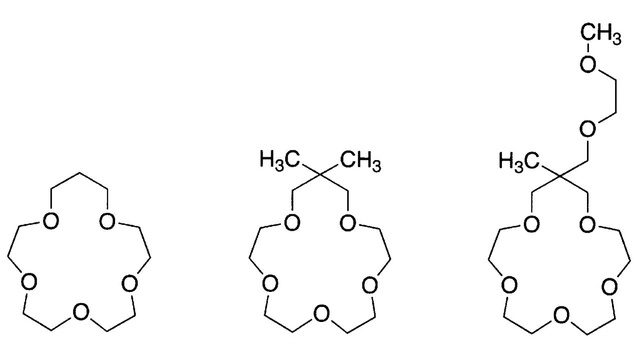
The stability constants of 1 : 1 complexes of 15,15-dimethyl-16-crown-5 (DM16C5) with Li^+, Na^+, K^+, Ag^+, Tl^+, Sr^{2+}, Ba^{2+}, and Pb^{2+} and of 16-crown-5 (16C5) with Li^+ have been determined by conductometry in water at 25 °C. The transfer activity coefficients ($^{s}\gamma^{H_2O}$) of the alkali metal ion complexes between nonaqueous solvents (s: acetonitrile, propylene carbonate, and methanol) and water have been calculated. These values have been compared with the literature values for 16C5 and 15-(2,5-dioxahexyl)-15-methyl-16-crown-5 (L16C5). In water, 16C5 and DM16C5 selectively complex Li^+ over Na^+ and K^+. The complexing ability of DM16C5 for a given metal ion is generally lower than that of 16C5 and L16C5. The alkali metal ion complexes of all the crown ethers are much less stable in water than in s, and the selectivity and the substituent effects also depend upon the solvent. The $^{s}\gamma^{H_2O}$ values provide the following information: the alkali metal ion and the ether oxygen atoms are greatly dehydrated upon complexation in water; the dehydration is most drastic for Na^+; the dehydration for Na^+ is hindered by the methyl groups of DM16C5 and facilitated by the electron-donating side arm of L16C5. The solvent effects upon complexation are explained in terms of solute–solvent interactions.

16-Crown-5 derivatives possessing various substituents have been synthesized.[1,2] There have been no reports on the stabilities in water of their complexes with metal ions, except for our previous studies on the complexes of 16-crown-5 (16C5, Fig. 1)[3] and 15-(2,5-dioxahexyl)-15-methyl-16-crown-5 (L16C5, Fig. 1).[4] Although L16C5 (lariat 16C5), which possess an electron-donating side arm, was originally designed to enhance the complexing ability of 16C5, it has been shown that the complex stability constants of L16C5 with several metal ions are comparable to those of 16C5 in water. A study of 15,15-dimethyl-16-crown-5 (DM16C5, Fig. 1) serves to elucidate the contribution of each substituent at the 15-position of L16C5. The stabilities of the alkali metal ion complexes with 16C5, L16C5, and DM16C5 in acetonitrile (AN), propylene carbonate (PC), and methanol (MeOH) were previously examined.[5–8]



16C5 DM16C5 L16C5

Fig. 1. Structures of 16C5, DM16C5, and L16C5.

In this paper, we report on the stability constants in water of the complexes of DM16C5 with Li^+, Na^+, K^+, Ag^+, Tl^+, Sr^{2+}, Ba^{2+}, and Pb^{2+} determined by a precise conductometric method. The transfer activity coefficients between a nonaqueous solvent (AN, PC, or MeOH) and water of the DM16C5-Li^+, -Na^+, and -K^+ complexes have been calculated to obtain quantitative information on the solvation of the complexes. Herein, the stability constant in water and the transfer activity coefficients of the 16C5-Li^+ complex are also reported for the first time. By comparing the results for DM16C5 with those for 16C5 and L16C5, the substituent effects on the stability and solvation of the complexes in water are discussed.

Experimental

DM16C5 and 16C5 were synthesized as described in a previous paper[1] and distilled several times at reduced pressure. $LiCl{\cdot}H_2O$, NaCl, and KCl (Merck, suprapur) were, prior to use, dried at 250 °C in vacuo. $Sr(NO_3)_2$, $Ba(NO_3)_2$, $AgNO_3$, $TlNO_3$ (Merck, suprapur or GR), and $Pb(NO_3)_2$ (Wako Pure Chemical Industries, 99.9%) were used without further purification. The purities of $AgNO_3$ and the other metal nitrates were checked by KCl and EDTA titrations, respectively. Water was distilled and further purified with a Milli-Q Labo system (Millipore). The conductivity of water was less than 8×10^{-7} S cm^{-1}.

Three conductivity cells (volume 350 cm^3) with cell constants of 0.1924, 0.2165, and 0.2691 cm^{-1} were used. In the cell, 200 cm^3 of the aqueous metal salt solution ($(2.0–3.9) \times 10^{-3}$ mol dm^{-3}) was placed and thermally equilibrated at 25 ± 0.02 °C; for $AgNO_3$ and $Pb(NO_3)_2$, the solution was acidified with nitric acid to pH 3.0–3.4 to prevent hydrolysis of the metal ions. The resistance was measured with a Fuso model 362B conductivity apparatus under a nitrogen atmosphere. Then, a known amount of the aqueous crown ether solution (4.3×10^{-2}–1.0×10^{-1} mol dm^{-3}) was added stepwise to the cell, and the resistance was measured after each addition. The apparent molar conductivity (Λ_{app}) was calculated by $\Lambda_{app} = (\kappa - \kappa_{H_2O}) / [M]_t$, where κ, κ_{H_2O}, and $[M]_t$ denote the conductivity of the solution, that of water, and the total concentration of the metal salt, respectively.

Results

Examples of the Λ_{app} vs. $[L]_t/[M]_t$ plots are shown in Fig. 2, where $[L]_t$ denotes the total concentration of the crown ether. In all of the systems studied, the Λ_{app} value decreased with an increase in $[L]_t$, indicating that the crown ether forms a metal-ion complex whose mobility is lower than that of the free metal ion. The stability constant (K_{ML}), defined as $[ML^{m+}] / [M^{m+}][L]$ (M^{m+} = metal ion and L = ligand), and the molar conductivity of the metal crown ether salt (Λ_{MLA_m}) were determined from an analysis of the conductivity data in the same manner as described previously.[8,9] In this analysis, it was assumed that the ligand forms only a 1:1 complex with the metal ion and that cation–anion association and viscosity changes are negligible. The solid lines in Fig. 2, which were calculated from the K_{ML} and Λ_{MLA_m} values obtained, are well fitted to the experimental points, supporting the validity of the analysis. The same is true for the 16C5-LiCl system. The log K_{ML} values together with the literature values[3–8] at 25 °C are summarized in Table 1. The diameters of the metal ions[10] are also listed in Table 1.

The transfer activity coefficient of a solute i between a nonaqueous solvent s and water (${}^{s}\gamma^{H_2O}(i)$) is related to the standard Gibbs free-energy change for the transfer of i from water to s ($\Delta G^{\circ}_{tr,H_2O\rightarrow s}(i)$) by $\log {}^{s}\gamma^{H_2O}(i) = -\Delta G^{\circ}_{tr,H_2O\rightarrow s}(i) / 2.303RT$. Therefore, the transfer activity coefficient of a crown ether–alkali metal ion 1:1 complex is calculated using the following equation:

$$\log {}^{s}\gamma^{H_2O}(ML^{+}) = \log K_{ML,s} - \log K_{ML,H_2O} + \log {}^{s}\gamma^{H_2O}(L) + \log {}^{s}\gamma^{H_2O}(M^{+}), \quad (1)$$

where $K_{ML,s}$ and K_{ML,H_2O} refer to K_{ML} in s and water, respectively. The ${}^{s}\gamma^{H_2O}(ML^{+})$ values for Li^+, Na^+, and K^+ were obtained from the K_{ML} values in Table 1 and the literature values of ${}^{s}\gamma^{H_2O}(L)$[4,5] and ${}^{s}\gamma^{H_2O}(M^{+})$.[11–13] The $\log {}^{s}\gamma^{H_2O}(ML^{+})$, $\log {}^{s}\gamma^{H_2O}(L)$, and $\log {}^{s}\gamma^{H_2O}(M^{+})$ values at 25 °C are summarized in Table 2.

Discussion

Transfer Activity Coefficients. The ${}^{s}\gamma^{H_2O}(i)$ can be regarded as a hypothetical partition constant of i between s and water, i.e., $[i]_s/[i]_{H_2O}$. The $\log {}^{s}\gamma^{H_2O}(L)$ value of DM16C5 is always positive and larger than the corresponding values of 16C5 and L16C5; this means that DM16C5 is more soluble in AN,

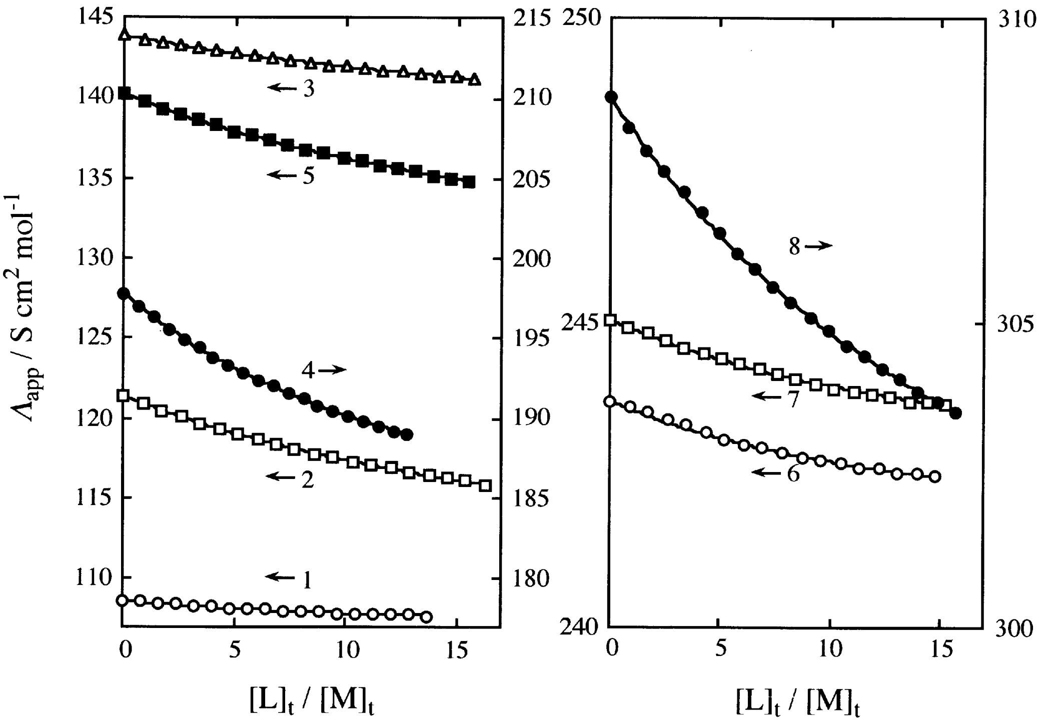


Fig. 2. Λ_{app} vs. $[L]_t/[M]_t$ plots for DM16C5–metal salt systems in water at 25 °C. Initial concentrations of electrolytes: (1) LiCl 3.0×10^{-3} mol dm^{-3}; (2) NaCl 2.8×10^{-3} mol dm^{-3}; (3) KCl 3.0×10^{-3} mol dm^{-3}; (4) $AgNO_3$ 3.0×10^{-3} mol dm^{-3}, HNO_3 5.1×10^{-4} mol dm^{-3}; (5) $TlNO_3$ 3.0×10^{-3} mol dm^{-3}; (6) $Sr(NO_3)_2$ 2.8×10^{-3} mol dm^{-3}; (7) $Ba(NO_3)_2$ 2.9×10^{-3} mol dm^{-3}; (8) $Pb(NO_3)_2$ 3.0×10^{-3} mol dm^{-3}, HNO_3 4.4×10^{-4} mol dm^{-3}.

Table 1. Stability Constants ($\log K_{\mathrm{ML}}$) at 25 °C

M^{m+}	d[a]/Å	H_2O			AN			PC			MeOH		
		L =16C5	DM16C5	L16C5[b]	16C5[c]	DM16C5[d]	L16C5[d]	16C5[c]	DM16C5[d]	L16C5[d]	16C5	DM16C5	L16C5
Li^+	1.52	1.05±0.05[e]	1.15±0.06[e]		4.4_8	4.1	4.45	3.2_5	3.13	3.06			
Na^+	2.04	0.78[f]	0.60±0.01[e]	0.65	5.3_9	4.3	5.0	5.7	4.0	5.2	4.10[c] 4.07[g]	3.54[g] 3.73[h]	3.70[g] 3.53[h]
K^+	2.76	0.40[f]	0.1±0.1[e]	0.3	3.5_7	3.13	3.06	3.3_4	2.89	2.88	2.9_2[c]	2.54[h]	2.43[h]
Ag^+	2.30	1.10[f]	0.92±0.01[e]	1.12									
Tl^+	3.00	0.73[f]	0.55±0.01[e]	0.56									
Sr^{2+}	2.36	2.08[f]	1.1±0.1[e]	2.18									
Ba^{2+}	2.70	1.84[f]	0.9±0.1[e]	1.84									
Pb^{2+}	2.38	0.74[f]	0.65±0.08[e]	1.27									

a) Cation diameters calculated from effective ionic radii (Ref. 10) for coordination number 6. b) Ref. 4. c) Ref. 7. d) Ref. 8. e) This work; average of 3 or 4 independent measurementes. f) Ref. 3. g) Ref. 6. h) Ref. 5.

Table 2. Transfer Activity Coefficients ($\log {}^{s}\gamma^{H_2O}(i)$, molar scale)[a] at 25°C

i	s = AN			PC			MeOH		
Li^+	−4.3[b]			−4.2[c]					
Na^+	−2.3[d]			-2.9_4[d]			−1.4[d]		
K^+	−1.3[d]			-1.5_4[d]			−1.7[d]		
	L = 16C5	DM16C5	L16C5	16C5	DM16C5	L16C5	16C5	DM16C5	L16C5
L	−0.64[e] −0.61[g]	0.43[f] 0.66[g]	0.17[f] −0.06[g]	−0.11[e] −0.13[g]	0.83[f] 0.70[g]	0.354[f] 0.48[g]	−0.88[e] −0.94[g]	0.40[f] 0.63[g]	−0.10[f] −0.32[g]
LiL^+	−1.5	−0.9		−2.1	−1.4				
NaL^+	1.7[e]	1.8	2.2[f]	1.9[e]	1.3	2.0[f]	1.0[e]	1.9	1.6
KL^+	1.2[e]	2.2	1.6[f]	1.2_9[e]	2.1	1.4[f]	−0.1[e]	1.1	0.3[f]

a) Based on the ${}^{s}\gamma^{H_2O}(Ph_4As^+) = {}^{s}\gamma^{H_2O}(BPh_4^-)$ assumption for single ions. b) Calculated from ${}^{AN}\gamma^{PC}(Li^+)$ (Ref. 11) and ${}^{PC}\gamma^{H_2O}(Li^+)$ (Ref. 12) values. c) Ref. 12. d) Ref. 13. e) Ref. 3. f) Ref. 4. g) Calculated from group contributions (see text).

PC, and MeOH than in water, and that DM16C5 is the most lipophilic of the three crown ethers. As reported previously,[3,14] the additivity of the group contribution to the $\log {}^{s}\gamma^{H_2O}(L)$ value is valid for these crown ethers; the contributions of a methylene group (π_{CH_2}), an ether oxygen atom (π_O), a methyl group (π_{CH_3}), and a quaternary carbon atom (π_C) are as follows: $\pi_{CH_2} = 0.34$, $\pi_O = -0.87$, $\pi_{CH_3} = 0.53$, and $\pi_C = 0.55$ for $\log {}^{AN}\gamma^{H_2O}(L)$; $\pi_{CH_2} = 0.12$, $\pi_O = -0.29$, $\pi_{CH_3} = 0.19$, and $\pi_C = 0.57$ for $\log {}^{PC}\gamma^{H_2O}(L)$; $\pi_{CH_2} = 0.41$, $\pi_O = -1.09$, $\pi_{CH_3} = 0.75$, and $\pi_C = 0.48$ for $\log {}^{MeOH}\gamma^{H_2O}(L)$. The $\log {}^{s}\gamma^{H_2O}(L)$ values calculated from the π values are in fair agreement with the experimental values (Table 2). The ether oxygen atom makes a hydrophilic contribution to the $\log {}^{s}\gamma^{H_2O}(L)$ value due to hydrogen bonding with water. The other fragments possessing no specific interactions with water are all lipophilic.

The $\log {}^{s}\gamma^{H_2O}(M^+)$ values are negatively large, indicating that the alkali metal ions are much more strongly solvated in water than in AN, PC, and MeOH. The $\log {}^{s}\gamma^{H_2O}(ML^+)$ value for DM16C5 is always much larger than the sum of the corresponding $\log {}^{s}\gamma^{H_2O}(M^+)$ and $\log {}^{s}\gamma^{H_2O}(L)$ values. The same is true for 16C5 and L16C5. The positive deviation from the additivity is ascribed to considerable dehydration of the metal ion and the crown-ether oxygen atoms upon complexation in water.[3,4] When $M^+ = Na^+$ and K^+, the $\log {}^{s}\gamma^{H_2O}(ML^+)$ values for the three crown ethers are positive and relatively large, except for a few cases. This indicates that the complexes are generally more soluble in the nonaqueous solvents than in water, in contrast to the free metal ions. The transfer activity coefficients of tetrapropylammonium (Pr_4N^+) and tetrabutylammonium (Bu_4N^+) ions have been reported as follows: $\log {}^{AN}\gamma^{H_2O} = 2.3$,[15] $\log {}^{PC}\gamma^{H_2O} = 3.8$,[16] and $\log {}^{MeOH}\gamma^{H_2O} = 1.50$[15] for Pr_4N^+; $\log {}^{AN}\gamma^{H_2O} = 5.8$,[12] $\log {}^{PC}\gamma^{H_2O} = 5.5$,[16] and $\log {}^{MeOH}\gamma^{H_2O} = 3.8$[12] for Bu_4N^+. The high lipophilicity of the tetraalkylammonium ions is explained in terms of hydrophobic hydration in water, the effect of which becomes greater with increasing size of the tetraalkylammonium ion.[12,15] The molar volumes of 16C5, DM16C5, and L16C5 in liquids at 25 °C, which were determined from the density measurements in this study, are 214.5 ± 0.1, 250.4 ± 0.2, and 311.5 ± 0.2 $cm^3\ mol^{-1}$, respectively; the intrinsic molar volumes of Na^+, K^+, Pr_4N^+, and Bu_4N^+ are 2.37, 5.93, 233, and 304 $cm^3\ mol^{-1}$,[17] respectively. It can be seen from the volume data that the complexes of these crown ethers with Na^+ and K^+ are comparable in size to Pr_4N^+ or Bu_4N^+. It follows from the above discussion that the Na^+ and K^+ complexes undergo hydrophobic hydration.

A comparison of the metal-ion dependence of $\log {}^{s}\gamma^{H_2O}(ML^+)$ with that of $\log {}^{s}\gamma^{H_2O}(M^+)$ provides information about the differences in the dehydration efficiency upon complexation among the metal ions. When s = AN and PC, the log ${}^{s}\gamma^{H_2O}(ML^+)$ values for 16C5 and L16C5 are larger for Na^+ than for K^+, whereas the reverse is true for the log ${}^{s}\gamma^{H_2O}(M^+)$ value. This indicates that the dehydration upon complexation is more effective for Na^+ than for K^+. In other cases (s = AN, PC, and MeOH and L = DM16C5; s = MeOH and L = 16C5, DM16C5, and L16C5), the log ${}^{s}\gamma^{H_2O}(ML^+)$ value for a given crown ether varies with the alkali metal ion in the same order of the log ${}^{s}\gamma^{H_2O}(M^+)$ value, i.e., $K^+ > Na^+ >> Li^+$ for s = AN and PC, and $Na^+ > K^+$ for s = MeOH; however, the difference in log ${}^{s}\gamma^{H_2O}(ML^+)$ between Li^+ and Na^+ is larger than that in the corresponding difference in log ${}^{s}\gamma^{H_2O}(M^+)$; the difference in log ${}^{s}\gamma^{H_2O}(ML^+)$ between Na^+ and K^+ is smaller than the corresponding difference in log ${}^{s}\gamma^{H_2O}(M^+)$ when s = AN and PC, and larger when s = MeOH. These results are in accord with the idea that, for all the ligands, the dehydration upon complexation is most drastic when $M^+ = Na^+$. This is presumably because Na^+ fits more closely into the 16C5 cavity (diameter 1.8 Å[18]) than Li^+ and K^+.

A comparison of the ligand dependence of log ${}^{s}\gamma^{H_2O}(ML^+)$ with that of log ${}^{s}\gamma^{H_2O}(L)$ provides information about the differences in the dehydration efficiency upon complexation among the ligands. For a given s, the log ${}^{s}\gamma^{H_2O}(KL^+)$ value is larger for DM16C5 than for 16C5, as is the log ${}^{s}\gamma^{H_2O}(L)$ value. This is attributed largely to the lipophilicity of the methyl groups, themselves, because the difference in log ${}^{s}\gamma^{H_2O}(KL^+)$ between DM16C5 and 16C5 is nearly equal to that in log ${}^{s}\gamma^{H_2O}(L)$. The log ${}^{s}\gamma^{H_2O}(LiL^+)$ value is also larger for DM16C5 than for 16C5, but the difference in log ${}^{s}\gamma^{H_2O}(LiL^+)$ between DM16C5 and 16C5 is smaller than the corresponding difference in log ${}^{s}\gamma^{H_2O}(L)$. The same is true for the log ${}^{MeOH}\gamma^{H_2O}(NaL^+)$ value. When s = AN and PC, the log ${}^{s}\gamma^{H_2O}(NaL^+)$ value of DM16C5 is comparable to, or smaller than, that of 16C5. Therefore, the hydration of the metal ion (Li^+ or Na^+) and the ether oxygens are more greatly decreased upon complexation of the metal ion with 16C5 than with DM16C5; such a trend is more obvious when $M^+ = Na^+$. Among the alkali metal ions, Li^+ is the second closest in size to the 16C5 cavity after Na^+. It appears that the more closely the alkali metal ion fits into the cavity, the more the methyl groups of DM16C5 hinder the dehydration of the metal ion and the ether oxygen atoms upon complexation.

The log ${}^{s}\gamma^{H_2O}(KL^+)$ value is always larger for DM16C5 than for L16C5, as is the log ${}^{s}\gamma^{H_2O}(L)$ value; the difference in log ${}^{s}\gamma^{H_2O}(KL^+)$ between DM16C5 and L16C5 is larger than the corresponding difference in log ${}^{s}\gamma^{H_2O}(L)$. The log ${}^{s}\gamma^{H_2O}(NaL^+)$ value, however, is smaller for DM16C5 than for L16C5 when s = AN and PC; although the log ${}^{MeOH}\gamma^{H_2O}(NaL^+)$ value is larger for DM16C5 than for L16C5, the difference in log ${}^{s}\gamma^{H_2O}(NaL^+)$ between DM16C5 and L16C5 is smaller than the corresponding difference in log ${}^{s}\gamma^{H_2O}(L)$. The above results indicate that the dehydration of the metal ion and the ether oxygens on complexation is greater for L16C5 than for DM16C5 when $M^+ = Na^+$, whereas the reverse holds for $M^+ = K^+$. This supports the previous suggestion that only the size-fitting cation accommodated in the cavity undergoes further ligation by the electron-donating side arm.[5]

Stability Constants in Water. The K_{ML} values in water of DM16C5 for the monovalent and divalent metal ions decrease in the orders $Li^+ > Ag^+ > Na^+ > Tl^+ > K^+$ and $Sr^{2+} \geq Ba^{2+} > Pb^{2+}$, respectively. These selectivity orders are almost the same as those of 16C5 and L16C5, except that the order for Li^+ and Ag^+ of DM16C5 is the reverse of that of 16C5.

We discuss the complexation selectivity in water of the 16C5 series for the alkali metal ions by breaking down the aqueous complexation into the following steps: (1) transfer of the metal ion from water to the gas phase (dehydration of the metal ion); (2) transfer of the crown ether from water to the gas phase (dehydration of the crown ether); (3) complexation in the gas phase; (4) transfer of the metal ion-crown ether complex from the gas phase into water (hydration of the complex). Steps (1), (3), and (4) are related to the metal-ion selectivity in water of the crown ether. At this stage, the selectivity in the gas phase of the 16C5 series is unknown. The standard Gibbs free energies of hydration[19] indicate that the strength of hydration of the alkali metal ions decreases in the order $Li^+ > Na^+ > K^+$. As described in the foregoing section, the metal ion and the ether oxygen atoms are most greatly dehydrated upon complexation when $M^+ = Na^+$. Therefore, it is expected that the hydrophilicity of Na^+ relative to that of K^+ is reduced by complexation, and that the combined contribution of steps (1) and (4) is negative to the selectivity in water for Na^+ over K^+; thus the selectivity order in the gas phase should be $Na^+ > K^+$ and govern that in water. The hydrophilicity of Li^+ relative to that of Na^+ is expected to be enhanced by complexation; the much stronger hydration of the Li^+ complex compared with the Na^+ one contributes to the higher stability of the former in water.

Although the introduction of the two methyl groups to 16C5 has no significant effect on the complex stability for Li^+ and Pb^{2+}, it obviously reduces the complex stability for the other metal ions. As a result, on going from 16C5 to DM16C5, the selectivity for Li^+ over the other monovalent metal ions is increased, but that for Sr^{2+} and Ba^{2+} over Pb^{2+} is decreased. On the whole, the complex stability is higher for L16C5 than for DM16C5; the positive effect of the electron-donating side arm is larger for Sr^{2+} and Ba^{2+} than for Pb^{2+}, resulting in the higher selectivity of L16C5 for Sr^{2+} and Ba^{2+} over Pb^{2+} compared with DM16C5. The substituent effects are generally larger for the divalent metal ions than for the monovalent ones.

The stability of a given DM16C5-alkali metal ion complex is much lower in water than in AN, PC, and MeOH. The same tendency is observed for the 16C5 and L16C5 complexes. The difference in log K_{ML} between a nonaqueous solvent s and water is expressed by the following equation derived from Eq. 1:

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

The much lower stability of the complex in water than in s ($\log K_{ML,s} - \log K_{ML,H_2O} >> 0$) is explained by the much larger log ${}^{s}\gamma^{H_2O}(ML^+)$ value than the sum of the log ${}^{s}\gamma^{H_2O}(M^+)$ and log ${}^{s}\gamma^{H_2O}(L)$ values, namely, the stronger solvation of the metal ion in water than in s, the hydrogen bonding of water to the ether oxygen atoms, and the dehydration of them on complexation in water.

In the nonaqueous solvents studied, the 16C5 series forms the most stable complex with Na^+ of all the alkali metal ions (Li^+–Cs^+).[5,7,8] On changing from the nonaqueous solvents to water, the selectivity for Li^+ and Na^+ is reversed, and the selectivity for Na^+ over K^+ is greatly decreased. The variations in the selectivity with the solvent come from the fact that, for a given crown ether, the $\log K_{\mathrm{ML,s}} - \log K_{\mathrm{ML,H_2O}}$ value is largest for Na^+. From Eq. 2, this is attributed to the largest $\log {}^{\mathrm{s}}\gamma^{\mathrm{H_2O}}(\mathrm{ML}^+) - \log {}^{\mathrm{s}}\gamma^{\mathrm{H_2O}}(\mathrm{M}^+)$ value for Na^+, namely, the most drastic dehydration upon complexation occurring for the size-fitting cation.

In the nonaqueous solvents, the negative effect of the methyl groups and the positive one of the electron-donating side arm on the complex stability are largest for Na^+ of all the alkali metal ions.[8] For Na^+, both of the effects are generally larger in the nonaqueous solvents than in water, which arises from the fact that the $\log K_{\mathrm{NaL,s}} - \log K_{\mathrm{NaL,H_2O}}$ value is smallest for DM16C5 of the three crown ethers. This is attributed to the smallest $\log {}^{\mathrm{s}}\gamma^{\mathrm{H_2O}}(\mathrm{NaL}^+) - \log {}^{\mathrm{s}}\gamma^{\mathrm{H_2O}}(\mathrm{L})$ value for DM16C5, namely, the lowest dehydration effect of the dimethyl analogue in complexation with Na^+.

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