Stabilities in Water and Transfer Activity Coefficients from Water to Nonaqueous Solvents of 15-Crown-5– and 16-Crown-5–Metal Ion Complexes

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Abstract. Stability constants of $1:1$ 16-crown-5 (16C5)–metal ion complexes were determined in water at 25°C by conductometry and potentiometry with ion-selective electrodes. The selectivity sequences of 16C5 in water for univalent and bivalent metal ions are $Ag^+ > Na^+ \geq Tl^+ > K^+$ and $Sr^{2+} > Ba^{2+} \gg Pb^{2+}$, respectively. The stability of a given 16C5–metal ion complex in water is much lower than might be expected on the basis of the solvation power (i.e. relative solubility of the metal ion) of water for the metal ion. The same tendency is observed for the cases of 15-crown-5 (15C5)–metal ion complexes. Transfer activity coefficients (γ) of 15C5 and 16C5 for tetradecane (TD)/water, TD/methanol, TD/acetonitrile, and propylene carbonate/water systems were determined at 25°C. From these data, contributions of a methylene group and an ether oxygen atom to the $\log \gamma$ value of a crown ether were then obtained. The γ values from water to acetonitrile, propylene carbonate, and methanol of 15C5– and 16C5–univalent metal ion complexes ($^s\gamma^{H_2O}(ML^+)$) were calculated, s, M^+, and L being a solvent, a univalent metal ion, and a crown ether, respectively. The $\log {}^s\gamma^{H_2O}(ML^+)$ value is greater than the corresponding $\log {}^s\gamma^{H_2O}(L)$ value. The $\log {}^s\gamma^{H_2O}(M^+)$ values are negative. This indicates that, although the M^+ ions are more soluble in water than in the nonaqueous solvents, when the crown ether forms a complex with the M^+ ion, the complex becomes more soluble in the nonaqueous solvents than in water, compared with the free crown ether. It was concluded from this finding that the unexpectedly low stability of the crown ether–M^+ complex in water is attributed to strong hydrogen bonding between ether oxygen atoms of the free crown ether and water.

Key words. Stability constant, transfer activity coefficient, 15-crown-5, 16-crown-5, metal ions, complexes, water, nonaqueous solvents.

1. Introduction

Both 15-crown-5 (15C5) and 16-crown-5 (16C5) have five donor ether oxygen atoms and have the most suitable cavity sizes for Na^+ of all the alkali metal ions. But, the structure of 15C5 is symmetric, whereas that of 16C5 is less symmetric because of the introduction of an extra methylene group into the 15C5 ring. Examination of CPK molecular models shows that Na^+ is better accommodated in the 16C5 cavity, and the donor ether oxygen atoms of 16C5 arrange more neatly around Na^+, compared with 15C5. Stabilities and solvation behavior of 15C5– and 16C5–metal ion complexes in nonaqueous solvents have been systematically studied by conductometry [1, 2]. In addition, the role of 15C5 and 16C5 in the metal ion extraction process have been clarified from the standpoint of equilibrium [3, 4]. In general, the selectivities of 15C5 and 16C5 for alkali metal ions show a correlation

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between size and fit in both homogeneous and solvent extraction systems. For the homogeneous system, the donor number of the solvent is a dominant factor governing the stability of the of 15C5– or 16C5–alkali metal ion complex; there is no relationship between the stability of the crown ether–alkali metal ion complex and the dielectric constant of the solvent. For the extraction system, the ion-pair extraction constant of 15C5 or 16C5 varies with a cation of the same charge held in the cavity (anion = picrate ion); namely, the crown ethers cannot effectively shield the cation.

The principal objects of this study are to obtain the contributions of a methylene group and an ether oxygen atom to a transfer activity coefficient of a crown ether and to clarify the factors responsible for the unexpectedly low stability of a crown ether–metal ion complex in water. Generally, the contribution of a methylene group to a partition constant of an organic compound has been determined from the slope of a straight line given by plots of ion-pair extraction constants of the tetraalkylammonium salt (or a cationic alkanesulfonate dye) against the number of carbon atoms of the tetraalkylammonium ion (or the alkanesulfonate ion). However, the overall ion-pair extraction process comprises one or two ionic reaction processes, for example an ion-association process of the cation with the anion in water. Consequently, 15C5 and 16C5 were chosen because they are electrically neutral and, moreover, 16C5 has an extra methylene group compared with 15C5. Scarcely any data on the stabilities of 16C5–metal ion complexes in water have been reported. In the present study, transfer activity coefficients of 15C5 and 16C5, and formation constants in water and transfer activitiy coefficients of 15C5– and 16C5–metal ion complexes are determined at 25°C. Effects on the stabilities in water and properties of the solute–solvent interaction of the crown ether complexes are discussed.

2. Experimental

2.1. MATERIALS

15-Crown-5 (Nisso Co., Ltd.) was purified by distillation under vacuum (bp. 129–131°C, 3 mmHg (1 mmHg ≃ 133.322 Pa)). The preparation of 16C5 was performed according to a reported procedure [5]. Extremely pure NaCl, KCl, RbCl, CsCl, $Sr(NO_3)_2$, $Ba(NO_3)_2$, and analytical grade $TINO_3$ were purchased from Merck Japan Ltd. They were used as received. Analytical grade $AgNO_3$, $Pb(NO_3)_2$, NaOH, and picric acid were obtained from Wako Pure Chemicals Ltd. The purities of $AgNO_3$ and $Pb(NO_3)_2$ were determined by KCl and EDTA titration, respectively. The concentrations of solutions of NaOH and picric acid were determined by neutralization titration.

Reagent grade propylene carbonate (PC) and analytical grade acetonitrile (AN), methanol, and $CHCl_3$ were Wako Pure Chemicals Ltd. products. The method of purification of AN [6], PC [1], and methanol [7] was as previously described. Chloroform was distilled once at atmospheric pressure. The middle 70% of the distillate of the solvents was used. Analytical grade tetradecane (TD) from Wako Pure Chemicals Ltd. was used without further purification. The conductivity of water was less than $3 \times 10^{-7} \, \Omega^{-1} \, cm^{-1}$.

2.2. APPARATUS AND PROCEDURE FOR CONDUCTOMETRY AND POTENTIOMETRY

The conductance measurements were performed with a Fuso conductivity apparatus (Model 362B) at $25 \pm 0.005°C$. Two cells were used, with cell constants of 0.09032 and $0.08137 \, cm^{-1}$. The experimental procedure to obtain the formation constants of the 16C5–Tl$^+$, Sr^{2+}, and Ba^{2+} complexes in water was almost the same as that described in a previous paper [1].

The emf measurements were conducted at $25 \pm 0.05°C$ with a Denki Kagaku Keiki ion meter apparatus (Model IOC-10) which permits readings to within 0.1 mV. For Na$^+$ and K$^+$, a Horiba 1512A-06T Na$^+$-selective electrode and a Toko Kagaku 1200 K$^+$-selective electrode were used, respectively. The Denki Kagaku Keiki 7080 Ag$^+$-selective electrode and the 7180 Pb^{2+}-selective electrode were used for Ag$^+$ and Pb^{2+}, respectively. Horiba 2535A-06T (Ag|AgCl electrode) and Denki Kagaku Keiki 4083 (Ag|AgCl electrode) were used as references for Na$^+$, K$^+$ measurements, and for Ag$^+$, Pb^{2+} measurements, respectively. Experiments for obtaining the formation constants of 16C5–Na$^+$, K$^+$, Ag$^+$, and Pb^{2+} complexes in water were carried out according to the method of Frensdorff [8].
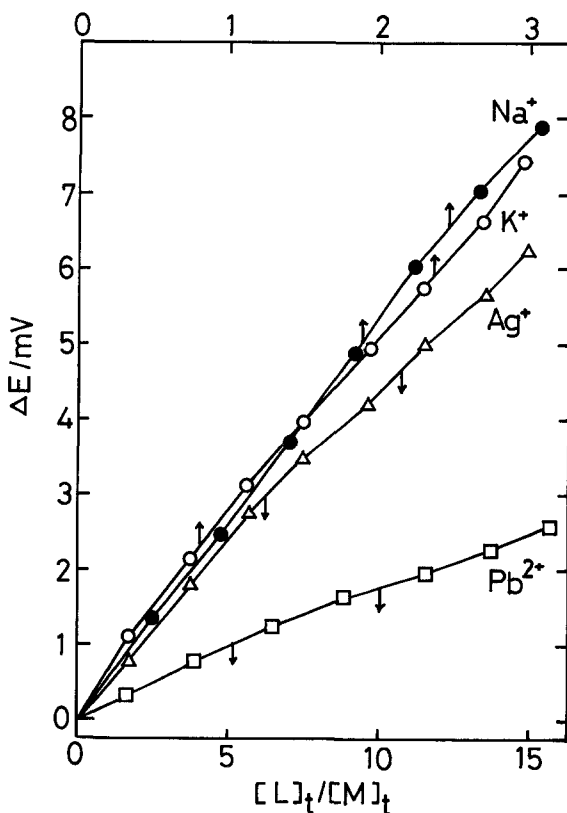

Fig. 1. Potentiometric titration curves for 16C5–NaCl, KCl, AgNO$_3$, and Pb(NO$_3$)$_2$ systems in H$_2$O at 25°C. [Na]$_t$ = 8.0×10^{-3} M. [K]$_t$ = 8.0×10^{-3} M. [Ag]$_t$ = 8.0×10^{-4} M. [Pb]$_t$ = 8.0×10^{-4} M.

Potentiometric titration curves for the 16C5–Na^+, K^+, Ag^+, and Pb^{2+} systems are shown in Figure 1. Here, ΔE is the difference in the emf between the metal salt solution and that containing 16C5; $[L]_t$ and $[M]_t$ denote total concentrations of 16C5 and the metal salt, respectively.

2.3. DISTRIBUTION COEFFICIENTS OF 15C5 AND 16C5

For the PC/water system, a 6 mL aqueous solution of the crown ether (1.5×10^{-5}–6.1×10^{-4}M: 1M = 1 mol dm^{-3}) and an equal volume of PC in a stoppered glass tube (volume 30 mL) were shaken in a thermostated water bath at $25 \pm 0.2°C$ for 2 h and centrifuged. A 5 mL portion of the aqueous phase, a 7 mL portion of an aqueous solution (pH 10.6–11.4) containing NaOH (1.1×10^{-1}M) and picric acid (1.0×10^{-1}M), and 12 mL CHCl$_3$ were placed in a stoppered glass tube (No. 1), agitated for 2 h at 0°C, and centrifuged. In order to complete the complexation with Na^+ of uncomplexed crown ether in the CHCl$_3$ phase in the No. 1 stoppered glass tube, a 6 mL portion of the CHCl$_3$ phase and an equal volume of an aqueous solution (pH 10.6–11.4) containing NaOH (1.1×10^{-1}M) and picric acid (1.0×10^{-1}M) were placed in a stoppered glass tube, agitated for 2 h at 0°C, and centrifuged. The picrate in the CHCl$_3$ phase was back-extracted into 0.01M NaOH aqueous solution and the picrate concentration was determined. No increased picrate extraction into the CHCl$_3$ phase was observed. A $(12 - 2n)$ mL portion of the aqueous phase in the stoppered glass tube (No. n) and an equal volume of CHCl$_3$ were placed in a stoppered glass tube (No. $(n + 1)$), shaken for 2 h at 0°C, and centrifuged. This procedure was repeated until $n = 2$ (or 3). The picrate in the CHCl$_3$ phase in the stoppered glass tube (No. n) was back-extracted into $(12 - 2n)$ mL of 0.01M NaOH aqueous solution (volume ratio 1 : 1), and the picrate concentration was determined spectrophotometrically ($\lambda_{max} = 356$ nm, $\varepsilon = 1.45 \times 10^4$ cm^{-1} M^{-1}). This procedure was repeated until $n = 3$ (or 4). The concentration of the crown ether which distributed itself into the 6 mL aqueous phase was calculated from the total concentration of the extracted crown ether–sodium picrate complex in a series of these extractions. The distribution coefficient values ($[L]_{s_1}/[L]_{s_2}$: see below) of 15C5 and 16C5 are given in Table I.

For the TD/water, TD/methanol, and TD/AN systems, a 7 mL aqueous, methanol, or acetonitrile solution of the crown ether (2.6×10^{-4}–5.8×10^{-2}M) and an equal volume of tetradecane in a stoppered glass tube were shaken in the thermostated water bath at $25 \pm 0.2°C$ for 2 h and centrifuged. A 6 mL portion of

Table I. Distribution constants of 15C5 and 16C5 at 25°C

System	15C5	16C5
TD^a/H$_2$O	$(2.2 \pm 0.1) \times 10^{-3}$	$(8.7 \pm 0.4) \times 10^{-3}$
TD^a/CH$_3$OH	$(4.33 \pm 0.06) \times 10^{-2}$	$(6.6 \pm 0.1) \times 10^{-2}$
TD^a/AN	$(2.1 \pm 0.1) \times 10^{-2}$	$(3.8 \pm 0.1) \times 10^{-2}$
PC/H$_2$O	0.59 ± 0.05	0.78 ± 0.04

^{a} TD denotes tetradecane. Each distribution constant value is the average of 9–15 measurements. The uncertainties are the standard deviations.

the TD phase and an equal volume of water were placed in a stoppered glass tube, agitated for 2 h at 25°C, and centrifuged. A 5 mL portion of the aqueous phase, a 7 mL portion of an aqueous solution (pH 10.6–11.4) containing NaOH (1.1×10^{-1}M) and picric acid (1.0×10^{-1}M), and 12 mL CHCl$_3$ were placed in a stoppered glass tube (No. 1), agitated for 2 h at 0°C, and centrifuged. The following procedure was almost the same as that described in the preceding section for the PC/water system. The extraction procedure and back-extraction procedure for the crown ether–sodium picrate complex were repeated until $n = 2$ and 3, respectively. The distribution coefficient values of 15C5 and 16C5 are listed in Table I.

3. Results

The analysis of the potentiometric data for obtaining the formation constants (K_{ML}) of 16C5 complexes with Na$^+$, K$^+$, Ag$^+$, and Pb^{2+} was the same as that described by Frensdorff [8] ($K_{ML} = [ML^{m+}]/[M^{m+}][L]$, M^{m+} being a metal ion). The analysis of the conductometric data for obtaining K_{ML} values of 16C5 complexes with Tl$^+$, Sr^{2+}, and Ba^{2+} was the same as that described elsewhere [1]. In this study, it is assumed that the association between a cation and an anion is negligible and that 16C5 forms a 1 : 1 complex with a metal ion. The log K_{ML} values are summarized in Table II.

Molar conductivity (Λ) vs. [L]$_t$/[M]$_t$ plots for the 16C5–Tl$^+$, Sr^{2+}, and Ba^{2+} systems are given in Figure 2. For the 16C5–RbCl and CsCl systems, there is a negligible change in Λ despite an increase in the 16C5 concentration. Consequently, the K_{ML} values could not be determined. This is attributed to either the unstable complex or nearly equal mobilities of the complex and the corresponding metal ion.
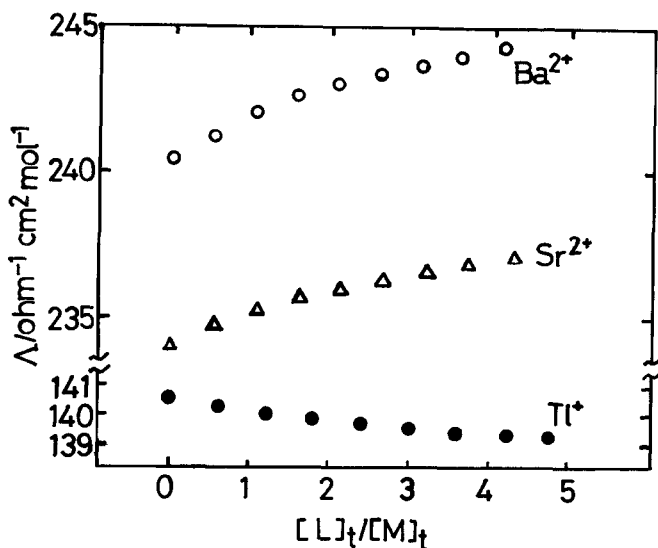

Fig. 2. Λ vs. [L]$_t$/[M]$_t$ curves for 16C5–TlNO$_3$, Sr(NO$_3$)$_2$, and Ba(NO$_3$)$_2$ systems in H$_2$O at 25°C. [Tl]$_t$ = (9.3–9.7) $\times$ 10^{-3} M. [Sr]$_t$ = 3.0 $\times$ 10^{-3} M. [Ba]$_t$ = 3.0 $\times$ 10^{-3} M.

Table II. Log(K_{ML}/mol^{-1} dm^3) values at 25°C

Metal ion	Ionic radius (Å)[a]	H$_2$O		AN [2]		PC		CH$_3$OH	
		16C5	15C5 [9]	16C5	15C5	16C5 [2]	15C5	16C5 [2]	15C5
Na$^+$	1.02	0.78 ± 0.04[b]	0.70	5.3_9	5.3_8	5.7	3.7 [2]	4.10	3.28[d]
K$^+$	1.38	0.40 ± 0.08[b]	0.74	3.5_7	3.9_8	3.3_4	3.4_1 [2]	2.9_2	3.3 [2]
Rb$^+$	1.49	–	0.62	2.9_4	3.4_2	2.5_9	3.0_4 [2]	2.4_6	2.7_2 [2]
Cs$^+$	1.70	–	0.8	2.3_8	3.1_4	2.1_7	2.6_9 [2]	2.0_9	2.6_6 [2]
Ag$^+$	1.15	1.10 ± 0.03[b]	0.94	–	–	–	5.67 [10]	–	3.62 [12]
Tl$^+$	1.50	0.73 ± 0.05[c]	1.23	–	–	–	5.29 [11]	–	–
Sr^{2+}	1.13	2.08 ± 0.06[c]	1.95	–	–	–	–	–	2.63 [12]
Ba^{2+}	1.36	1.84 ± 0.05[c]	1.71	–	–	–	–	–	–
Pb^{2+}	1.19	0.74 ± 0.04[b]	1.85	–	–	–	–	–	–

Each log K_{ML} value of 16C5 in water is the average of 6–8 measurements. The uncertainties are the standard deviations.

[a] R. D. Shannon and C. T. Prewitt: *Acta Crystallogr., Sect. B*, **25**, 925 (1969).

[b] This study, ion selective electrode. Errors were minimized by extending titration runs to large excess of 16C5. When ΔE was small, the log K_{ML} value was determined by the curve-fitting method.

[c] This study, conductometry.

[d] The average of literature values (3.48 [12], 3.30 [13], 3.14 [14], 3.25 [15], 3.24 [16], 3.27 [17], 3.31 [18]).

For the Tl^+ system, the Λ vs. $[L]_t/[M]_t$ plot shows a decrease in Λ with an increase in $[L]_t$, and the reverse is true for the Sr^{2+} and Ba^{2+} systems. In the case of Tl^+, the 16C5 complex is less mobile than the uncomplexed cation, whereas the reverse holds for the cases of Sr^{2+} and Ba^{2+}. This is attributable to the much stronger hydration of the bivalent cation compared with the monovalent cation. It follows from this finding that dehydration of the free metal ion occurs upon complexation. Values of $[Sr]_t$ and $[Ba]_t$ are nearly equal and the Λ value of the Ba system at the point of large $[L]_t/[M]_t$ value is larger than that of the Sr system (Figure 2). This reflects the difference between the interaction with water of Sr^{2+} in the 16C5 complex and that of Ba^{2+} in the 16C5 complex.

4. Discussion

4.1. STABILITY OF CROWN ETHER COMPLEXES

Table II shows that the selectivity sequences of 16C5 in water for univalent and bivalent metal ions are $Ag^+ > Na^+ \geq Tl^+ > K^+$ and $Sr^{2+} > Ba^{2+} \gg Pb^{2+}$, respectively. From 15C5 to 16C5, the selectivity of the crown ether for Na^+ over K^+ is enhanced. This is due to the lower stability of the $16C5-K^+$ complex compared with the $15C5-K^+$ complex. The selectivity sequence of 16C5 for Ag^+ and Tl^+ is the reverse of that of 15C5. Except for Pb^{2+}, the selectivity sequence of 16C5 for the bivalent metal ions in water is identical with that of 15C5. The stability of the $16C5-Pb^{2+}$ complex is much lower than expectations based on stabilities of the other 16C5– and $15C5-M^{2+}$ complexes. The ionic size of Pb^{2+} is nearly equal to that of Sr^{2+}. The Gibbs free energy of hydration $(\Delta G_h^0/kJ\,mol^{-1})$ of Pb^{2+} $(-1497\,kJ\,mol^{-1}$ [19]) and Sr^{2+} $(-1447\,kJ\,mol^{-1}$ [19]) are almost the same. But 16C5 forms a much more stable complex with Sr^{2+} in water than it does with Pb^{2+}, whereas the stabilities of the $15C5-Sr^{2+}$ and $-Pb^{2+}$ complexes are much the same.

The 16C5 complex in water is slightly more stable for Na^+, Ag^+, Sr^{2+}, or Ba^{2+} and less stable for K^+, Tl^+, or Pb^{2+} than the corresponding 15C5 complex. It has been reported, on the basis of an examination of CPK molecular models, that Na^+ is more suited to the size of the 16C5 cavity (0.9 Å) than the 15C5 cavity (0.85 Å), and the donor oxygen atoms of 16C5 are more closely arranged around Na^+ in comparison with 15C5; however, the lower symmetry of 16C5 causes a more unfavorable orientation of the donor oxygen atoms for the less well fitting cations Li^+, K^+, Rb^+, and Cs^+ [2]. Ag^+ is nearly equal to Na^+ in ionic size. Tl^+ and Ba^{2+} are less well fitting cations. Sr^{2+} and Pb^{2+} have sizes more suitable for the 16C5 cavity than the 15C5 cavity. Thus, this explanation holds for the stability tendency for the 16C5– and $15C5-M^+$ complexes in water, but does not always hold for the cases of M^{2+}. The unexpected behavior of the Ba^{2+} and Pb^{2+} complexes cannot be explained at the present time.

The difference in the log K_{ML} values in water between Ba^{2+} and K^+ is increased from 15C5 to 16C5. In the case of 15C5, the Ag^+ complex is less stable in water than the Pb^{2+} complex, but the reverse is true for the case of 16C5. Although the ionic sizes of K^+ and Ba^{2+} and those of Ag^+ and Pb^{2+} are almost the same, a remarkable enhancement of selectivity in water for Ba^{2+} and Ag^+ over K^+ and Pb^{2+}, respectively, is caused by an extra methylene group in the 16C5 ring.

Table II shows that the stability of a given 16C5–metal ion complex in water is by far the lowest of all the solvents. The same tendency is observed for the cases of 15C5–metal ion systems. This is attributed to the highest solvation power of water of all the solvents for a metal ion (i.e. the relative solubility of the metal ion), which is derived from the data on transfer activity coefficients of the metal ion [20]. However, the stability of the crown ether–metal ion complex in water is much lower than might be expected on the basis of the solvation power of water for the metal ion. Log K_{ML} values of the 15C5–Na$^+$ complex at 25°C are 1.97 in DMF and 1.31 in DMSO [21]. Although the solvation power of water for Na$^+$ is lower than that of DMF and DMSO [22], the 15C5–Na$^+$ complex is less stable in water (log $K_{ML} = 0.70$) than in DMF and DMSO. Hydrogen bonds between ether oxygen atoms of the crown ether and water are responsible for the much lower stability of the crown ether–metal ion complex in water than in all the other solvents.

4.2. TRANSFER ACTIVITY COEFFICIENTS OF CROWN ETHERS

The transfer activity coefficient ($^{s_1}\gamma^{s_2}(L)$) of a crown ether (L) between solvent s_1 and solvent s_2 is defined as follows:

$$^{s_1}\gamma^{s_2}(L) = [L]_{s_1}/[L]_{s_2}.$$

This is the partition constant of the crown ether.

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 $^{s_1}\gamma^{s_2}(L)$ values of 15C5 and 16C5; namely, $\Pi_{CH_2} = \log ^{s_1}\gamma^{s_2}(16C5) - \log ^{s_1}\gamma^{s_2}(15C5)$ and $\Pi_O = (\log ^{s_1}\gamma^{s_2}(L) - \Pi_{CH_2} \times a) \div b$, where a and b denote the number of methylene groups and ether oxygen atoms, respectively. The contribution of a benzo group ($\Pi_{C_6H_4}$) to log $^{s_1}\gamma^{s_2}(L)$ between s_1 and s_2 at 25°C can be calculated from log $^{s_1}\gamma^{s_2}(L)$ values of benzo– and dibenzo–crown ethers by using the Π_{CH_2} and Π_O values; that is, $\Pi_{C_6H_4} = \{\log ^{s_1}\gamma^{s_2}(L) - \Pi_{CH_2} \times a - \Pi_O \times b\} \div c$, c being the number of benzo groups. The Π_{CH_2}, Π_O, and $\Pi_{C_6H_4}$ values are summarized in Table III, together with experimental log $^{s_1}\gamma^{s_2}(L)$ values of crown ethers at 25°C and those estimated from the empirical parameters. Except for the cases of 18C6, B18C6, and DB21C7 for the PC/H$_2$O system, B18C6 for the AN/H$_2$O system, and DB18C6 for the CH$_3$OH/H$_2$O system, experimental and calculated log $^{s_1}\gamma^{s_2}(L)$ values of a given crown ether are consistent with each other within an error of ± 0.22. The additivity of the contribution of a functional group to the log $^{s_1}\gamma^{s_2}(L)$ value of a crown ether is valid.

The solubility of an ether oxygen atom, a methylene group, and a benzo group increases in the order TD < CH$_3$OH < AN < PC < H$_2$O, H$_2$O < PC < AN < CH$_3$OH < TD, and H$_2$O ≪ PC ≪ CH$_3$OH < AN, respectively. The solubility sequences of the first two for the solvents are completely the reverse of each other. The ether oxygen atom is hydrophilic, whereas methylene and benzo groups are hydrophobic. The benzo group is much more lipophilic than the methylene group. The hydrophilicity of the ether oxygen atom is due to hydrogen bonding between the ether oxygen atom and water. The lower than expected solubility of the ether oxygen atom and the higher than expected solubility of the methylene group in CH$_3$OH cannot be explained at the present stage of our investigation.

Table III. Π_{CH_2}, Π_O, $\Pi_{C_6H_4}$, and $\log {}^{s_1}\gamma^{s_2}(L)$ values at 25°C

	Π_{CH_2}	Π_O[c]	$\Pi_{C_6H_4}$[d]	$\log {}^{s_1}\gamma^{s_2}(L)$							
				15C5		16C5		18C6		B15C5	
				Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
TD[a]/H_2O[b]	0.60	-1.73	—	-2.66	-2.65	-2.06	-2.05	—	—	—	—
TD[a]/CH_3OH[b]	0.18	-0.64	—	-1.364	-1.40	-1.18	-1.22	—	—	—	—
TD[a]/AN[b]	0.26	-0.85	—	-1.68	-1.65	-1.42	-1.39	—	—	—	—
PC[a]/H_2O[b]	0.12	-0.29	1.75	-0.23	-0.25	-0.11	-0.13	-1.32[e,f]	-0.30	1.04[g]	1.26
AN[a]/H_2O[b]	0.34	-0.87	3.00	-0.98	-0.95	-0.64	-0.61	-0.97[e,f]	-1.14	1.24[g]	1.37
CH_3OH[a]/H_2O[b]	0.41	-1.09	2.85	-1.29	-1.35	-0.88	-0.94	-1.66[e]	-1.62	0.56[g]	0.68

	$\log {}^{s_1}\gamma^{s_2}(L)$									
	B18C6		DB18C6		DB21C7		DB24C8		DB30C10	
	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
TD[a]/H_2O[b]	—	—	—	—	—	—	—	—	—	—
TD[a]/CH_3OH[b]	—	—	—	—	—	—	—	—	—	—
TD[a]/AN[b]	—	—	—	—	—	—	—	—	—	—
PC[a]/H_2O[b]	0.41[h]	1.21	2.89[i]	2.72	3.024[f]	2.67	2.72[f,j] 2.715[f]	2.62	2.339[f] 2.367[f,k]	2.52
AN[a]/H_2O[b]	-0.53[h]	1.18	3.50[i]	3.50	3.367[f]	3.31	3.06[f,j] 3.044[f]	3.12	2.896[f] 2.959[f,k]	2.74
CH_3OH[a]/H_2O[b]	0.49[h]	0.41	1.84[i]	2.44	2.036[f]	2.17	1.88[f,j] 1.832[f]	1.90	1.492[f] 1.560[f,k]	1.36

[a] Solvent s_1.

[b] Solvent s_2.

[c] The respective Π_O value is the average of Π_O values calculated from $\log {}^{s_1}\gamma^{s_2}(L)$ values of 15C5 and 16C5.

[d] The respective $\Pi_{C_6H_4}$ value is the average of $\Pi_{C_6H_4}$ values calculated from $\log {}^{s_1}\gamma^{s_2}(L)$ values of benzo- and dibenzo-crown ethers; for the PC/H_2O and AN/H_2O systems, L = B15C5, DB18C6, DB21C7, DB24C8, and DB30C10; for the CH_3OH/H_2O system, L = B15C5, B18C6, DB21C7, DB24C8, and DB30C10.

[e] Ref. [23]. [f] Ref. [24]. [g] Ref. [25]. [h] Ref. [26]. [i] Ref. [27]. [j] Ref. [20]. [j] Ref. [28]. [k] Ref. [28].

4.3. TRANSFER ACTIVITY COEFFICIENTS OF CROWN ETHER–METAL ION COMPLEXES

The logarithm of the transfer activity coefficient of a crown ether–metal ion complex between solvent s_1 and solvent s_2 ($\log {}^{s_1}\gamma^{s_2}(ML^{m+})$ [29]) is calculated as follows:

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

(1)

where ${}^{s_1}\gamma^{s_2}(M^{m+})$ [29] denotes the transfer activity coefficient of a metal ion between solvent s_1 and solvent s_2; $(\log K_{ML})_s$ refers to the $\log K_{ML}$ value in solvent s. A positive $\log {}^{s_1}\gamma^{s_2}(ML^{m+})$ value means that the ML^{m+} complex undergoes stronger solvation in s_1 than in s_2. The reverse holds for the negative $\log {}^{s_1}\gamma^{s_2}(ML^{m+})$ value. The $\log {}^{s}\gamma^{H_2O}(ML^+)$ and $\log {}^{s}\gamma^{H_2O}(M^+)$ values at 25°C are summarized in Table IV.

In each case of 15C5 and 16C5, the $\log {}^{s}\gamma^{H_2O}(ML^+)$ value for a given solvent s varies with the univalent metal ion in the complex. This reflects the difference in interactions with solvents of univalent metal ions in the complexes among the univalent metal ions. Neither 15C5 nor 16C5 can effectively shield the univalent metal ion trapped in the cavity from surrounding solvents. For the AN/H_2O and PC/H_2O systems, the smaller an alkali metal ion, the more soluble it is in water. For the CH_3OH/H_2O system, K^+ and Rb^+ are more soluble in water than in CH_3OH compared with Na^+ and Cs^+. However, except for the 15C5–Na^+ complex in PC, the hydrophobicity of the crown ether–alkali metal ion complex increases from Cs^+ to Na^+. This indicates that the more closely the alkali metal ion fits into the crown ether cavity, the more effectively the crown ether shields the alkali metal ion from water.

The $\log {}^{s}\gamma^{H_2O}(ML^+)$ value is larger than the corresponding $\log {}^{s}\gamma^{H_2O}(M^+)$ value, indicating that when a monovalent metal ion forms a complex with 15C5 or 16C5,

Table IV.   Log ${}^{s}\gamma^{H_2O}(ML^+)$ and log ${}^{s}\gamma^{H_2O}(M^+)$ values at 25°C

s =	AN		PC		CH$_3$OH	
log ${}^{s}\gamma^{H_2O}(M^+)$ [20]						
Na$^+$	-2.3		-2.9_4		-1.4	
K$^+$	-1.3		-1.5_4		-1.7	
Rb$^+$	-1.1		-1.2_2		-1.7	
Cs$^+$	-0.8		-0.9_4		-1.6	
Ag$^+$	3.9		-3.8		-1.2	
Tl$^+$	-1.5		-1.6_5		-0.6	
L =	16C5	15C5	16C5	15C5	16C5	15C5
log ${}^{s}\gamma^{H_2O}(ML^+)$						
Na$^+$	1.7	1.4	1.9	-0.2	1.0	-0.1
K$^+$	1.2	1.0	1.2_9	0.9_0	-0.1	-0.4
Rb$^+$	–	0.7	–	0.9_7	–	-0.9
Cs$^+$	–	0.6	–	0.7	–	-1.0
Ag$^+$	–	–	–	0.7	–	0.2
Tl$^+$	–	–	–	2.1_8	–	–

the complex becomes more soluble in the nonaqueous solvents than in water, compared with the monovalent metal ion. Except for Ag^+ in AN, the M^+ ion is most strongly solvated in H_2O among all the solvents. Thus, both 15C5 and 16C5 effectively screen the M^+ ion in the complex from water, and raise the lipophilicity of the M^+ ion. The difference in the value of $\log{}^s\gamma^{H_2O}(ML^+) - \log{}^s\gamma^{H_2O}(M^+)$ between Na^+ and K^+ is greater for 16C5 than for 15C5. It follows from this that 16C5 more effectively screens Na^+ than K^+ compared with 15C5. Table IV shows that the 16C5–M^+ complex is more lipophilic than the corresponding 15C5–M^+ complex. Except for the cases of Na^+ complexes when $s = PC$ and CH_3OH, the difference in the $\log{}^s\gamma^{H_2O}(ML^+)$ value between 16C5 and 15C5 is roughly equal to the corresponding Π_{CH_2} value. This is attributed only to the lipophilicity of the extra methylene group in the 16C5 ring. In the cases of the Na^+ complexes when $s = PC$ and CH_3OH, the lipophilicity of the extra methylene group and specific solute–solvent interactions of the Na^+ complexes are responsible for the unexpectedly larger lipophilicity of the 16C5–Na^+ complex compared with the 15C5 complex.

The $\log{}^s\gamma^{H_2O}(ML^+)$ value is greater than the corresponding $\log{}^s\gamma^{H_2O}(L)$ value. Although the M^+ ions in Table IV are more soluble in water than in the nonaqueous solvents, when the crown ether forms a complex with the M^+ ion, the complex becomes more soluble in the nonaqueous solvents than in water, compared with the free crown ether. It has been reported that, upon complexation of a crown ether with a M^{m+} ion, hydrogen bonding to the ether oxygen atoms is greatly decreased as a result of ionic M^{m+}—O bonding [23]. It can be concluded that the higher lipophilicity of the crown ether–M^+ complex compared with the uncomplexed crown ether is attributable to an enforcement of the hydrogen-bonded structure of water for the bulky crown ether complex caused by the considerably reduced hydrogen bonding between ether oxygen atoms and water. The above discussion strongly supports the conclusion in the preceding section that the strong hydrogen bonding between the ether oxygen atoms of the free crown ether and water causes the unexpected lowest stability of the crown ether–metal ion complex in water of all the solvents.

From the $\log{}^{CH_3OH}\gamma^s(ML^+)$ values, all the ML^+ complexes are less soluble in CH_3OH than in AN and PC except for the 15C5–Na^+ complex in PC. Except for the 15C5–Na^+ complex, the $\log{}^{PC}\gamma^{AN}(ML^+)$ values vary from -0.1 to 0.2_7. This indicates that the solvation ability of AN for the ML^+ complex is almost the same as that of PC.

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29. $^{s_1}\gamma^{s_2}(X) = [X]_{s_1}/[X]_{s_2}$, X being ML^{m+} or M^{m+}.