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Stability and Solvation of 1:1 Complexes of Dibenzo-21-crown-7 with Alkali Metal Ions in Polar Solvents

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Stability constants of 1:1 complexes of dibenzo-21-crown-7 (DB21C7) with alkali metal ions have been determined at 25 °C in nitromethane, acetonitrile, propylene carbonate, and water by conductometry or capillary electrophoresis. The stability constants in acetonitrile, propylene carbonate, and water vary as $Na^+ \ll K^+ \leq Rb^+ > Cs^+$; this selectivity pattern is the same as that previously reported in methanol. In these solvents, the K^+/Na^+ selectivity of DB21C7 is higher than that of dibenzo-18-crown-6 (DB18C6) and dibenzo-24-crown-8 (DB24C8). The stability constant in nitromethane, which has the weakest solvation power for the metal ions, decreases with increasing ionic size ($Na^+ > K^+ > Rb^+ > Cs^+$), reflecting the gas-phase selectivity governed by the electrostatic interaction between the ether oxygen atoms and the metal ion. The transfer activity coefficients of DB21C7 and its alkali metal ion complexes from nitromethane to the other solvents have been determined to evaluate the solvation of these solutes. It is shown that DB21C7 shields the alkali metal ions effectively from the solvents; the shielding by DB21C7 is generally more effective than by DB18C6 but less effective than by DB24C8.

Introduction

Complexation between a metal ion and a crown ether in a solvent can be considered to consist of the following steps: (i) desolvation of the metal ion; (ii) desolvation of the crown ether; (iii) complexation between the metal ion and the crown ether in the gas phase; and (iv) solvation of the complex. The thermodynamic contribution of each step must be evaluated to understand the factors governing the complexing ability and selectivity of the crown ether. We previously studied the complexation of alkali metal ions with dibenzo-18-crown-6 (DB18C6) and dibenzo-24-crown-8 (DB24C8) through the determination of the complex stability constants and the transfer activity coefficients in several solvents.[1] It was shown from the stability constants in nitromethane having a weak solvation ability for the metal ions that the intrinsic selectivity (i.e., the selectivity in the gas phase) of the crown ethers is $Na^+ > K^+ > Rb^+ > Cs^+$. The selectivities of DB18C6 and DB24C8 for the alkali metal ions in some other polar solvents, which apparently obey the ion/cavity size-fit concept, receive a large contribution from the metal ion solvation. It was also shown that each alkali metal ion is more effectively desolvated and shielded from the solvents by complexation with DB24C8 than with DB18C6.

Dibenzo-21-crown-7 (DB21C7) is intermediate between DB18C6 and DB24C8 in ring size and number of oxygen atoms. The complexation behavior of DB21C7 has not been well characterized so far. In this study, we have determined the stability constants and the transfer activity coefficients of the DB21C7−alkali metal ion complexes in several solvents to further elucidate the relationship of the ring size and oxygen atom number of the crown ether to the stability and solvation of the complexes. The solvents used are nitromethane ($MeNO_2$), acetonitrile (MeCN), propylene carbonate (PC), and water (H_2O). The characteristics of the DB21C7 complexes are discussed by comparing the present results with the published ones for the DB18C6 and DB24C8 complexes. The structures of the crown ethers are shown in Figure 1.

Experimental Section

Chemicals. DB21C7 (Aldrich, 97% purity) was recrystallized from hexane and dried over P_2O_5 in vacuum at room temperature. Alkali metal chlorides (Merck, Suprapur grade) were dried in vacuum at 250 °C. $RbClO_4$ and $CsClO_4$ were prepared by adding a small excess of perchloric acid to aqueous solutions of RbCl and CsCl and recrystallized three times from deionized water; these products and commercially obtained $NaClO_4{\cdot}H_2O$ and $KClO_4$ (Merck, GR grade) were dried in vacuum at 150 °C. $MeNO_2$, MeCN, and PC (Kanto Chemical, GR grade) were dried over 4 Å molecular sieves and distilled twice just before use under atmospheric pressure (MeCN) or reduced pressure ($MeNO_2$, PC); the solvent conductivities were lower than (3×10^{-7}, 5×10^{-8}, and 2×10^{-8}) $S{\cdot}cm^{-1}$ for $MeNO_2$, MeCN, and PC, respectively. Water was distilled and deionized with a Milli-Q system (Millipore). Other reagents were GR grade and used as received.

Procedures. The stability constants in $MeNO_2$, MeCN, and PC were determined by a conductometric titration method. Conductance measurements were carried out with custom-made two-electrode cells (inner volume, 300 cm^3) at (25 ± 0.02) °C under a nitrogen atmosphere; the cell constants were (0.2036, 0.2040, 0.2184, and 0.2196) cm^{-1}. A solution (200 cm^3) of an alkali metal perchlorate {(5.0×10^{-5} to 2.0×10^{-4}) $mol{\cdot}dm^{-3}$ in $MeNO_2$; (5.6×10^{-4} to 1.3×10^{-3}) $mol{\cdot}dm^{-3}$ in MeCN and PC} was placed in the cell, and the resistance was measured with a conductance bridge (Fuso HECS-362B). A known volume of a DB21C7 solution {(1.8×10^{-4} to 1.7×10^{-3}) $mol{\cdot}dm^{-3}$ in $MeNO_2$ and (5.2 to 9.4) $\times 10^{-3}$ $mol{\cdot}dm^{-3}$ in MeCN and PC} was added stepwise to the cell, and the resistance was mea-

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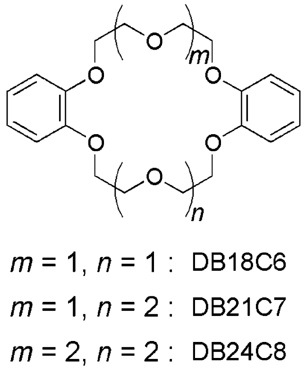

Figure 1. Structural formulas of the dibenzo crown ethers.

sured after each addition. The total volume of the crown ether solution added did not exceed 95 cm^3. The water content of the solution after the run was checked by Karl Fischer titration: <0.07% by mass for MeCN and <0.02% by mass for $MeNO_2$ and PC.

The stability constants in H_2O, which could not be determined by conductometry because of the low aqueous solubility of DB21C7, were determined by a capillary electrophoresis method. Electrophoresis was performed in a fused-silica capillary tube (620 mm total length, 500 mm from the anodic end to the detection section, 50 μm i.d., 375 μm o.d.) at (25 ± 0.1) °C; the instruments were the same as previously described.[2] The running aqueous solution containing an alkali metal chloride {(0.085 to 0.10) $mol \cdot dm^{-3}$ for NaCl; (2.2 to 5.0) $\times 10^{-2}$ $mol \cdot dm^{-3}$ for KCl, RbCl, and CsCl} was buffered at pH 6.7 to 6.9 with MH_2PO_4 and M_2HPO_4 (2.5×10^{-3} $mol \cdot dm^{-3}$ for each) when M = Na and K and with MOH (7.3×10^{-3} $mol \cdot dm^{-3}$) and H_3PO_4 (5.0×10^{-3} $mol \cdot dm^{-3}$) when M = Rb and Cs. A sample solution (ca. 4×10^{-5} cm^3), which was the same in electrolyte composition as the running solution but contained DB21C7 (1×10^{-5} $mol \cdot dm^{-3}$) and benzene (5×10^{-4} $mol \cdot dm^{-3}$), was injected from the anodic end of the capillary by siphoning with a 5 cm height difference for 20 s. A voltage of 8.0 kV or 10.0 kV was applied {current: (12 to 30) μA}, and the crown ether and benzene were detected by UV absorption at 200 nm to determine the mobilities.

To obtain the transfer activity coefficients of DB21C7, its solubility in $MeNO_2$ was measured in the following manner. A suspension of DB21C7 in the solvent was stirred at (25 ± 0.2) °C for (3 to 7) days. After centrifugation, a portion of the supernatant solution was transferred into a beaker and evaporated to dryness under reduced pressure. The residue was redissolved in MeCN, and the DB21C7 concentration was determined spectrophotometrically (λ_{max} = 275.5 nm, $\epsilon = 5.29 \times 10^3$ $mol^{-1} \cdot dm^3 \cdot cm^{-1}$). It was confirmed that the solubility was independent of the stirring time.

Results

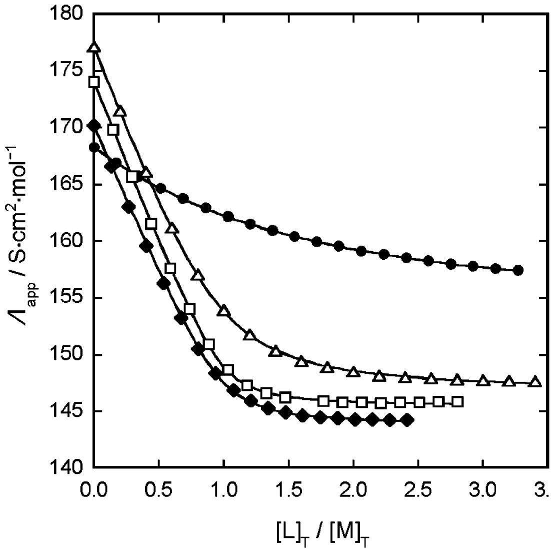

Figure 2. Conductometric titration curves for DB21C7−alkali metal perchlorate systems in MeCN at 25 °C. Metal salts: ●, $NaClO_4$ (9.8×10^{-4} $mol \cdot dm^{-3}$); ♦, $KClO_4$ (9.7×10^{-4} $mol \cdot dm^{-3}$); □, $RbClO_4$ (1.0×10^{-3} $mol \cdot dm^{-3}$); △, $CsClO_4$ (8.3×10^{-4} $mol \cdot dm^{-3}$). The values in parentheses are the initial concentrations of the salts.

Determination of Stability Constants in Nonaqueous Solvents. The apparent molar conductivity (Λ_{app}) of each alkali metal salt (MA; M^+ = alkali metal ion, A^- = counteranion) in the nonaqueous solvent containing the crown ether (L) was obtained as a function of $[L]_T/[M]_T$, where $[L]_T$ and $[M]_T$ are the total concentrations of L and MA, respectively. Examples of the Λ_{app} versus $[L]_T/[M]_T$ plots in MeCN are shown in Figure 2. The Λ_{app} value always decreases with an increase of $[L]_T/[M]_T$, showing that the alkali metal ions become less mobile upon complexation with DB21C7. For the $NaClO_4$, $KClO_4$, and $RbClO_4$ systems, the slope of each curve changes sharply at $[L]_T/[M]_T = 1$; this is proof that a stable 1:1 complex (ML^+) is formed. Such a sharp change of the slope is not observed for the $CsClO_4$ system, owing to the relatively low stability of the $Cs(DB21C7)^+$ complex. When the metal ion and the crown ether form only a 1:1 complex and the cation−anion association is negligible, the Λ_{app} value is expressed as[1]

$$\Lambda_{app} = \frac{\Lambda_{MLA} - \Lambda_{MA}}{2[M]_T}\Big\{([M]_T + [L]_T + K_{ML}^{-1}) - \sqrt{([M]_T + [L]_T + K_{ML}^{-1})^2 - 4[L]_T[M]_T}\Big\} + \Lambda_{MA} \quad (1)$$

where Λ_{MA} and Λ_{MLA} are the molar conductivities of MA and MLA, respectively. $[M]_T$ and $[L]_T$ can be expressed as $[M]_T = [M]_0/\{1 + ([M]_0/[L]_0)x\}$ and $[L]_T = [M]_0x/\{1 + ([M]_0/[L]_0)x\}$, where $x = [L]_T/[M]_T$ and $[L]_0$ and $[M]_0$ denote the L concentration in the titrant solution and the initial MA concentration in the titrated solution, respectively. Although the total salt concentration decreases with the addition of the ligand solution to the salt solution, the Λ_{MA}, Λ_{MLA}, and K_{ML} values were assumed to be constant during the titration because of the low salt concentrations ($\leq 1 \times 10^{-3}$ $mol \cdot dm^{-3}$) and the low dilution factors (<1.5). It was confirmed that the variation of Λ_{MA} was generally less than 1%. The K_{ML} and Λ_{MLA} values were determined by a nonlinear least-squares analysis of the Λ_{app} versus $[L]_T/[M]_T$ plot based on eq 1. The regression curves (solid lines in Figure 2) all fit well with the data points. More than three independent experiments with different $[M]_0$ values were performed for each system, and it was confirmed that a constant K_{ML} value was obtained. The log K_{ML} values obtained in $MeNO_2$, MeCN, and PC are listed in Table 1, together with literature values in MeOH and DMF.[3−7]

Determination of Stability Constants in Water. In capillary electrophoresis using a fused-silica capillary, uncharged molecules migrate with the electroosmotic flow from anode to cathode. When a neutral crown ether forms cationic complexes with an alkali metal ion, the apparent mobility (μ_{app}) of the crown ether in the presence of the metal ion becomes higher than the electroosmotic flow

Table 1. Stability Constants of 1:1 Complexes of DB21C7 with Alkali Metal Ions in Polar Solvents at 25 °C

	$\log K_{ML}$ [a]					
M^+	$MeNO_2$	MeCN	PC	H_2O	MeOH	DMF
Na^+	6.04 ± 0.07[b]	2.96 ± 0.01[c] 2.88[f]	3.145 ± 0.009[c]	-0.3 ± 0.2[d]	2.40[e]	
K^+	5.70 ± 0.06[b]	4.643 ± 0.007[c] 4.47[f]	4.53 ± 0.02[c] 4.38[f]	1.37 ± 0.01[d]	4.30[e] 4.19[g]	2.40[f]
Rb^+	5.40 ± 0.03[b]	4.70 ± 0.03[c]	4.58 ± 0.03[c]	1.71 ± 0.01[d]	4.4[h]	2.73[i]
Cs^+	4.65 ± 0.01[b]	4.23 ± 0.01[c]	3.971 ± 0.006[c]	1.47 ± 0.01[d]	4.20[e] 4.25,[g] 4.2[h]	2.46[i]

[a] The uncertainties for the H_2O system are standard errors, and those for the other systems are standard deviations. [b] Conductivity; $I < 2 \times 10^{-4}$. [c] Conductivity; $I < 1 \times 10^{-3}$. [d] Capillary electrophoresis; $I = 0.08-0.11$ (MCl) for $M^+ = Na^+$ and $0.03-0.06$ (MCl) for $M^+ = K^+$, Rb^+, and Cs^+. [e] Reference 3; potentiometry. [f] Reference 4 (the values were supplied directly from the authors); solubility method. [g] Reference 5; calorimetry. [h] Reference 6; potentiometry. [i] Reference 7; ^{133}Cs NMR (27 °C).

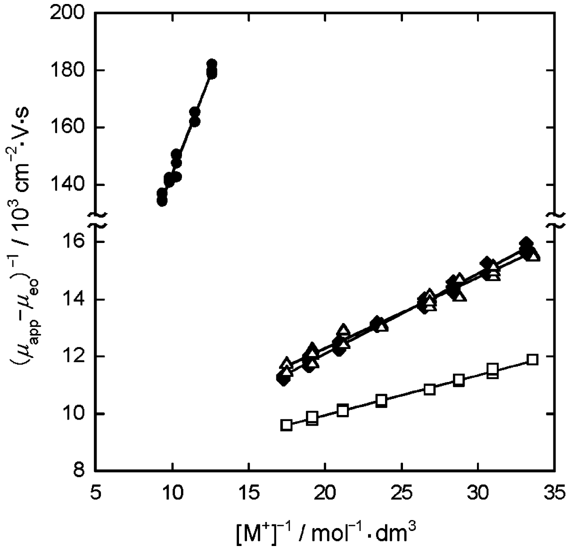

Figure 3. Plots of $(\mu_{app} - \mu_{eo})^{-1}$ vs $[M^+]^{-1}$ for DB21C7−alkali metal chloride systems in H_2O at 25 °C. Metal salts: ●, NaCl; ♦, KCl; □, RbCl; △, CsCl.

mobility (μ_{eo}) by electrophoresis of the complexes. Assuming the formation of a 1:1 complex and no cation−anion association, the following equation is derived[2]

$$\frac{1}{\mu_{app} - \mu_{eo}} = \frac{1}{K_{ML}\mu_{ep,ML}[M^+]} + \frac{1}{\mu_{ep,ML}} \tag{2}$$

where $\mu_{ep,ML}$ represents the electrophoretic mobility of the ML^+ complex. The $\mu_{app} - \mu_{eo}$ value was calculated from the migration times of the crown ether (t_L) and benzene as an electroosmotic flow marker (t_{eo}): $\mu_{app} - \mu_{eo} = L_T L_D(t_{eo} - t_L)/Vt_{eo}t_L$, where L_T, L_D, and V are the total capillary length, the capillary length from the injection end to the detection section, and the applied voltage, respectively. The equilibrium concentration, $[M^+]$, was practically equal to the total concentration of the metal ion because the total concentration was much higher for the metal ion than for the crown ether. The $(\mu_{app} - \mu_{eo})^{-1}$ versus $[M^+]^{-1}$ plots are shown in Figure 3, and the aqueous K_{ML} values determined from the linear relationships are given in Table 1. The reliability of this method was certified by the good agreement between the K_{ML} values of K(benzo-18-crown-6)$^+$ from conductivity and capillary electrophoresis experiments.[2] The $\mu_{ep,ML}$ values were almost the same for the Na(DB21C7)$^+$, K(DB21C7)$^+$, Rb(DB21C7)$^+$, and Cs(DB21C7)$^+$ complexes (i.e., $(1.5 \pm 0.9) \times 10^{-4}$, $(1.53 \pm 0.03) \times 10^{-4}$, $(1.40 \pm 0.01) \times 10^{-4}$, and $(1.36 \pm 0.03) \times 10^{-4}$ cm^2·V^{-1}·s^{-1}, respectively). The experiments for Na^+ were conducted at a higher concentration of the metal salt than those for K^+, Rb^+, and Cs^+ because of the much lower K_{ML} value of the Na(DB21C7)$^+$ complex. It was previously confirmed for the Na(DB18C6)$^+$ complex in H_2O that the K_{ML} and $\mu_{ep,ML}$ values are insensitive to the ionic strength.[2]

Determination of Transfer Activity Coefficients. We considered a Gibbs free energy cycle as shown in Figure 4, where $\Delta G°_{c,MeNO_2}$ and $\Delta G°_{c,S}$ are the standard molar Gibbs energies for complexation in $MeNO_2$ and S, respectively; $\Delta G°_{t,MeNO_2\rightarrow S}(M^+)$, $\Delta G°_{t,MeNO_2\rightarrow S}(L)$, and $\Delta G°_{t,MeNO_2\rightarrow S}(ML^+)$ are the standard molar Gibbs energies for transfer from $MeNO_2$ to S of M^+, L, and ML^+, respectively. The $\Delta G°_{c,S} - \Delta G°_{c,MeNO_2}$ value is expressed as

$$\Delta G°_{c,S} - \Delta G°_{c,MeNO_2} = \Delta G°_{t,MeNO_2\rightarrow S}(ML^+) - \Delta G°_{t,MeNO_2\rightarrow S}(L) - \Delta G°_{t,MeNO_2\rightarrow S}(M^+) \tag{3}$$

Equation 3 is transformed into eq 4 using the stability constants of ML^+ in S and $MeNO_2$ and the transfer activity coefficients ($^{S}\gamma^{MeNO_2}$) of M^+, L, and ML^+:

$$\log K_{ML,S} - \log K_{ML,MeNO_2} = \log {}^{S}\gamma^{MeNO_2}(ML^+) - \log {}^{S}\gamma^{MeNO_2}(L) - \log {}^{S}\gamma^{MeNO_2}(M^+) \tag{4}$$

where the transfer activity coefficient of a solute is the hypothetical partition constant between the two solvents and is equal to $\exp\{-\Delta G°_{t,MeNO_2\rightarrow S}(\text{solute})/RT\}$. The $^{S}\gamma^{MeNO_2}(ML^+)$ value can be determined from the relation of eq 4 using the known values of $K_{ML,S}$, $K_{ML,MeNO_2}$, $^{S}\gamma^{MeNO_2}(L)$, and $^{S}\gamma^{MeNO_2}(M^+)$. The $^{S}\gamma^{MeNO_2}(L)$ values were determined in this study from the crown ether solubilities (S_L) (i.e., $^{S}\gamma^{MeNO_2}(L) = S_{L,S}/S_{L,MeNO_2}$). The S_L values of DB21C7 were 0.160 ± 0.001 mol·dm^{-3} in $MeNO_2$ (obtained from three independent measurements), 0.242 mol·dm^{-3} in MeCN,[4] 0.110 mol·dm^{-3} in PC,[4] 1.04×10^{-4} mol·dm^{-3} in H_2O,[4] 1.13×10^{-2} mol·dm^{-3} in MeOH,[4] and 0.285 mol·dm^{-3} in DMF.[4] The $^{S}\gamma^{MeNO_2}(M^+)$ values were calculated using the literature values of $^{S}\gamma^{H_2O}(M^+)$[8] and $\Delta G°_{t,H_2O\rightarrow MeNO_2}(M^+)$.[9] The transfer activity coefficient values are summarized in Table 2.

Discussion

Stability of DB21C7−Alkali Metal Ion Complexes. The results in Table 1 show that the stability of a given DB21C7−alkali metal ion complex varies with the solvent in the following order: for Na^+, $MeNO_2 \gg PC \approx MeCN > MeOH \gg H_2O$; for K^+, $MeNO_2 \gg MeCN \approx PC \approx MeOH \gg DMF \gg H_2O$; for Rb^+, $MeNO_2 > MeCN \approx PC \approx MeOH \gg DMF \gg H_2O$; and for Cs^+, $MeNO_2 > MeCN \approx MeOH \approx PC \gg DMF \gg H_2O$. From the $^{S}\gamma^{MeNO_2}(M^+)$ values (Table

$$\begin{tikzcd}
\mathrm{MeNO_2:} & \mathrm{M^+} \arrow[d, "{\Delta G^\circ_{t,\,MeNO_2\to S}(M^+)}"] & + & \mathrm{L} \arrow[rr, "{\Delta G^\circ_{c,\,MeNO_2}}"] \arrow[d, "{\Delta G^\circ_{t,\,MeNO_2\to S}(L)}"] & & \mathrm{ML^+} \arrow[d, "{\Delta G^\circ_{t,\,MeNO_2\to S}(ML^+)}"] \\
\mathrm{S:} & \mathrm{M^+} & + & \mathrm{L} \arrow[rr, "{\Delta G^\circ_{c,\,S}}"'] & & \mathrm{ML^+}
\end{tikzcd}$$

Figure 4. Thermodynamic cycle for complexation of M^+ with L in a polar solvent S by regarding $MeNO_2$ as a reference solvent.

Table 2. Transfer Activity Coefficients of Alkali Metal Ions, Crown Ethers, and Their 1:1 Complexes at 25 °C (Molar Scale)[a]

	$\log {}^{S}\gamma^{MeNO_2}$														
solute	S = MeCN			PC			H_2O			MeOH			DMF		
Na^+	3.2[b]			2.6[b]			5.5[c]			4.1[b]			7.2[b]		
K^+	1.4[b]			1.2[b]			2.70[c]			1.0[b]			4.5[b]		
Rb^+	0.8[b]			0.7[b]			1.93[c]			0.2[b]			3.8[b]		
Cs^+	0.2[b]			0.1[b]			0.99[c]			−0.6[b]			2.7[b]		
L =	I[d]	II	III[d]	I[d]	II	III[d]	I[d]	II	III[d]	I[d]	II	III[d]	I[d]	II	III[d]
L	0.179	0.180	−0.42	−0.430	−0.163	−0.77	−3.32	−3.187	−3.45	−1.483	−1.151	−1.61	0.12	0.251	−0.387
NaL^+	1.2	0.3	−0.9	0.4	−0.5	−1.8	−3.6	−4.0	−6.0	0.0	−0.7	−3.0	3.0		
KL^+	0.4	0.5	−0.6	0.0	−0.1	−1.3	−4.82	−4.82	−5.54	−1.3	−1.6	−2.5	1.8	1.5	0.5
RbL^+	0.1	0.3	−0.7	−0.4	−0.3	−1.4	−4.74	−4.95	−5.61	−1.6	−2.0	−2.5	1.8	1.4	0.2
CsL^+	0.2	0.0	−0.7	−0.2	−0.7	−1.6	−4.57	−5.38	−5.87	−1.8	−2.2	−2.7	1.2	0.8	0.2

[a] I = DB18C6, II = DB21C7, and III = DB24C8. The values for single ions are based on the Ph_4As^+/BPh_4^- assumption. [b] Calculated from the values of ${}^{S}\gamma^{H_2O}(M^+)$ (ref 8) and $\Delta G^\circ_{t,H_2O\to MeNO_2}(M^+)$ (ref 9). [c] Reference 9. [d] Reference 1.

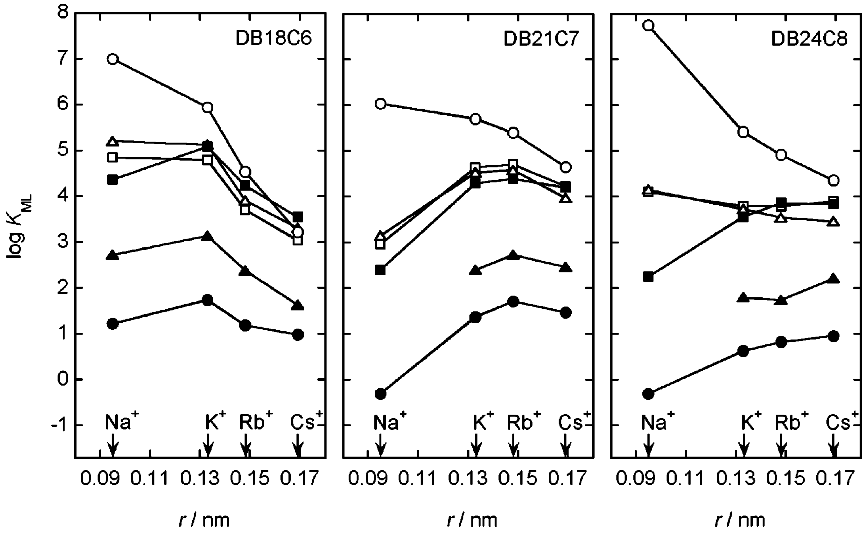

Figure 5. Plots of log K_{ML} vs the metal ion radius (r) for alkali metal ion complexes with DB18C6, DB21C7, and DB24C8. The log K_{ML} values for DB18C6 and DB24C8 are cited from the literature (ref 1). Solvents: ○, $MeNO_2$; □, MeCN; △, PC; ●, H_2O; ■, MeOH; ▲, DMF.

2), the solvation-power order of the solvents for an alkali metal ion is as follows: for Na^+, DMF ≫ H_2O ≫ MeOH > MeCN > PC ≫ $MeNO_2$; for K^+, DMF ≫ H_2O ≫ MeCN ≈ PC ≈ MeOH ≫ $MeNO_2$; for Rb^+, DMF ≫ H_2O ≫ MeCN ≈ PC > MeOH ≈ $MeNO_2$; and for Cs^+, DMF ≫ H_2O > MeCN ≈ PC ≈ $MeNO_2$ > MeOH. When the solvent is aprotic ($MeNO_2$, MeCN, PC, or DMF), the stability of a given complex tends to be lower in the solvent that solvates the alkali metal ion more strongly. In general, the complex stability in MeOH or H_2O is lower or much lower, respectively, than that expected from the solvation power.

In Figure 5, the log K_{ML} values of the alkali metal ion complexes with DB18C6, DB21C7, and DB24C8 are plotted against the ionic radius[10] of each metal. In MeCN, PC, H_2O, MeOH, and DMF, the K_{ML} value for DB21C7 varies with the metal ion as follows: Na^+ (the data in DMF is lacked) ≪ K^+ ≈ or < Rb^+ > Cs^+. This selectivity pattern is partially different from that of DB24C8 or DB18C6 in the same solvents. As for the selectivity between Na^+ and K^+, all three crown ethers form more stable complexes with K^+ in H_2O, MeOH, and DMF; the $K_{ML}(K^+)/K_{ML}(Na^+)$ value is greatest for DB21C7. In MeCN and PC, DB24C8 and DB18C6 show no K^+/Na^+ selectivity, whereas DB21C7 is still highly selective for K^+ over Na^+. Therefore, DB21C7 is superior in K^+/Na^+ selectivity to DB24C8 and DB18C6 in the solvents other than $MeNO_2$.

In $MeNO_2$ which has the weakest solvation power for the alkali metal ions, the K_{ML} value for DB21C7 decreases monotonically with an increase in the metal ion size (i.e., Na^+ > K^+ > Rb^+ > Cs^+). The same is true for DB24C8 and DB18C6. Although the smaller ion is more strongly solvated in every solvent, the metal ion dependence of the solvation free energy is smallest in $MeNO_2$.[1] It is expected that as the difference in the solvation free energy between two metal ions decreases the complex of the smaller metal ion is relatively more stabilized. It follows that the selectivity sequence in the absence of a solvent (i.e., in the gas phase) should approach that observed in $MeNO_2$. The sequence shows that the intrinsic selectivity of these crown ethers is primarily governed by the electrostatic interaction between the alkali metal ion and the ether oxygen atoms, regardless of the crown ether size. A feature of the DB21C7 complexation in $MeNO_2$ is that the Na^+ complex is remarkably unstable as compared to the corresponding complexes of DB18C6 and DB24C8; the reason is not clear at this stage.

Solvation of DB21C7. The solubility of DB21C7 decreases in the following solvent sequence: DMF ≈ MeCN > $MeNO_2$ > PC ≫ MeOH ≫ H_2O. Similar sequences are observed for DB24C8 ($MeNO_2$ > DMF ≈ MeCN > PC > MeOH ≫ H_2O) and DB18C6 (MeCN ≈ DMF > $MeNO_2$ > PC ≫ MeOH ≫ H_2O).[1] The solvent dependence of the solubility is discussed using the Scatchard−Hildebrand equation in its general form: the activity coefficient of a neutral solute i (f_i, mole fraction scale) at infinite dilution in a solvent j can be written as[11,12]

$$RT \ln f_i = V_i(C_i + C_j - 2C_{i,j}) + RT\left(\ln\frac{V_i}{V_j} + 1 - \frac{V_i}{V_j}\right) \quad (5)$$

where V_x and C_x ($x = i$ or j) denote the molar volume and cohesive energy density of a pure liquid x, respectively; $C_{i,j}$ is the cohesive energy density for the pair interaction between i and j molecules. By using eq 5, the standard Gibbs energy for transfer of a crown ether L from $MeNO_2$ to a polar solvent S (molar scale) can be expressed as follows:

$$-\Delta G^\circ_{t,MeNO_2\rightarrow S}(L) = RT \ln {}^{S}\gamma^{MeNO_2}(L)$$

$$= V_L\left[RT\left(\frac{1}{V_S} - \frac{1}{V_{MeNO_2}}\right) + (C_{MeNO_2} - C_S) + 2(C_{S,L} - C_{MeNO_2,L})\right] \quad (6)$$

For a given crown ether, the larger $-\Delta G^\circ_{t,MeNO_2\rightarrow S}(L)$ value corresponds to the higher solubility in S; the terms $RT({V_S}^{-1} - {V_{MeNO_2}}^{-1})$, $C_{MeNO_2} - C_S$, and $2(C_{S,L} - C_{MeNO_2,L})$ on the right side correspond to the contributions (per unit volume of the crown ether) of the entropy of solution, the energy needed to break the solvent−solvent interaction, and the energy needed to form the solute−solvent interaction, respectively. The values of the molar volume and cohesive energy density of the solvents are as follows: for $MeNO_2$, $V = 54.3$ $cm^3{\cdot}mol^{-1}$ and $C = 630$ MPa; for MeCN, $V = 52.6$ $cm^3{\cdot}mol^{-1}$ and $C = 595$ MPa; for PC, $V = 85.0$ $cm^3{\cdot}mol^{-1}$ and $C = 745$ MPa; for H_2O, $V = 18.0$ $cm^3{\cdot}mol^{-1}$ and $C = 2280$ MPa; for MeOH, $V = 40.7$ $cm^3{\cdot}mol^{-1}$ and $C = 6876$ MPa; and for DMF, $V = 77.0$ $cm^3{\cdot}mol^{-1}$ and $C = 615$ MPa.[12] The V_L value of DB21C7 was estimated to be 307 $cm^3{\cdot}mol^{-1}$ from the V_L values of DB18C6 (288 $cm^3{\cdot}mol^{-1}$)[13] and DB24C8 (325 $cm^3{\cdot}mol^{-1}$),[14] assuming the additivity of group contributions. The $RT({V_S}^{-1} - {V_{MeNO_2}}^{-1})$, $C_{MeNO_2} - C_S$, and $2(C_{S,L} - C_{MeNO_2,L})$ values calculated for DB21C7 are, respectively, (1, 35, and −33) MPa when S = MeCN; (−16, −115, and 128) MPa when S = PC; (92.1, -1.65×10^3, and 1.50×10^3) MPa when S = H_2O; (15, −246, and 210) MPa when S = MeOH; and (−13, 15, and 3) MPa when S = DMF. The variations of the $C_{MeNO_2} - C_S$ and $2(C_{S,L} - C_{MeNO_2,L})$ values with S are generally much larger than the corresponding variation of the $RT({V_S}^{-1} - {V_{MeNO_2}}^{-1})$ value. The $2(C_{S,L} - C_{MeNO_2,L})$ value decreases in the following sequence of S: H_2O ≫ MeOH > PC > DMF ≈ $MeNO_2$ (the value equals zero) > MeCN, where the greater $2(C_{S,L} - C_{MeNO_2,L})$ value means a stronger interaction between the crown ether and S. It is shown that the protic solvents (particularly H_2O) have a much stronger interaction with the crown ether than the aprotic ones; this is explained by hydrogen bonding of the protic solvents to the ether oxygen atoms. The relatively strong interaction of PC with the crown ether may be due to the high dipolarity of PC; the dipole moments in Debye units (1 D = 3.336×10^{-30} C·m) of the solvents are 3.56, 3.53, 4.94, 1.82, 2.87, and 3.24 for $MeNO_2$, MeCN, PC, H_2O, MeOH, and DMF, respectively.[15] The solvent sequence for the $2(C_{S,L} - C_{MeNO_2,L})$ value, however, is quite different from that for the solubility. On the other hand, the $C_{MeNO_2} - C_S$ value decreases in the sequence MeCN > DMF > $MeNO_2$ > PC > MeOH ≫ H_2O, which is almost consistent with the solubility sequence. It can be concluded from the above that the DB21C7 solubility is governed by the cohesive energy density of the solvent itself; the crown ether is generally less soluble in the solvent where the energy for breaking the solvent−solvent interaction to accommodate the solute molecule is greater. The same conclusion is reached for the other dibenzo crown ethers as well.

Solvation of DB21C7−Alkali Metal Ion Complexes. The ${}^{S}\gamma^{MeNO_2}(ML^+)$ values (Table 2) show that the solvation-power sequences for the DB21C7−alkali metal ion complexes are greatly different from those for the parent metal ions: for $Na(DB21C7)^+$, MeCN > $MeNO_2$ > PC ≈ MeOH ≫ H_2O; for $K(DB21C7)^+$, DMF ≫ MeCN > $MeNO_2$ ≈ PC ≫ MeOH ≫ H_2O; for $Rb(DB21C7)^+$, DMF ≫ MeCN > $MeNO_2$ > PC ≫ MeOH ≫ H_2O; and for $Cs(DB21C7)^+$, DMF > MeCN = $MeNO_2$ > PC ≫ MeOH ≫ H_2O. An almost identical sequence is found for all of the complexes, and the sequence is the same as that for the free crown ether. Thus the relative solubility of the DB21C7−alkali metal ion complex in the different solvents is mostly determined by that of DB21C7. It appears that the alkali metal ion in the DB21C7 complex is effectively shielded from the solvents. Indeed, the log ${}^{S}\gamma^{MeNO_2}(ML^+)$ value for L = DB21C7 is generally comparable to the log ${}^{S}\gamma^{MeNO_2}(L)$ value when S = MeCN and PC. However, when S = DMF, having strong solvation power for the alkali metal ions, the log ${}^{S}\gamma^{MeNO_2}(ML^+)$ value is larger than the log ${}^{S}\gamma^{MeNO_2}(L)$ value, showing that the alkali metal ion in the DB21C7 complex is not completely shielded and interacts with DMF; it is known that the alkali metal ions in the cryptand complexes are well shielded even in strong donor solvents such as DMF and dimethyl sulfoxide.[16−18] In contrast, when S = H_2O and MeOH, the log ${}^{S}\gamma^{MeNO_2}(ML^+)$ value is generally smaller than the log ${}^{S}\gamma^{MeNO_2}(L)$ value although the alkali metal ion is more strongly solvated in that solvent than in $MeNO_2$; the decrease from log ${}^{S}\gamma^{MeNO_2}(L)$ to log ${}^{S}\gamma^{MeNO_2}(ML^+)$ is attributable to the reduction of the hydrogen bonds between the solvent molecules and the ether oxygen atoms upon complexation. This is responsible for the lower complex stability in the protic solvents than that expected from the solvation power for the alkali metal ions. The increase from log ${}^{DMF}\gamma^{MeNO_2}(L)$ to log ${}^{DMF}\gamma^{MeNO_2}(ML^+)$ when S = DMF and the decrease from log ${}^{S}\gamma^{MeNO_2}(L)$ to log ${}^{S}\gamma^{MeNO_2}(ML^+)$ when S = H_2O and MeOH are also found for the DB18C6 and DB24C8 complexes. The magnitude of the increase or decrease of the log ${}^{S}\gamma^{MeNO_2}$ value generally becomes smaller or greater as the crown ether size increases, respectively. It appears that the larger crown ether more effectively shields the alkali metal ion by coordination of more oxygen atoms to the metal ion.

For a given S, the ${}^{S}\gamma^{MeNO_2}(M^+)$ value decreases in the order $Na^+ \gg K^+ > Rb^+ > Cs^+$, reflecting that the difference in the solvation free energy between S and $MeNO_2$ is greater for the smaller alkali metal ion. The ${}^{S}\gamma^{MeNO_2}(ML^+)$ values for all of the crown ethers are always less sensitive to the kind of central metal ion, which is reasonable as a result of effective shielding of the metal ion from solvents by the crown ethers. For DB24C8, the ${}^{S}\gamma^{MeNO_2}(ML^+)$ value is nearly independent of the central metal ion. The same is true for DB18C6, except for the Na^+ complex; the ${}^{S}\gamma^{MeNO_2}(M(DB18C6)^+)$ value is clearly larger for the Na^+ complex than for the other alkali metal ion complexes regardless of the kind of S, indicating the remaining interaction of each S with the central Na^+ ion. In the case of DB21C7, such a positive deviation in ${}^{S}\gamma^{MeNO_2}(ML^+)$ is observed for the Na^+ complex when S = H_2O and MeOH but not when S = MeCN and PC. These results support the idea that the larger crown ether more effectively shields the alkali metal ion in the complex.

The change of selectivity for different alkali metal ions, M_I^+ and M_{II}^+, on going from $MeNO_2$ to the other solvent S is written by the following equation derived from eq 4:

$$\log\left\{\frac{K_{ML,S}(M_IL^+)}{K_{ML,S}(M_{II}L^+)}\right\} - \log\left\{\frac{K_{ML,MeNO_2}(M_IL^+)}{K_{ML,MeNO_2}(M_{II}L^+)}\right\} = \log\left\{\frac{{}^{S}\gamma^{MeNO_2}(M_IL^+)}{{}^{S}\gamma^{MeNO_2}(M_{II}L^+)}\right\} - \log\left\{\frac{{}^{S}\gamma^{MeNO_2}(M_I^+)}{{}^{S}\gamma^{MeNO_2}(M_{II}^+)}\right\} \quad (7)$$

Because the log ${}^{S}\gamma^{MeNO_2}\{M(DB21C7)^+\}$ value is less dependent on the kind of the metal ion than the log ${}^{S}\gamma^{MeNO_2}(M^+)$ value, the variation of the selectivity of DB21C7 with the solvent is governed by that of the solvation of the free alkali metal ions. For example, the inversion of the Na^+-K^+ selectivity on going from $MeNO_2$ ($K_{ML,MeNO_2}(Na^+)/K_{ML,MeNO_2}(K^+) > 1$) to the other solvent S ($K_{ML,S}(Na^+)/K_{ML,S}(K^+) < 1$) is attributed to the fact that the relative solvation of Na^+ compared to K^+ is much stronger in S than in $MeNO_2$ (i.e., ${}^{S}\gamma^{MeNO_2}(Na^+)/{}^{S}\gamma^{MeNO_2}(K^+) > 1$). The same is true for DB24C8 and DB18C6. Thus, it can be concluded that the differences in the selectivity of these crown ethers in a solvent are mainly caused by those in the intrinsic selectivity in the gas phase.

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