March, 1988] © *1988 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *61*, 627—632 (1988)

A Conductance Study of 1:1 Complexes of 15-Crown-5, 16-Crown-5, and Benzo-15-crown-5 with Alkali Metal Ions in Nonaqueous Solvents

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(Received June 18, 1987)

Conductivities of alkali metal salts in the presence of 15-crown-5 (15C5), 16-crown-5 (16C5), and benzo-15-crown-5 (B15C5) were measured at 25 °C in acetonitrile, propylene carbonate, and methanol. Formation constants (K_{ML^+}) of 1:1 complexes of 15C5 and 16C5 with alkali metal ions and conductance parameters (λ^0 and $\mathring{a}$) of the Na$^+$ complexes of 15C5, 16C5, and B15C5 were determined, λ^0 and $\mathring{a}$ being limiting ionic molar conductivity and distance of closest approach of ions, respectively. In general, selectivities of 15C5 and 16C5 for alkali metal ions show the size-fit correlation. In contrast to 15C5, 16C5 forms much the most stable complex with Na$^+$ in every solvent. Generally, K_{ML^+}-value sequences of a given crown ether complex for the solvents are the reverse of donor-number sequences of the solvents. Value of $\mathring{a}$ increases with an increase in the cationic size (Na$^+$→Na(15C5)$^+$→Na(16C5)$^+$→Na(B15C5)$^+$). Mobility of the Na$^+$–crown ether complex decreases with an increase in the size of the crown ether. From λ^0 values and Walden products of these Na(crown ether)$^+$ complexes and a tetrapropylammonium ion, it seems likely that Na(15C5)$^+$ and Na(16C5)$^+$ act as structure breakers in hydrogen-bonding solvents, whereas Na(B15C5)$^+$ as a structure maker.

Conductance measurements of a solution of alkali metal salt in the presence of crown ether provide two valuable information; that is, (1) stability of the crown ether–alkali metal ion complex, and (2) transport phenomena of the crown ether–alkali metal salt complex in the solution.[1] Many data have been reported on stabilities of 15-crown-5 (15C5)- and benzo-15-crown-5 (B15C5)-alkali metal ion complexes in solutions, but a few data on solvation behavior of the crown ether complexes in solutions.[2] It has recently been presented that 16-crown-5 (16C5), possessing the same number of donor oxygen atoms but reduced symmetry, exhibits much higher selectivity for Na$^+$ among alkali metal ions than 15C5.[3,20] In the present study, in order to obtain systematic and detailed information on stabilities and solvation behavior of 15C5-, 16C5-, and B15C5-alkali metal ion complexes, conductivities of alkali metal salts in the presence of these three crown ethers were measured at 25 °C in acetonitrile, propylene carbonate, and methanol.

Experimental

Materials. 15-Crown-5 (Nisso Co., Ltd.) was purified twice by distillation under vacuum (bp 128.5—129.5 °C, 2.5 mmHg (1 mmHg≈133.322 Pa)). The preparation of 16C5 was just the same as that described in the previous paper.[3] Benzo-15-crown-5 (Merck Japan Ltd.) was dissolved in heptane, and filtered while hot. Then it was recrystallized from heptane three times and, prior to use, dried at 40 °C in vacuo for 50 h.

Extremely pure $LiCl \cdot H_2O$, NaCl, KCl, RbCl, and CsCl were purchased from Merck Japan Ltd., and were used without further purification. Rubidium and caesium perchlorates were prepared by adding a little excess of perchloric acid to aqueous solutions of the RbCl and CsCl, respectively. Lithium, sodium, and potassium perchlorates were obtained from Merck Japan Ltd. All the perchlorates were recrystallized four times from distilled water and, prior to use, dried at 150 °C in a vacuum oven.

The method of purification of acetonitrile,[4] propylene carbonate,[5] and methanol[6] was previously described. Middle 70% of distillate of the solvents was used. Conductivities of the purified acetonitrile, propylene carbonate, and methanol were less than 3×10^{-7}, 6×10^{-8}, and 2×10^{-7} $\Omega^{-1}\,cm^{-1}$, respectively.

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

Apparatus and Procedure. The conductance measurements were made on a Fuso conductivity apparatus, model 362A, in a water bath thermostated at 25±0.005 °C.

The experimental procedure to obtain formation constants of crown ether complexes with alkali metal ions was almost the same as that described in a previous paper.[5]

The experimental procedure to obtain molar conductivities (Λ) of the crown ether–sodium salt complexes was as follows. A solution of crown ether (6×10^{-3} mol dm^{-3}, 200 cm^3) was placed in the cell and the resistance of the solution was measured. Then a step-by-step increase in the sodium salt concentration was effected by a rapid transfer from a solution of the sodium salt (1×10^{-2} mol dm^{-3}) to the cell with a pipet, until the total concentration of the crown ether was about five times as large as that of the sodium salt. The resistance of the solution in the cell was remeasured after each transfer.

Results

The molar conductivity vs. $[L]_t/[M]_t$ plots of the $16C5/LiClO_4$/propylene carbonate system show an increase in Λ with an increase in the 16C5 concentration, $[L]_t$ and $[M]_t$ denoting total concentrations of the crown ether and the alkali metal, respectively. This indicates that a 16C5–Li$^+$ complex is more mobile in propylene carbonate than a free Li^+ ion. For 15C5 and 16C5/LiCl/CH_3OH and 15C5/NaCl/CH_3OH systems, there is a negligible change in Λ in spite of an increase in the crown ether concentration. Consequently, the complex-formation constants could not be determined. When the complex is unstable or mobilities of the complex and the corresponding alkali metal ion are equal, conductometric determination of the complex-formation constant is impossible. For all the other systems, Λ vs. $[L]_t/[M]_t$ plots show a decrease in Λ with an increase in the crown ether concentration. This reveals that the crown ether complex is less mobile than the corresponding free alkali metal ion. By way of example, Λ vs. $[L]_t/[M]_t$ plots for 15C5/ and 16C5/acetonitrile systems at 25 °C are given in Figs. 1 and 2, respectively.

From Figs. 1 and 2, in the cases of 15C5/ and 16C5/$NaClO_4$ systems, the slope of each curve changes sharply at $[L]_t/[M]_t=1$. The same tendency was observed for 16C5/$NaClO_4$/propylene carbonate system. It follows from this that the crown ethers form 1:1 complexes with Na^+. For the other systems, no such clear breaking point was observed.

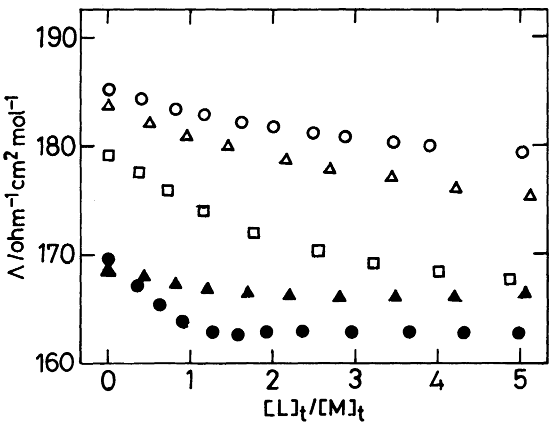

Fig. 1. Λ vs. $[L]_t/[M]_t$ curves for 15C5–alkali metal perchlorate systems in acetonitrile at 25 °C
▲ Li, ● Na, □ K, △ Rb, ○ Cs, $[M]_t=6\times10^{-4}$ M.

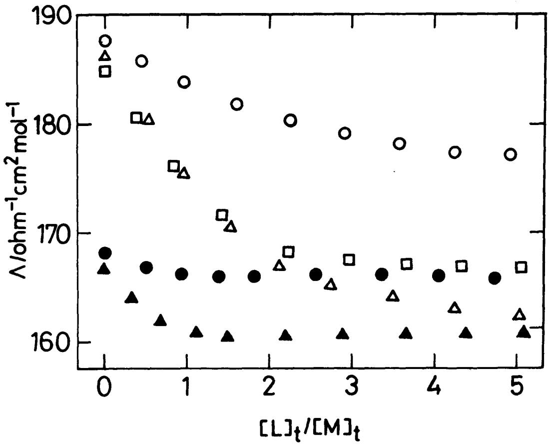

Fig. 2. Λ vs. $[L]_t/[M]_t$ curves for 16C5–alkali metal perchlorate systems in acetonitrile at 25 °C
● Li, ▲ Na, △ K, □ Rb, ○ Cs, $[M]_t=6\times10^{-4}$ M.

When a crown ether forms a 1:1 complex with an alkali metal ion, the equilibrium equation is written as

$$\begin{array}{ccccc} M^+ & + & L & \rightleftarrows & ML^+ \\ \alpha[M]_t & & [L]_t-(1-\alpha)[M]_t & & (1-\alpha)[M]_t, \end{array} \qquad (1)$$

where M^+, L, and α are the alkali metal ion, crown ether, and the fraction of free alkali metal ions. Thus, the complex-formation constant, K_{ML^+}, is defined by

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

The observed conductivity, κ, is given by

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

where A^- denotes an anion, and κ_{MA} and κ_{MLA} refer to conductivities of alkali metal salt and alkali metal crown ether salt, respectively. The molar conductivities are as follows.

$$\begin{aligned} \Lambda_{MA} &= \kappa_{MA}/[M^+] \\ &= \kappa_{MA}/\alpha[M]_t, \end{aligned} \qquad (4)$$

$$\begin{aligned} \Lambda_{MLA} &= \kappa_{MLA}/[ML^+] \\ &= \kappa_{MLA}/(1-\alpha)[M]_t, \end{aligned} \qquad (5)$$

Λ_{MA} and Λ_{MLA} designating molar conductivities of alkali metal salt and alkali metal crown ether salt, respectively. As a consequence of Eqs. 4 and 5, Eq. 3 can be transformed into

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

In this study, corrections for viscosity changes were neglected. As a consequence of Eq. 6, Eq. 2 can be transformed into

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

where $[L]=[L]_t-[M]_t(\Lambda_{MA}-\Lambda)/(\Lambda_{MA}-\Lambda_{MLA})$. The K_{ML^+} value can be obtained by the following procedure. The Λ_{MLA} value is estimated from the Λ values at the points of large $[L]_t$ to $[M]_t$ ratios. Using this Λ_{MLA} value, the K_{ML^+} value in Eq. 7 is calculated. The actual K_{ML^+} and Λ_{MLA} values are calculated by a successive approximation method. The actual Λ_{MLA} values at nearly equal $[M]_t$ values are listed in Table 1. The log K_{ML^+} values are summarized in Table 2.

Conductance data of crown ether–sodium salt complexes (NaLA) were analyzed by the Fuoss–Onsager equations:[21]

$$\Lambda = \Lambda_0 - SC^{1/2} + EC\log C + JC \qquad (8)$$

for unassociated electrolytes, and

$$\Lambda = \Lambda_0 - S(C\gamma)^{1/2} + EC\gamma \log C\gamma + JC\gamma - K_A\Lambda_0 f^2 C\gamma \tag{9}$$

for associated electrolytes, where K_A is ion-pair association constant and the other symbols have their usual meaning. In order to obtain the parameters of Eqs. 8 and 9, values of dielectric constants and viscosities listed in Table 6 were employed. It was found that every crown ether–sodium salt complex (NaLA) completely dissociates into cation and anion in the solvents. Limiting molar conductivities (Λ_0) and ion-size parameters (å) obtained in this work are summarized in Table 3.

Table 1. Λ_{MLA} Values at 25 °C

L	Solvent	MA	$\Lambda_{MLA}/\Omega^{-1}\,cm^2\,mol^{-1}$	$[M]_t\times 10^4/mol\,dm^{-3}$
15C5	AN[a]	$LiClO_4$	163.67	3.9866
		$NaClO_4$	163.64	3.8645
		$KClO_4$	159.38	4.0249
		$CsClO_4$	161.13	4.0809
	CH_3OH	NaCl	89.18	8.5552
		CsCl	89.39	8.0501
16C5	AN[a]	$LiClO_4$	160.52	5.8525
		$NaClO_4$	160.11	3.8457
			159.41	5.6345
		$KClO_4$	159.24	4.8213
		$RbClO_4$	164.04	4.0587
		$CsClO_4$	162.52	4.8808
	PC[b]	$NaClO_4$	26.55	4.7872
		$KClO_4$	27.17	4.7476
		$RbClO_4$	27.04	4.8989
		$CsClO_4$	28.30	4.6545

a) Acetonitrile. b) Propylene carbonate.

Table 2. Log ($K_{ML^+}/mol^{-1}\,dm^3$) Values at 25 °C

	CH_3CN		Propylene carbonate		CH_3OH	
	15C5	16C5	15C5	16C5	15C5	16C5
Li^+	5.3_4 3.60[a,7] >4[b,8]	4.4_8	4.2_6[5] >4[b,8]	3.2_5	1.23[b,8]	—
Na^+	5.3_8 4.9[9] 5.28[c,7] >4[10]	5.3_9	3.7[5]	5.7	3.48[11] 3.30[12,15] 3.14[13] 3.25[14] 3.24[16] 3.27[17] 3.31[18]	4.10 3.51[20]
K^+	3.9_8 2.9_8[d,7]	3.5_7	3.4_1[5]	3.3_4	3.3 3.77[11] 3.35[12] 3.1[19] 3.61[13] 3.34[15,18] 3.43[16]	2.9_2 2.63[20]
Rb^+	3.4_2	2.9_4	3.0_4[5]	2.5_9	2.7_2	2.4_6
Cs^+	3.1_4	2.3_8	2.6_9[5]	2.1_7	2.6_6 2.62[12] 2.18[11]	2.0_9

a) LiI. b) At 27±1 °C, $LiClO_4$. c) $NaBPh_4$. d) $KBPh_4$.

Table 3. Values of Λ_0, K_A, and $\mathring{a}$ at 25 °C in Nonaqueous Solvents

Salt	Solvent	Λ_0/Ω^{-1} cm^2 mol^{-1}	K_A/mol^{-1} dm^3	$\mathring{a}$/Å
$NaClO_4$ 22)	AN a)	180.63	11	3.7
Na(15C5)ClO_4	AN a)	170.43±0.36		4.12±0.08
Na(16C5)ClO_4	AN a)	165.84±0.04		5.5±0.3
Na(B15C5)ClO_4	AN a)	164.59±0.12		6.5±0.5
Bu_4NClO_4 23)	AN a)	165.06±0.01		3.57
$NaClO_4$	PC b)	27.98±0.01		2.9±0.1
$NaClO_4$ 24)	PC b)	27.89±0.01	−1.1	
		27.89±0.002	−1.3	
Na(15C5)ClO_4	PC b)	28.32±0.02		4.3±0.2
Na(16C5)ClO_4	PC b)	27.17±0.03		5.1±0.2
Na(B15C5)ClO_4	PC b)	26.64±0.02		5.7±0.1
NaCl 25)	CH_3OH	97.53		3.73
Na(15C5)Cl	CH_3OH	96.48±0.05		4.97±0.36
Na(16C5)Cl	CH_3OH	93.50±0.04		5.5±0.2
Na(B15C5)Cl	CH_3OH	90.06±0.01		6.2±0.2
Bu_4NCl 26)	CH_3OH	91.38	0.0	3.9

a) Acetonitrile. b) Propylene carbonate.

Table 4. Crystal Ionic Radii of Alkali Metals and Cavity Radius of Crown Ethers (Å)

Cation	Crystal ionic radius 27)	Crown ether	Cavity radius a)
Li^+	0.60	15C5	0.85
Na^+	0.95	16C5	0.9
K^+	1.33		
Rb^+	1.48		
Cs^+	1.69		

a) Estimated by CPK space-filling molecular models.

Discussion

Stability of Crown Ether Complexes. As can be seen from Tables 2 and 4, selectivity of 15C5 for alkali metal ions shows the size-fit correlation except for the cases of Li^+ in acetonitrile and propylene carbonate and Na^+ in CH_3OH. In comparison with the case of 16C5, Li^+–15C5 complex is very stable among alkali metal ion–15C5 complexes in acetonitrile and propylene carbonate. It is interesting that, in contrast to 15C5, 16C5 forms much the most stable complex with Na^+ of all the alkali metal ions in every solvent. In particular, selectivity of 16C5 for Na^+ in propylene carbonate is the most striking of all the systems. Moreover, the 16C5–Na^+ complex in propylene carbonate is the most stable among all the 15C5 and 16C5 complexes. Thus, a remarkable enhancement of selectivity for Na^+ is caused by an extra methylene group in the 16C5 ring. The more closely an alkali metal ion fits into the 16C5 cavity, the more stable is the 16C5–alkali metal ion complex. This tendency can be explained by the size-fit concept.

Log K_{ML^+}-value sequences of a given crown ether–alkali metal ion complex for the solvents are acetonitrile>propylene carbonate>CH_3OH only except for those of 16C5–Na^+ complex for propylene carbonate and acetonitrile (Table 2). The log K_{ML^+}-value sequences are completely the reverse of donor-number sequences of the solvents (acetonitrile<propylene carbonate<CH_3OH, from Table 6). Donor number of the solvent seems to be a dominant factor governing the stability of the crown ether–alkali metal ion complex.1) From Table 6, ε_r values of the solvents increase in the order CH_3OH<acetonitrile<propylene carbonate. This indicates that there is no relationship between stability of the crown ether–alkali metal ion complex and dielectric constant of the solvent.

A 15C5–alkali metal ion complex is more stable than the corresponding 16C5 complex except for the case of Na^+. In propylene carbonate and CH_3OH, the reverse is true of 15C5- and 16C5–Na^+ complexes. In acetonitrile, log K_{ML^+} values of 15C5- and 16C5–Na^+ complexes are almost the same. This tendency may be explained in terms of examination of CPK molecular models, that is, Na^+ has a more suitable size for the cavity of 16C5 than that of 15C5, and the donor oxygen atoms of 16C5 arrange more nicely around Na^+ compared to 15C5. However, lower symmetry of 16C5 causes more unfavorable orientation of the donor oxygen atoms for the less size-fitted cations, Li^+, K^+, Rb^+, and Cs^+.

Behavior of Crown Ether Complexes in Solutions. From Table 3, a slight association to ion-pairs is found for $NaClO_4$ in acetonitrile, but all the crown ether–sodium salt complexes completely dissociate into ions. Since mobilities of these three crown ether–Na^+ complexes are much smaller than that of a Na^+ ion in acetonitrile (Table 5), an apparent cationic size is much larger for the crown ether–Na^+ complexes

Table 5. Limiting Ionic Molar Conductivities (λ^0) in Various Solvents at 25 °C

	$\lambda^0/\Omega^{-1}\,\mathrm{cm^2\,mol^{-1}}$		
	AN[a]	PC[b]	CH_3OH
Na^+	76.9[29]	9.7_0 9.45[24]	45.17[25]
$Na(15C5)^+$	66.7_3 65.5[30]	10.0_4	44.12
$Na(16C5)^+$	62.1_4	8.8_9	41.14
$Na(B15C5)^+$	60.8_9	8.3_6	37.70
Pr_4N^+	70.3[29]	11.0_0[31]	46.08[26]
Cl^-	—	—	52.36[32]
ClO_4^-	103.7[29]	18.2_8[31]	—

a) Acetonitrile. b) Propylene carbonate.

Table 6. Walden Products at 25 °C

	AN[d]	PC[e]	CH_3OH
η_0/mP[a] (at 25 °C)	3.39[37]	25.3[38]	5.42[39]
DN[b,36]	14.1	15.1	19
ε_r[c] (at 25 °C)	35.95[29]	64.4[38]	32.6[39]
$Na(15C5)^+$	0.226	0.254	0.239
$Na(16C5)^+$	0.211	0.22_5	0.223
$Na(B15C5)^+$	0.206	0.21_2	0.204
Pr_4N^+	0.238	0.278	0.250

a) η_0 denotes viscosity and 1P=0.1 Pa s. b) DN denotes donor number. c) ε_r denotes dielectric constant. d) Acetonitrile. e) Propylene carbonate.

than for the Na^+ ion. This is responsible for a complete dissociation of crown ether–$NaClO_4$ complexes into ions and a slight association of $NaClO_4$ to ion-pairs in acetonitrile.

Table 3 shows that å value increases with an increase in the cationic size ($Na^+ \rightarrow Na(15C5)^+ \rightarrow Na(16C5)^+ \rightarrow Na(B15C5)^+$) regardless of a variety of anions and solvents. It follows from this finding that the anion does not always approach the sodium ion trapped in the cavity in a direction perpendicular to the plane of the crown ether ring.

By using ionic radii of $Na(15C5)^+$ (4.6 Å[5]), ClO_4^- (2.26 Å[28]), and Cl^- (1.81 Å[27]), center-to-center distance of the cation and the anion is calculated to be 6.86 Å for $Na(15C5)ClO_4$ and 6.41 Å for $Na(15C5)Cl$, which are greater than the largest å values of B15C5–sodium salt complexes.

For 15C5 and 16C5, å values of the crown ether–$NaClO_4$ complex in acetonitrile and propylene carbonate are much the same. Although ionic radius of Cl^- is 0.45 Å smaller than that of ClO_4^-, å value of the crown ether–sodium salt complex in CH_3OH is larger than or nearly equal to those in aprotic solvents. The same behavior is observed for both sodium and tetrabutyl ammonium salts (Table 3). This may be attributed to much stronger solvation of Cl^- in CH_3OH compared to ClO_4^-.

It can be seen from Table 5 that the mobility of Na^+–crown ether complex decreases with an increase in the size of crown ether, indicating that the mobility of the complexed sodium ion is governed completely by the size of the complex. It is of interest to note that only an additional methylene group causes the lower mobility of $Na(16C5)^+$ compared to $Na(15C5)^+$. Mobilities of Na^+ in acetonitrile and CH_3OH show the same tendency as stated above, but that in propylene carbonate the opposite trend. It has been reported that the degree of solvation of large ions is determined predominantly by the dipole moment of solvent molecules, whereas that of small ions by the acid-base properties of solvent molecules.[22] Although propylene carbonate has a slightly larger and smaller donor number than acetonitrile and CH_3OH, respectively (Table 6), and has a larger dipole moment (4.94 D[33]) than acetonitrile (3.37 D[33]) and CH_3OH (1.73 D[33]), $Na(15C5)^+$ is more mobile than Na^+ in propylene carbonate, and the reverse is true of acetonitrile and CH_3OH. The lower mobility (the larger moving entity) of Na^+ in propylene carbonate may be attributed to the larger size of the propylene carbonate molecule (molecular radii of propylene carbonate, acetonitrile, and CH_3OH are 3.23, 2.75, and 2.52 Å, respectively[31]).

Although the ionic radius of $Na(15C5)^+$ is nearly equal to that of tetrapropylammonium ion (Pr_4N^+) (4.52 Å[34]), $Na(15C5)^+$ is less mobile than Pr_4N^+. For $Na(15C5)^+$, there exists a possible interaction of the central Na^+ with solvent molecules on two axial sides of the 15C5 plane, whereas, for Pr_4N^+, the charge of the nitrogen atom is effectively screened by four propyl groups. Consequently, the interaction of $Na(15C5)^+$ with solvent dipole seems to be stronger than that of Pr_4N^+. This may be responsible for the lower mobility of $Na(15C5)^+$ compared to Pr_4N^+.

In the cases of L=15C5 and 16C5, sequences of $|\lambda^0(Pr_4N^+)/\lambda^0(NaL^+)-1|$ value for the solvents are $CH_3OH < CH_3CN <$ propylene carbonate. This shows that a difference in mobility in CH_3OH between NaL^+ and Pr_4N^+ is the smallest of all the solvents. The same behavior was observed for the case of $K(18C6^{**})^+$ complex and tetrabutylammonium ion (Bu_4N^+).[4] In the previous papers,[4,35] it was reported that $K(18C6)^+$ acts as a structure breaker in hydrogen-bonding solvents. From Walden products of Pr_4N^+ in Table 6, Pr_4N^+ is more mobile in CH_3OH than in acetonitrile. It thus appears that hydrogen-bonded structure of CH_3OH scarcely decreases the mobility of Pr_4N^+. Although hydrogen bonds of ether oxygen atoms of 15C5 and 16C5 with methanol molecules would decrease mobilities of $Na(15C5)^+$ and $Na(16C5)^+$ complexes, the mobility of NaL^+(L=15C5 and 16C5) approaches that of Pr_4N^+ most closely in CH_3OH of

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**18C6=18-crown-6.

all the solvents. Therefore, it can be considered that $Na(15C5)^+$ and $Na(16C5)^+$ in CH_3OH are more mobile than expected. This is supported by the data in Table 6; namely, Walden products of $Na(15C5)^+$ and $Na(16C5)^+$ in CH_3OH are larger than those in acetonitrile. Consequently, from the data of $K(18C6)^+$ [4,35] and the above discussion, it seems likely that $Na(15C5)^+$ and $Na(16C5)^+$ act as structure breakers in hydrogen-bonding solvents.

For $Na(B15C5)^+$, sequences of $\lambda^0(Pr_4N^+)/\lambda^0(Na(B15C5)^+)$ value for the solvents are $CH_3CN<CH_3OH<$propylene carbonate. The order of CH_3CN and CH_3OH for $Na(B15C5)^+$ is in the reverse of that for $Na(15C5)^+$ and $Na(16C5)^+$. This indicates that the mobility of $Na(B15C5)^+$ in CH_3OH is lower than expected on the basis of those of $Na(15C5)^+$ and $Na(16C5)^+$. Enforcement of a hydrogen-bonded structure of CH_3OH for the benzo group may decrease the mobility of $Na(B15C5)^+$. This is supported by the data of Walden products of $Na(B15C5)^+$ in Table 6; the $\lambda^0\eta_0$ value of CH_3OH of $Na(B15C5)^+$ is the smallest of all the solvents. This suggests that, on account of the benzo group, $Na(B15C5)^+$ acts as a structure maker in hydrogen-bonding solvents.

For these three Na(crown ether)$^+$ complexes as well as Pr_4N^+, Walden products in propylene carbonate, which has the greatest ε_r value, are the largest.

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