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A Conductance Study of 1 : 1 Complexes of 1,2-Bis[2-(2-methoxyethoxy)ethoxy]benzene (Noncyclic Polyether) with Alkali Metal Ions in Nonaqueous Solvents

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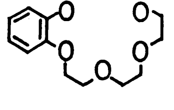
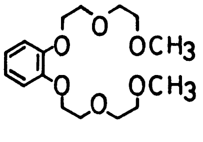
Conductivities of alkali metal salts in the presence of 1,2-bis[2-(2-methoxyethoxy)ethoxy]benzene (AC·B18C6), which is a linear counterpart of benzo-18-crown-6 (B18C6), were measured at 25 °C in acetonitrile, propylene carbonate, and methanol. Formation constants and limiting ionic molar conductivities of the 1 : 1 AC·B18C6-alkali metal ion complexes were determined. Selectivity of AC·B18C6 for alkali metal ions is lower than that of B18C6. The selectivity order of AC·B18C6 for K^+, Rb^+, and Cs^+ is consistent entirely with that of B18C6 ($K^+>Rb^+>Cs^+$), but the selectivity order of AC·B18C6 for Na^+ differs from that of B18C6. The AC·B18C6-alkali metal ion complex is less stable than the corresponding B18C6 complex. The AC·B18C6 complex may be entropy-destabilized due to the two flexible arms. The AC·B18C6-alkali metal ion complex is more mobile than the corresponding B18C6 complex; the mobility of the AC·B18C6 complex is less sensitive to a variety of the alkali metal ions in the complexes than that of the B18C6 complex. This indicates that the alkali metal ion in the AC·B18C6 complex is coordinated with the two arms and the surface charge of the alkali metal ion in the AC·B18C6 complex is more effectively shielded than that in the B18C6 complex.

In order to clarify the macrocyclic effect (i.e., enhanced stabilities of crown compound-cationic species complexes), complexation reactions of crown compounds and their corresponding open-chain analogs with metal ions have been studied from thermodynamic and kinetic points of view.[1] However, few data on solvation behavior and structures in solutions of the resulting complexes have been reported. In this study, conductivities of alkali metal salts in the presence of 1,2-bis[2-(2-methoxyethoxy)ethoxy]benzene (AC·B18C6), which is a linear counterpart of benzo-18-crown-6 (B18C6), were measured at 25 °C in acetonitrile, propylene carbonate, and methanol. Formation constants and limiting ionic molar conductivities of the 1 : 1 AC·B18C6-alkali metal ion complexes were determined. Stabilities and mobilities of the AC·B18C6 complexes in the solvents were compared with those of the B18C6 complexes to obtain information on the macrocyclic effect of B18C6, and solvation properties and structures in solutions of the AC·B18C6 complexes.



B18C6



AC·B18C6

Experimental

Materials. AC·B18C6 was prepared by the reaction of catechol with 2-(2-methoxyethoxy)ethyl chloride in aqueous sodium hydroxide-1-butanol mixture according to the literature method.[2,3] The crude light yellow oil was distilled three times to give colorless viscous oil: 65%; bp 225—230 °C/19 Torr (1 Torr≃133.322 Pa); MS *m/z*, 314 (M^+). Found: C, 60.97; H, 8.20%. Calcd for $C_{16}H_{26}O_6$: C, 61.13; H, 8.34%. Extremely pure $LiCl \cdot H_2O$, NaCl, KCl, RbCl, and CsCl were obtained 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 purchased from Merck Japan Ltd. All the perchlorates were recrystallized four times from distilled water. The alkali metal chlorides and perchlorates were, 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 3×10^{-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. Three cells were used with cell constants of 0.13545, 0.090741, and 0.031112 cm^{-1}.

The experimental procedure to obtain formation constants and limiting ionic molar conductivities of AC·B18C6-alkali metal ion complexes was almost the same as that described in a previous paper.[5]

Results and Discussion

The procedure for obtaining formation constants (K_{ML^+}) and limiting ionic molar conductivities (λ^0) of AC·B18C6-alkali metal ion complexes was just the same as that reported in a previous paper,[5] where $K_{ML^+}=[ML^+]/[M^+][L]$. M^+ and L denote an alkali metal ion and AC·B18C6, respectively. In this study, it is assumed that the association between a cation and an anion is negligible and that AC·B18C6 forms the 1 : 1 complex with an alkali metal ion. Corrections for viscosity changes were neglected. The $\log K_{ML^+}$ and λ^0

Table 1. Log (K_{ML^+}/mol^{-1} dm^3) Values of AC·B18C6- and B18C6-Alkali Metal Ion Complexes at 25 °C

	AN[a)]		PC[b)]		CH$_3$OH	
	AC·B18C6	B18C6	AC·B18C6	B18C6	AC·B18C6	B18C6
Li$^+$	—	—	1.93±0.08	—	—	—
Na$^+$	2.85±0.02	4.9[7]	3.07±0.03	5.3[7]	1.44[3]	4.5[7]
K$^+$	2.619±0.005	5.3[7]	2.544±0.009	5.4[7]	2.25±0.03 2.15[3]	5.7[7]
Rb$^+$	2.403±0.006	4.4[7]	2.12±0.02	4.5[7]	2.116±0.008	5.1[7]
Cs$^+$	1.75±0.11	3.8[7]	1.82±0.06	3.6[7]	1.83±0.03 1.66[3]	4.1[7]

a) Acetonitrile. b) Propylene carbonate.

Table 2. λ^0/Ω^{-1} cm^2 mol^{-1} Values of AC·B18C6- and B18C6-Alkali Metal Ion Complexes at 25 °C

	AN[a)]		PC[b)]	
	AC·B18C6	B18C6	AC·B18C6	B18C6
Na$^+$	$58._6$	$53._1$[8]	8.1_7	7.2_9[8]
K$^+$	$58._1$	$56._5$[8]	8.5_3	7.9_0[8]
ClO$_4^-$	103.7[9]		18.2_8[10]	

a) Acetonitrile. b) Propylene carbonate.

values of the AC·B18C6-alkali metal ion complexes are summarized in Tables 1 and 2, respectively, together with the literature values.

The molar conductivity (Λ) vs. $[L]_t/[M]_t$ plots in acetonitrile, propylene carbonate, and methanol are given in Figs. 1, 2, and 3, $[L]_t$ and $[M]_t$ being total concentrations of AC·B18C6 and an alkali metal ion, respectively. The Λ vs. $[L]_t/[M]_t$ plots show a decrease in Λ with an increase in the AC·B18C6 concentration, except for all the Li$^+$ systems and the Na$^+$-CH$_3$OH system. This indicates that the moving entity of the AC·B18C6-alkali metal ion complex is larger than that of the corresponding alkali metal ion. In the case of the Li$^+$ system, a small increase in Λ is found with an increase in the AC·B18C6 concentration, indicating that, if a complex is formed between AC·B18C6 and Li$^+$, the moving entity of the AC·B18C6-Li$^+$ complex is smaller than that of Li$^+$. For the Na$^+$-CH$_3$OH system, scarcely any change in Λ is observed in spite of an increase in the AC·B18C6 concentration. Consequently, the conductometric determination of the complex-formation constant is impossible for the Li$^+$-acetonitrile and -methanol systems and the Na$^+$-methanol system. From the fact that the AC·B18C6-Na$^+$ complex is formed in CH$_3$OH,[3] the changeless Λ may be caused by low stability of the AC·B18C6 complex and/or nearly equal mobilities of the AC·B18C6 complex and Na$^+$ in CH$_3$OH.

It can be seen from Figs. 1, 2, and 3 that no clear breaking point is observed at $[L]_t/[M]_t=1$; whereas, the reverse holds for B18C6 systems.[7] This is attributed largely to much lower stabilities of AC·B18C6-alkali metal ion complexes compared with B18C6-alkali metal ion complexes (Table 1).

Stabilities of AC·B18C6 Complexes. The difference in logK_{ML^+} values of AC·B18C6 between neighboring alkali metal ions in the periodic table in the same solvent is smaller than that of B18C6 except for the cases of Rb$^+$, Cs$^+$ in acetonitrile and Na$^+$, K$^+$ in propylene carbonate. The difference between the

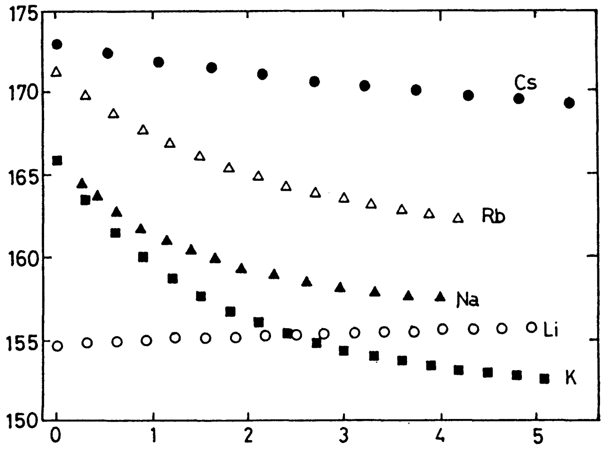


Fig. 1. Λ vs. $[L]_t/[M]_t$ curves for AC·B18C6-alkali metal perchlorate systems in acetonitrile at 25 °C. $[M]_t$=1.5×10^{-3} mol dm^{-3}.

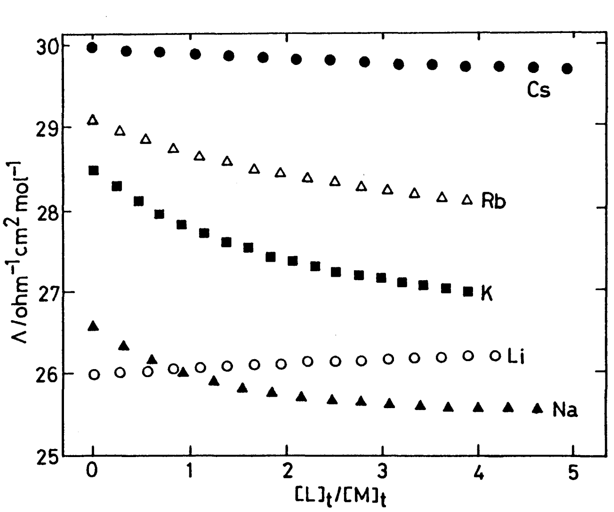


Fig. 2. Λ vs. $[L]_t/[M]_t$ curves for AC·B18C6-alkali metal perchlorate systems in propylene carbonate at 25 °C. $[M]_t$=1.5×10^{-3} mol dm^{-3}.

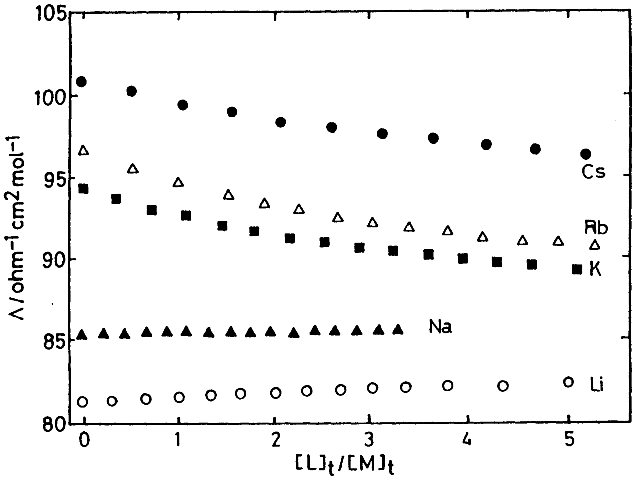


Fig. 3. Λ vs. $[L]_t/[M]_t$ curves for AC·B18C6-alkali metal chloride systems in methanol at 25 °C. $[M]_t=1.5\times10^{-3}$ mol dm^{-3}.

largest and the smallest $\log K_{ML^+}$ values of AC·B18C6 complexes among alkali metal ions in a given solvent is smaller than that of B18C6. Thus, the selectivity of AC·B18C6 for alkali metal ions is lower than that of B18C6. Since AC·B18C6 has two relatively flexible arms, each of which contains three donor ether oxygen atoms, AC·B18C6 may trap the alkali metal ion with the two arms and adopt the most favorable conformation according to the size of the alkali metal ion at the complexation reaction. Thus, since smaller alkali metal ions may attract the donor oxygen atoms of the two arms of AC·B18C6 more strongly than larger alkali metal ions, values of both enthalpy (ΔH°) and entropy (ΔS°) of complexation are expected to be negative and small for smaller alkali metal ions and are expected to be negative and large for larger alkali metal ions. By way of example, values of thermodynamic quantities of pentaethylene glycol dimethyl ether-Na$^+$ and K$^+$ complexes in 99 wt.% methanol at 25 °C are as follows.

	$\log K_{ML^+}$	ΔH°/kJ mol^{-1}	$T\Delta S^\circ$/kJ mol^{-1}
Na$^+$ [11]	1.0	−38.2	−32
K$^+$ [12]	2.27	−34.1	−21.2

However, it seems that differences in ΔH° and ΔS° among AC·B18C6-alkali metal ion complexes are not so large on account of its flexible structure compared with the case of rigid B18C6. The same tendency for ΔH° and ΔS° values is found for relatively rigid 18C6- and flexible dibenzo-24-crown-8-alkali metal ion complexes.[1] Consequently, enthalpy and entropy changes compensate each other, resulting in lower selectivity of AC·B18C6 for alkali metal ions.

The selectivity order of AC·B18C6 for K$^+$, Rb$^+$, and Cs$^+$ is consistent entirely with that of B18C6 (K$^+$> Rb$^+$>Cs$^+$), but the selectivity order of AC·B18C6 for Na$^+$ among alkali metal ions differs from that of B18C6. This shows that, in the cases of K$^+$, Rb$^+$, and Cs$^+$, the size and shape of a pseudocavity formed by the two arms at the ortho position may be similar to those of the B18C6 cavity, and that a smaller Na$^+$ ion may cause a larger conformational change on complexation with AC·B18C6 than K$^+$, Rb$^+$, and Cs$^+$ compared with the case of B18C6.

As can be seen from Table 1, an AC·B18C6-alkali metal ion complex is less stable than the corresponding B18C6 complex in the same solvent. Since the two arms of AC·B18C6 are flexible, the entropy contribution seems to play a more dominant role in destabilizing the AC·B18C6-alkali metal ion complex compared with the case of the corresponding B18C6 complex.

For each of the AC·B18C6-Na$^+$, K$^+$, and Rb$^+$ complexes, the $\log K_{ML^+}$ value in CH_3OH is the smallest of all the solvents, and $\log K_{ML^+}$ values in the three solvents of the AC·B18C6-Cs$^+$ complex are almost the same; however, for each of the B18C6-K$^+$, Rb$^+$, and Cs$^+$ complexes, the $\log K_{ML^+}$ value in CH_3OH is the largest. This may be attributed to stronger hydrogen bonding between uncomplexed AC·B18C6 and CH_3OH compared with the case of B18C6. On the basis of a thermodynamic study on Ni^{2+} complexes in water of tetramine ligands, Hinz and Margerum proposed that a cyclic ligand, being much more compact, is less solvated than a noncyclic, and consequently less energy is expended at its desolvation step.[13] It was reported that, from the data of transfer activity coefficients of Na$^+$, Na$^+$ is solvated most strongly in CH_3OH among all the solvents used here.[7] This may be responsible for the fact that $\log K_{ML^+}$ value of the B18C6-Na$^+$ complex in CH_3OH is the smallest of all the solvents.

Transport Phenomena of AC·B18C6 Complexes. Limiting molar conductivities (Λ_0) of AC·B18C6 complexes determined in this study are as follows:

Λ_0/Ω^{-1} cm^2 mol^{-1} values at 25 °C

	Propylene carbonate	Acetonitrile
(Na·AC·B18C6)ClO_4	26.45±0.09	162.3±0.9
(K·AC·B18C6)ClO_4	26.81±0.08	161.8±0.7

Although, when the two arms of AC·B18C6 form a pseudocavity, the size and shape of AC·B18C6 are similar to those of B18C6, an AC·B18C6-alkali metal ion complex is more mobile than the corresponding B18C6 complex (Table 2). This indicates that the alkali metal ion in the AC·B18C6 complex is coordinated with the two arms, and the surface charge of the alkali metal ion in the AC·B18C6 complex is more effectively shielded than that in the B18C6 complex. The effective shielding seems to be ascribed to high flexibility of the two arms. For Na$^+$, λ^0 values of the complex increase from B18C6 to AC·B18C6 by $10._3$ and $12._0$% in acetonitrile and propylene carbonate, respectively; for K$^+$, λ^0 values of the complex increase from B18C6 to AC·B18C6 by 2.8_3 and 7.9_7% in acetonitrile and propylene carbonate, respectively. For the rate of increase in λ^0 values of the complex from B18C6 to AC·B18C6, Na^+ is much larger than K^+. Since Na^+ is smaller than K^+, Na^+ may attract the two flexible arms of AC·B18C6 more strongly than K^+, resulting in more efficient shielding of Na^+ in the complex by the two arms from surrounding solvent molecules on going from B18C6 to AC·B18C6 compared with the case of K^+.

Mobilities of AC·B18C6-Na^+ and K^+ complexes in acetonitrile are almost the same; λ^0 values of AC·B18C6 and B18C6 complexes in propylene carbonate increase from Na^+ to K^+ by 4.4 and 8.4%, respectively; the λ^0 value of the B18C6 complex in acetonitrile increases by 6.4%. Mobilities of the B18C6 complexes vary with a variety of metal ions in the complexes much more than those of the AC·B18C6 complexes. These data support the above discussion, i.e., much more effective shielding of surface charge of the metal ion in the AC·B18C6 complex owing to the two flexible arms compared with the case of B18C6.

Walden products of the AC·B18C6 complexes with Na^+ and K^+ at 25 °C are as follows:

	Acetonitrile	Propylene carbonate
η_0/mP	3.39[14)]	25.3[14)]
Na^+	0.19_8	0.20_6
K^+	0.19_6	0.21_5

where η_0 denotes viscosity and 1 P = 0.1 Pa s. Walden products of the AC·B18C6-alkali metal ion complexes in propylene carbonate, dielectric constant of which (64.4 at 25 °C[14)]) is larger than that of acetonitrile (35.95 at 25 °C[14)]), are slightly greater than those in acetonitrile.

References

1) G. A. Melson, "Coordination Chemistry of Macrocyclic Compounds," Plenum Press, New York (1979).

2) C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967).

3) G. Chaput, G. Jeminet, and J. Juillard, *Can. J. Chem.*, **53**, 2240 (1975).

4) Y. Takeda, *Bull. Chem. Soc. Jpn.*, **56**, 866 (1983).

5) Y. Takeda, H. Yano, M. Ishibashi, and H. Isozumi, *Bull. Chem. Soc. Jpn.*, **53**, 72 (1980).

6) Y. Takeda and H. Yano, *Bull. Chem. Soc. Jpn.*, **53**, 1720 (1980).

7) Y. Takeda, Y. Ohyagi, and S. Akabori, *Bull. Chem. Soc. Jpn.*, **57**, 3381 (1984).

8) Y. Takeda, *Bull. Chem. Soc. Jpn.*, **58**, 1259 (1985).

9) C. H. Springer, J. F. Coetzee, and R. L. Kay, *J. Phys. Chem.*, **73**, 471 (1969).

10) N. Matsuura, K. Umemoto, and Y. Takeda, *Bull. Chem. Soc. Jpn.*, **48**, 2253 (1975).

11) P. U. Früh and W. Simon, "Protides of the Biological Fluids-20th Colloquium," ed by H. Peeters, Pergamon Press, New York (1973).

12) J. D. Lamb, Ph. D. Dissertation, Brigham Young University, Provo, Utah (1978).

13) F. P. Hinz and D. W. Margerum, *Inorg. Chem.*, **13**, 2941 (1974).

14) G. J. Janz and R. P. T. Tomkins, "Nonaqueous Electrolytes Handbook," Academic Press, New York and London (1972), Vol. 1.