Bull. Chem. Soc. Jpn., *58,* *1259—1261 (1985)*

A Conductance Study of Benzo-18-crown-6- and Its Analogs-Alkali Metal Ion Complexes in Various Solvents

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(Received November 10, 1984)

Limiting ionic molar conductivities of benzo-18-crown-6 (B18C6)-alkali metal ion complexes in various nonaqueous solvents were determined at 25 °C. The mobilities of the B18C6 complexes were compared with those of 18-crown-6 (18C6)- and dibenzo-18-crown-6 (DB18C6)-alkali metal ion complexes. Regardless of varieties of alkali metal ions held in the crown ether cavity, the larger is the size of the crown ether complex, the less mobile the complex is. For aprotic solvents (acetonitrile, DMF, DMSO, propylene carbonate), the mobility of the B18C6-K$^+$ complex is smaller than that of $(n\text{-}C_4H_9)_4N^+$; however, for the protic solvent (methanol), they are almost the same. Walden product value of the B18C6-K$^+$ complex as well as 18C6- and DB18C6-K$^+$ complexes somewhat changes with the variation of solvents. For these three crown ether-K$^+$ complexes, Walden product values of acetonitrile and propylene carbonate are larger than or nearly equal to those of DMF and DMSO. This may indicate that, for the aprotic solvents, donicity is a very important factor in determining the magnitude of mobility of the crown ether-K$^+$ complexes. The B18C6-K$^+$ complex as well as 18C6- and DB18C6-K$^+$ complexes seems to act as a structure breaker in a hydrogen-bonding solvent.

In a previous paper,1) solvation behavior of 1:1 complexes of benzo-18-crown-6 (B18C6) with alkali metal ions in various nonaqueous solvents was studied by transfer activity coefficients. The B18C6–alkali metal ion complex is more strongly solvated in DMF and DMSO than in acetonitrile and propylene carbonate. In methanol, owing to hydrogen bonds between ether oxygen atoms of B18C6 and methanol, the B18C6 complex is more strongly solvated than the corresponding free alkali metal ion, compared to the case of the aprotic solvents.

In this work, in order to investigate solvation property for B18C6–alkali metal ion complexes from the viewpoint of transport phenomena, limiting ionic molar conductivities of B18C6–alkali metal ion complexes in various nonaqueous solvents were determined at 25 °C. The limiting ionic molar conductivities of the B18C6 complexes were compared with those of 18-crown-6 (18C6)- and dibenzo-18-crown-6 (DB18C6)–alkali metal ion complexes, and, moreover, Walden products of these three crown ether complexes were discussed in detail.

Experimental

Most of the reagents, solvents, and procedures were the same as those described previously.1–5) The conductivities of final products of acetonitrile, propylene carbonate, methanol, DMF, and DMSO were less than 2×10^{-7}, 6×10^{-8}, 3×10^{-7}, 3×10^{-7}, and 6×10^{-8} $\Omega^{-1}\,cm^{-1}$, respectively. Alkali metal chlorides were used for the methanol system and perchlorates for the other solvent systems. The conductance measurements were made on a Fuso conductivity apparatus, model 362A, in a water bath thermostated at 25±0.005 °C. Two cells were used with cell constants of 0.059709 and 0.097766 cm^{-1}.

Results and Discussion

Limiting ionic molar conductivities (λ°) of B18C6 complexes with alkali metal ions were obtained in the same way as previously described.2) In this study, it is assumed that the association between a cation and an anion is negligible (total concentration of an alkali metal ion $\approx6\times10^{-4}$ M; 1 M=1 mol dm^{-3}) and that B18C6 forms a 1:1 complex with an alkali metal ion. Corrections for viscosity changes were neglected (total concentration of B18C6$<2.5\times10^{-3}$ M). The λ° values of B18C6 complexes with alkali metal ions in various solvents are listed in Table 1.

It is seen from Table 1 that, for acetonitrile and propylene carbonate, B18C6–alkali metal ion complexes, where the alkali metal ions closely fit into the

Table 1. λ° values in various solvents at 25 °C

	$\lambda^\circ/\Omega^{-1}\,cm^2\,mol^{-1}$				
	CH_3OH	CH_3CN	DMF	DMSO	PC$^{a)}$
18C6-K$^+$	$39.{}_9$$^{5)}$	$59$$^{5)}$ $61.1$$^{6)}$	$24.{}_6$$^{4)}$	$10.{}_0$$^{5)}$	$8.9_1$$^{2)}$
B18C6-Na$^+$	—	$53.{}_1$	—	—	7.2_9
B18C6-K$^+$	$38.{}_4$	$56.{}_5$	$23.{}_0$	$8.{}_7$	7.9_0
B18C6-Rb$^+$	—	$56.{}_1$	—	—	8.1_6
B18C6-Cs$^+$	—	$54.{}_3$	—	—	7.8_8
DB18C6-K$^+$	$35.{}_5$$^{5)}$ $35.63$$^{7)}$ $36.69$$^{7)}$	$53$$^{5)}$ $54.2$$^{6)}$	$22.{}_3$$^{5)}$	$8.{}_2$$^{5)}$	$7.{}_3$$^{5)}$
$(n\text{-}C_4H_9)_4N^+$	$38.94$$^{8)}$	$61.4$$^{9)}$	$26.9$$^{10)}$	$11.2_9$$^{10)}$	$9.32$$^{10)}$
Cl$^-$	$52.36$$^{8)}$	—	—	—	—
ClO_4^-	—	$103.7$$^{9)}$	$52.8_3$$^{4)}$	$24.52$$^{11)}$	$18.2_8$$^{10)}$

a) Propylene carbonate.

TABLE 2. WALDEN PRODUCTS AT 25 °C

	C_2H_5OH	CH_3OH	$C_6H_5NO_2$	CH_3CN	DMF	DMSO	PC[a]	H_2O
η_o/mP* (at 25 °C)[b]	10.84	5.42	18.11	3.39	7.96	19.6	25.3	8.903
DN**[13]	20	19	4.4	14.1	26.6	29.8	15.1	18.0
ε_r*** (at 25 °C)[b]	24.3	32.6	34.82	35.95	36.71	46.6	64.4	78.54
18C6–K^+[5]	—	0.21_6	—	0.20	0.19_5	0.19_6	0.22_5	0.22_5
B18C6–K^+	—	0.20_8	—	0.19_1	0.18_3	0.1_7	0.19_9	—
DB18C6–K^+[5]	0.1995	0.19_2	0.17	0.18	0.17_7	0.16	0.18	—
$(n\text{-}C_4H_9)_4N^+$[5]	0.2132	0.211	0.216	0.208	0.214	0.221	0.236	0.1719

* η_o denotes viscosity and 1 P=0.1 Pa s. ** DN denotes donor number. *** ε_r denotes dielectric constant. a) Propylene carbonate. b) G. J. Janz and R. P. T. Tomkins, "Nonaqueous Electrolytes Handbook," Academic Press, New York and London (1972), Vol. 1.

B18C6 cavity, have larger mobilities. Mobilities of free alkali metal ions in acetonitrile and propylene carbonate increase in the order $Na^+ < K^+ < Rb^+ < Cs^+$.[2,12] This indicates that the central alkali metal ion, which has the optimum size for the B18C6 cavity, is effectively screened by the B18C6 from surrounding solvent molecules; for a smaller or larger alkali metal ion than the B18C6 cavity, the interaction between the ion trapped in the B18C6 cavity and solvent molecules may decrease the mobility of the B18C6–alkali metal ion complex.

The size sequences of the three crown ethers are 18C6<B18C6<DB18C6. For the same solvent, the $\lambda°$ value series of the K^+–crown ether complexes are given in the order DB18C6<B18C6<18C6. This indicates that the mobility sequences of the K^+–crown ether complexes are determined completely by the size ones of the complexes (*i.e.*, the larger is the complex size, the less mobile it is). Limiting ionic molar conductivities at 25 °C of 18C6–Na^+, Rb^+, Cs^+ complexes in propylene carbonate[2] and DB18C6–Na^+, Rb^+ complexes in acetonitrile[6] are 8.5_1, 8.8_6, 8.7_8 and 52.7, 55.5, respectively. It can be seen from these data and Table 1 that a B18C6–alkali metal ion complex is less and more mobile than the corresponding 18C6 complex in propylene carbonate and the corresponding DB18C6 complex in acetonitrile, respectively. This shows that, regardless of varieties of central alkali metal ions, the smaller crown ether–alkali metal ion complex is more mobile than the corresponding larger one.

It is interesting to compare the mobility of a B18C6–K^+ complex with that of $(n\text{-}C_4H_9)_4N^+$. For aprotic solvents (acetonitrile, DMF, DMSO, and propylene carbonate), the $\lambda°$ value of the B18C6–K^+ complex is smaller than that of $(n\text{-}C_4H_9)_4N^+$; however, for the protic solvent (methanol), they are almost the same. A similar tendency was observed for the case of a 18C6–K^+ complex and $(n\text{-}C_4H_9)_4N^+$ and that of a DB18C6–K^+ complex and $(n\text{-}C_5H_{11})_4N^+$.[5] The size of a 18C6–$K^+$ complex is nearly identical with that of $(n\text{-}C_4H_9)_4N^+$.[2] Thus, it can be considered that the B18C6–K^+ complex is larger than $(n\text{-}C_4H_9)_4N^+$ by a benzene ring. For $(n\text{-}C_4H_9)_4N^+$, it is symmetrical and the charge of the nitrogen atom is well shielded; while, for the B18C6–K^+ complex, it is unsymmetrical and there exists a possible interaction of the central K^+ with solvent molecules on two axial sides of the B18C6 plane. From the above discussion, the fact that the B18C6–K^+ complex is less mobile than $(n\text{-}C_4H_9)_4N^+$ in the aprotic solvents may be attributed to the differences in the size and the structure between the B18C6–K^+ complex and $(n\text{-}C_4H_9)_4N^+$. From the results for methanol, it seems that enforcement of the hydrogen-bonded structure for the B18C6–K^+ complex is weaker than that for $(n\text{-}C_4H_9)_4N^+$.

Walden products at 25 °C of the B18C6–K^+ complex for various solvents are compiled in Table 2, together with those from the literature. From the more detailed examination of the data in Table 2, it was concluded that $\lambda°\eta_o$ value of the same crown ether–K^+ complex as well as $(n\text{-}C_4H_9)_4N^+$ somewhat changes with the variation of solvents. For the same crown ether–K^+ complex, $\lambda°\eta_o$ value of DMSO is the smallest and that of DMF is smaller than those of the other solvents except DMSO and nitrobenzene of the DB18C6–K^+ system; $\lambda°\eta_o$ values of acetonitrile and propylene carbonate are larger than or nearly equal to those of DMF and DMSO. Dimethyl sulfoxide and DMF have extremely strong donicity compared to the other solvents listed in Table 2.[13] It thus appears that, for the aprotic solvents (CH_3CN, PC, DMF, DMSO), donicity is a very important factor in determining the magnitude of mobility of the crown ether–K^+ complexes. For $(n\text{-}C_4H_9)_4N^+$, the $\lambda°\eta_o$ value of the aprotic solvent increases with an increase in dielectric constant except nitrobenzene (Table 2). The dielectric constant of nitrobenzene, however, is nearly equal to those of acetonitrile and DMF; the $\lambda°\eta_o$ value of nitrobenzene is smaller than those of propylene carbonate and DMSO, and is slightly larger than that of DMF. Consequently, for the aprotic solvents, the magnitude of mobility of $(n\text{-}C_4H_9)_4N^+$ is considered to be governed largely by the dielectric constant. The difference in factors influencing mobilities of the crown ether–K^+ complexes and $(n\text{-}C_4H_9)_4N^+$ in the aprotic solvents may be attributed to the difference in structures of the cations as mentioned above. For the B18C6–alkali metal ion complex other than the B18C6–K^+ complex, $\lambda°\eta_o$ value of propylene carbonate is larger than or nearly equal to that of acetonitrile. This is the same tendency for the B18C6–K^+ complex.

Generally, mobilities of 18C6-, B18C6-, and DB18C6–K^+ complexes in protic solvents are greater than those in aprotic solvents, and contrary holds for $(n\text{-}C_4H_9)_4N^+$

(Table 2). These results may be caused by the effect of hydrogen-bonded structure of the protic solvents. Methanol and ethanol have larger donicities than propylene carbonate, acetonitrile, and nitrobenzene, and have the smallest dielectric constants of all the solvents; hydrogen bonds between protic solvent molecules and ether oxygen atoms of these crown ethers would decrease the mobility of the crown ether–K^+ complexes; however, for B18C6- and DB18C6–K^+ complexes, $\lambda^\circ\eta_0$ values of the protic solvents are the largest of all the solvents. This suggests that the crown ether–K^+ complexes act as a structure breaker in the protic solvents. For the 18C6–K^+ complex, $\lambda^\circ\eta_0$ value of methanol is smaller than that of propylene carbonate, and on the contrary for B18C6- and DB18C6–K^+ complexes. For B18C6- and DB18C6–K^+ complexes, the difference in $\lambda^\circ\eta_0$ value between methanol and propylene carbonate increases on moving from B18C6 to DB18C6. A possible explanation for this is as follows. On account of lower basicity of aromatic ether oxygen atoms compared to aliphatic ones and steric hindrance caused by a benzo group, the interaction between ether oxygen atoms and methanol molecules may decrease in the order 18C6–K^+>B18C6–K^+> DB18C6–K^+. Thus, the mobility of the 18C6–K^+ complex in propylene carbonate is greater than that in methanol, and the reverse is true for B18C6- and DB18C6–K^+ complexes; moreover, the difference in the mobility of the K^+ complex between methanol and propylene carbonate increases on going from B18C6 to DB18C6. The fact that $\lambda^\circ\eta_0$ value of the 18C6–K^+ complex for water is higher than that for methanol may reflect the difference in characteristics of hydrogen bonds for water (three-dimentional structure) and methanol (one-dimentional structure). The 18C6–K^+ complex seems to act as a structure breaker more effectively in water than in methanol, resulting in the excess mobility in water.

The author would like to thank Professor Sadatoshi Akabori of Toho University for the generous gift of benzo-18-crown-6.

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