A Conductance Study of 18-Crown-6 and Dibenzo-18-crown-6 Complexes with K^+ in Various Solvents

Yasuyuki Takeda
Department of Chemistry, Faculty of Science, Chiba University, Yayoi-chō, Chiba 260

(Received July 7, 1982)

Limiting ionic molar conductivities (λ°) of 18-crown-6 (18C6) and dibenzo-18-crown-6 (DB18C6) complexes with K^+ in several protic and aprotic solvents have been determined at 25 °C. The crystal ionic radius of 18C6 complex with K^+ is nearly identical with that of tetrabutylammonium ion ($(n\text{-}C_4H_9)_4N^+$). For CH_3OH, the mobility of the 18C6 complex with K^+ is nearly equal to that of $(n\text{-}C_4H_9)_4N^+$. However, for H_2O, the former is much larger than the latter, but the contrary is true for aprotic solvents. Walden products of 18C6 complexes with K^+ for the solvents are nearly equal to each other. For acetonitrile and DMSO, the λ° value of the DB18C6 complex with K^+ is smaller than those for the tetrapentylammonium ion ($(n\text{-}C_5H_{11})_4N^+$) and for the tetraisopentylammonium ion ($(i\text{-}C_5H_{11})_4N^+$). For nitrobenzene and propylene carbonate, that of the DB18C6 complex with K^+ is smaller than those of $(n\text{-}C_5H_{11})_4N^+$ and $(i\text{-}C_5H_{11})_4N^+$, respectively. In contrast to the case of the aprotic solvents, the λ° value of the DB18C6 complex with K^+ for CH_3OH is nearly equal to those of $(n\text{-}C_5H_{11})_4N^+$ and $(i\text{-}C_5H_{11})_4N^+$. Walden products of the DB18C6 complexes with K^+ for the solvents are nearly equal to each other. From the above data, it appears that a solute which contains a unit of 18C6 in its structure does not enforce a hydrogen-bonded structure for a protic solvent.

Stabilities and selectivities on complexation of 18-crown-6 (18C6) and dibenzo-18-crown-6 (DB18C6) with alkali metal ions in various solvents have been studied in detail.[1-5] However, the behavior of these crown ether complexes in various solvents has scarcely been investigated systematically.

In the present work, limiting ionic molar conductivities of 18C6 and DB18C6 complexes with K^+ in several protic and aprotic solvents have been determined at 25 °C; the limiting ionic molar conductivities of the crown ether complexes have been compared with those of tetraalkylammonium ions in order to investigate the behavior of the crown ether complexes in the solutions.

Experimental

Materials. 18-Crown-6 (Nisso Co., Ltd.) was recrystallized three times from acetonitrile and dried at 70 °C in a vacuum oven before use. DB18C6 (Aldrich Chemical Co., Inc.) was dissolved in chloroform, and filtered while hot. It was then recrystallized four times from benzene and dried at 60 °C in a vacuum oven prior to use. Potassium perchlorate and chloride were obtained from Merck Japan Ltd. The potassium perchlorate was recrystallized twice from water and dried at 150 °C in a vacuum oven prior to use. The potassium chloride was used without further purification. The method of purification of *N,N*-dimethylformamide (DMF),[5] methanol,[6] and propylene carbonate[3] was as has previously been described. Acetonitrile and dimethyl sulfoxide (DMSO) were allowed to stand in contact with molecular sieves for several days. The acetonitrile was then distilled twice and DMSO twice under nitrogen at about 1.8 kPa. In the case of each of these five solvents, the middle 70% of the distillate was used. The water contents of the purified acetonitrile, propylene carbonate, DMF, and DMSO determined by means of the Karl Fischer titration were less than 0.01%, and, in the case of CH_3OH, less than 0.03%. The conductivities of these final products of acetonitrile, propylene carbonate, H_2O, CH_3OH, DMF, and DMSO were less than 2×10^{-7}, 5×10^{-8}, 5×10^{-7}, 2×10^{-7}, 3×10^{-7}, and $8\times10^{-8}\ \Omega^{-1}\ cm^{-1}$, respectively.

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 0.059707, 0.093936, and 0.20461 cm^{-1}. The experimental procedure to obtain complex-formation constants and limiting ionic molar conductivities of 18C6 and DB18C6 complexes with a potassium ion was described in the previous paper.[3]

Results and Discussion

The procedure for obtaining the complex-formation constants, K_{ML^+}, and limiting ionic molar conductivities, λ°, of 18C6 and DB18C6 complexes with K^+ was the same as that described in the previous study.[3] M^+ and L denote an alkali metal ion and a crown ether respectively. In this work, it is assumed that the association between a cation and an anion is negligible under these highly dilute experimental conditions and that crown ethers form 1:1 complexes with K^+. Since concentrations of crown ethers were kept low ($<2.0\times10^{-3}$ M; 1 M=1 mol dm^{-3}) during these experiments, corrections for viscosity changes were neglected. The K_{ML^+} and the limiting molar conductivity, Λ°, values of 18C6 and DB18C6 complexes with potassium salts in various solvents are listed in Table 1.

As can be seen from Table 2, in the cases of K^+, 18C6 and DB18C6 complexes with K^+, the λ° value decreases with an increase in the size of the cation for each solvent system. It is interesting to note that the 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane ((2,2)) complex with K^+ is more mobile than the 18C6 complex with K^+ in acetonitrile, although the size and cavity size of (2,2) are nearly the same as those of 18C6. The author cannot explain this phenomenon at present. Both dibenzo-24-crown-8 (DB24C8) and DB18C6 have two benzene rings, and DB24C8 is larger than DB18C6. However, the λ° value of DB24C8 complex with K^+ in propylene carbonate is nearly equal to that of DB18C6 complex. Since DB24C8 has a flexible structure and a large cavity, the potassium ion trapped in the cavity is surrounded by DB24C8. Thus, the potassium ion held in the DB24C8

Table 1. K_{ML^+} and Λ° values of 18C6 and DB18C6 complexes with potassium salts in various solvents at 25 °C

Solvent	Crown ether–Salt	K_{ML^+} / $mol^{-1}\,dm^3$	Λ° / $\Omega^{-1}\,cm^2\,mol^{-1}$
CH_3CN	18C6–$KClO_4$	5.2×10^5	163
	DB18C6–$KClO_4$	6.3×10^4	157
PC[a)]	18C6–$KClO_4$	1.6×10^6 [3)]	27.1_9[3)]
	DB18C6–$KClO_4$	1.4×10^5 [4)]	$25._6$
H_2O	18C6–KCl	1.11×10^2 [2)]	$101._7$
CH_3OH	18C6–KCl	1.2×10^6	$92._3$
	DB18C6–KCl	1.2×10^5	$87._9$
DMF	18C6–$KClO_4$	2.0×10^4 [5)]	$77._4$[5)]
	DB18C6–$KClO_4$	6.3×10^2 [4)]	$75._1$
DMSO	18C6–$KClO_4$	1.9×10^3	$34._6$
	DB18C6–$KClO_4$	3.3×10^2	$32._8$

a) Propylene carbonate.

cavity may be effectively screened by DB24C8. On the contrary, since DB18C6 has a rigid structure and an optimum cavity size for K^+, solvent molecules may be able to interact with central K^+ in the DB18C6 cavity in the direction perpendicular to the plane of the DB18C6. This is the reason why the mobilities of the DB24C8 and the DB18C6 complexes with K^+ in propylene carbonate are nearly equal.

The crystal ionic radius of 18C6 complex with K^+ (4.9 Å[3)]) is nearly identical with that of tetrabutylammonium ion, $(n\text{-}C_4H_9)_4N^+$, (4.94 Å[20)]). For CH_3OH, the mobility of the 18C6 complex with K^+ is nearly equal to that of $(n\text{-}C_4H_9)_4N^+$; however, for H_2O, the former is much larger than the latter, contrary to the aprotic solvents (acetonitrile, DMF, DMSO, and propylene carbonate) (Table 2). In the case of $(n\text{-}C_4H_9)_4N^+$, the surface charge of the central nitrogen atom is effectively shielded by four butyl groups, while, for the 18C6 complex with K^+, K^+ trapped in the 18C6 cavity is exposed to solvent molecules on two axial sides of the 18C6 plane. Thus, the interaction between cation and solvent dipole seems to be stronger for 18C6 complex with K^+ than for $(n\text{-}C_4H_9)_4N^+$. Consequently, since the aprotic solvents have no hydrogen-bonded structures, $(n\text{-}C_4H_9)_4N^+$ is more mobile than 18C6 complex with K^+ in these aprotic solvents. In hydrogen-bonding solvents such as H_2O and CH_3OH, enforcement of a hydrogen-bonded structure for hydrophobic butyl groups of $(n\text{-}C_4H_9)_4N^+$ decreases the mobility of $(n\text{-}C_4H_9)_4N^+$. Although the 18C6 complex with K^+ would undergo specific solvation than $(n\text{-}C_4H_9)$ N^+ much more strongly as is stated above and, moreover, hydrogen bonds between protic solvent molecules and ether oxygen atoms of 18C6 would decrease the mobility of the 18C6 complex with K^+, the 18C6 complex is much more mobile than $(n\text{-}C_4H_9)_4N^+$ in H_2O and is nearly as mobile as $(n\text{-}C_4H_9)_4N^+$ in CH_3OH (Table 2). This indicates that the 18C6 complex with K^+ in H_2O and CH_3OH does not enforce the hydrogen-bonded structure around the complexed ion like $(n\text{-}C_4H_9)_4N^+$ does. This is supported by the data in Table 3. As can be seen from Table 3, Walden products of 18C6 complexes with K^+ for the solvents are nearly equal to each other, while, that of $(n\text{-}C_4H_9)_4N^+$ for H_2O is much smaller than those of $(n\text{-}C_4H_9)_4N^+$ for the other solvents and those of $(n\text{-}C_4H_9)_4N^+$ for the other solvents are nearly identical. Judging from the above observations, the 18C6 complex with K^+ appears to act as a structure breaker in hydrogen-bonding solvents, and the complex shows almost the same behavior for transport phenomena in all the solvents in Table 3. The ratio of λ° value of the 18C6 complex with K^+ to that of $(n\text{-}C_4H_9)_4N^+$ for H_2O (1.3) is much larger than that for CH_3OH (1.0) (Table 2). This may reflect a difference in characteristics of hydrogen bonds for H_2O and CH_3OH. Since H_2O forms three-dimentional structures *via* hydrogen bonding, while, CH_3OH can form only one-dimentional structures *via* hydrogen bonding, the effect of hydrogen-bonded structure enforcement on the mobility of $(n\text{-}C_4H_9)_4N^+$ appears to be much greater for H_2O than for CH_3OH.

As can be seen from Table 2, for acetonitrile and DMSO, the λ° value of DB18C6 complex with K^+ is smaller than those of tetrapentylammonium ion ($(n\text{-}C_5H_{11})_4N^+$) and tetraisopentylammonium ion ($(i\text{-}C_5H_{11})_4N^+$); for nitrobenzene and propylene carbonate, that of DB18C6 complex with K^+ is smaller

Table 2. λ° values in various solvents at 25 °C

	$\lambda^\circ/\Omega^{-1}\,cm^2\,mol^{-1}$							
	C_2H_5OH	CH_3OH	$C_6H_5NO_2$	CH_3CN	DMF	DMSO	PC[a)]	H_2O
K^+	23.55[7)]	52.44[7)]	17.53[8)]	83.6[9)]	30.6_7[5)]	14.69[10)]	11.9_8[3)]	73.55[7)]
18C6–K^+	—	$39._9$	—	59	$24._6$[5)]	$10._0$	8.9_1[3)]	$25._3$
DB18C6–K^+	18.40[11)]	$35._5$	9.6[12)]	53	$22._3$	$8._2$	$7._3$	—
(2,2)–K^+	—	—	—	62.4[13)]	—	—	—	—
DB24C8–K^+	—	—	—	—	—	—	7.4_2[3)]	—
$(n\text{-}C_4H_9)_4N^+$	19.67[14)]	38.94[7)]	11.9[15)]	61.4[9)]	26.9[16)]	11.2_9[16)]	9.32[16)]	19.31[7)]
$(n\text{-}C_5H_{11})_4N^+$	—	34.8[17)]	10.6[18)]	55.1[19)]	—	10.41[20)]	—	—
$(i\text{-}C_5H_{11})_4N^+$	—	35.2_6[21)]	—	57.24[8)]	—	10.61[20)]	8.185[22)]	—
$(n\text{-}C_7H_{15})_4N^+$	14.93[14)]	—	—	—	—	9.18[20)]	—	—
ClO_4^-	—	—	—	103.7[9)]	52.8_3[5)]	24.52[10)]	18.2_8[16)]	67.2[23)]
Cl^-	—	52.36[7)]	—	—	—	—	—	76.39[7)]

a) Propylene carbonate.

TABLE 3. WALDEN PRODUCTS AND VISCOSITIES (η_0) AT 25 °C

	C_2H_5OH	CH_3OH	$C_6H_5NO_2$	CH_3CN	DMF	DMSO	PC[a)]	H_2O
η_0/mP*	10.84[14]	5.42[24]	18.11[24]	3.39[24]	7.96[24]	19.6[24]	25.3[24]	8.903[24]
18C6-K^+	—	0.21_6	—	0.20	0.19_5[5]	0.19_6	0.22_5[3]	0.22_5
DB18C6-K^+	0.1995[11]	0.19_2	0.17[12]	0.18	0.17_7	0.16	0.18	—
$(n\text{-}C_4H_9)_4N^+$	0.2132[14]	0.211[7]	0.216[15]	0.208[9]	0.214[16]	0.221[16]	0.236[16]	0.1719[7]

* 1 P=0.1 Pa s. a) Propylene carbonate.

than those of $(n\text{-}C_5H_{11})_4N^+$ and $(i\text{-}C_5H_{11})_4N^+$, respectively. In contrast to the cases of aprotic solvents, the λ° value of DB18C6 complex with K^+ for CH_3OH is nearly equal to those of $(n\text{-}C_5H_{11})_4N^+$ and $(i\text{-}C_5H_{11})_4N^+$. For DMSO, the DB18C6 complex with K^+ is not so mobile as tetraheptylammonium ion ($(n\text{-}C_7H_{15})_4N^+$), and contrary holds for C_2H_5OH. The fact that, for every aprotic solvent, the DB18C6 complex with K^+ is less mobile than these tetraalkylammonium ions can be attributed to the fact that the former would undergo specific solvation much more strongly than the latter, as is stated above. The results for protic solvents indicate that the effect of hydrogen-bonded structure enforcement on the mobility is very much larger for these tetraalkylammonium ions than for the DB18C6 complex with K^+. Walden products of DB18C6 complexes with K^+ are nearly equal to each other (Table 3). Thus, it seems that the behavior of the DB18C6 complex with K^+ for transport phenomena is much the same in the various solvents.

From the above discussion, it appears that a solute which contains a unit of 18C6 in its structure does not enforce hydrogen-bonded structure of a protic solvent.

References

1) D. F. Evans, S. L. Wellington, J. A. Nadis, and E. L. Cussler, *J. Solution Chem.*, **1**, 499 (1972).

2) H. Høiland, J. A. Ringseth, and T. S. Brun, *J. Solution Chem.*, **8**, 779 (1979).

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

4) I. M. Kolthoff and M. K. Chantooni, Jr., *Anal. Chem.*, **52**, 1039 (1980).

5) Y. Takeda, *Bull. Chem. Soc. Jpn.*, **54**, 3133 (1981).

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

7) R. L. Kay and D. F. Evans, *J. Phys. Chem.*, **70**, 2325 (1966).

8) J. F. Coetzee and G. P. Cunningham, *J. Am. Chem. Soc.*, **87**, 2529 (1965).

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

10) R. Gopal and J. S. Jha, *J. Phys. Chem.*, **78**, 2405 (1974).

11) M. S. Frant and J. W. Ross, *Science*, **167**, 987 (1970).

12) T. Iwachido, M. Kimura, and K. Tōei, *Chem. Lett.*, **1976**, 1101.

13) S. Kulstad and L. Å. Malmsten, *J. Inorg. Nucl. Chem.*, **42**, 573 (1980).

14) D. F. Evans and P. Gardam, *J. Phys. Chem.*, **72**, 3281 (1968).

15) C. R. Wischonke and C. A. Kraus, *J. Am. Chem. Soc.*, **69**, 2472 (1947).

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

17) R. L. Kay, C. Zawoyski, and D. F. Evans, *J. Phys. Chem.*, **69**, 4208 (1965).

18) E. G. Taylor and C. A. Kraus, *J. Am. Chem. Soc.*, **69**, 1731 (1947).

19) A. C. Harkness and H. M. Daggett, Jr., *Can. J. Chem.*, **43**, 1215 (1965).

20) D. E. Arrington and E. Griswold, *J. Phys. Chem.*, **74**, 123 (1970).

21) R. L. Kay, D. F. Evans, and G. P. Cunningham, *J. Phys. Chem.*, **73**, 3322 (1969).

22) L. M. Mukherjee, D. P. Boden, and R. Liendauer, *J. Phys. Chem.*, **74**, 1942 (1970).

23) A. D'Aprano, *J. Phys. Chem.*, **75**, 3290 (1971).

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