October, 1981] © *1981 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 54, 3133—3136 (1981)* 3133

A Conductance Study of Alkali Metal Ion-18-Crown-6 Complexes in *N,N*-Dimethylformamide

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(Received February 5, 1981)

The formation constants, K_{ML^+}, for 1 : 1 complexes of 18-crown-6 (18C6) with alkali metal ions (Na^+, K^+, Rb^+, and Cs^+) and the limiting ionic molar conductivities, λ°, of the complexed cations in *N,N*-dimethylformamide have been determined conductometrically at 25 °C. The K_{ML^+} sequences of the alkali metal ions with 18C6 are $K^+ > Rb^+ > Cs^+ > Na^+$. The stabilities and selectivities on complexation are governed by the solvent medium and the relative sizes of the cation and the 18C6 cavity. The λ° values of the 18C6 complexes with the alkali metal ions are all approximately equal except for Cs^+, suggesting that, in the cases of Na^+, K^+, and Rb^+, the charge of the alkali metal ion trapped in the 18C6 cavity is effectively screened by 18C6, while this is not true in the case of Cs^+. The ratio of the size of the alkali metal ion to that of the 18C6 cavity appears to be an important factor in determining the magnitude of λ° for alkali metal ion–18C6 complexes.

Complexation reactions of 18-crown-6 (18C6) with alkali metal ions in various solvents have been investigated from the thermodynamic point of view by several different methods, *e.g.* conductance,[1,2] calorimetry,[3,4] potentiometry,[5,6] and spectroscopy.[7,8] The stabilities and selectivities on complexation are governed by the solvent medium and the relative sizes of the cation and the 18C6 cavity.

In the present study, the formation constants for 1 : 1 complexes of 18C6 with alkali metal ions and the limiting ionic molar conductivities of the alkali metal ion–18C6 complexes in *N,N*-dimethylformamide (DMF) have been determined conductometrically at 25 °C; the complex-formation constants have been compared with those in other solvents in order to clarify the factors influencing the magnitude of the complex-formation constant; on the basis of the data for the limiting ionic molar conductivities of the alkali metal ion–18C6 complexes, the behavior of the complexes in DMF has been discussed.

Experimental

Materials. 18C6 (Nisso Co., Ltd.) was recrystallized from acetonitrile and, prior to use, dried at 70 °C in a vacuum oven. The rubidium and caesium perchlorates were prepared by adding an equimolar perchloric acid solution to aqueous solutions of rubidium and caesium chlorides respectively. The lithium, sodium, and potassium perchlorates were purchased commercially. All the perchlorates were recrystallized from water four times and, prior to use, dried at 150 °C in a vacuum oven. The DMF was distilled twice under nitrogen at approx. 12 mmHg.† The middle 70% of the distillate was used. The water content of the finally purified DMF, as determined by Karl Fischer titration, was less than 0.01%. The conductivity of the final product was less than 1×10^{-7} Ω^{-1} cm^{-1}.

Apparatus and Procedure. The conductance measurements were conducted on a Yanagimoto conductivity apparatus, model MY-7, in a water bath thermostated at 25.00±0.01 °C. Three cells were used with cell constants of 0.05971, 0.09393, and 0.09776 cm^{-1}.

The experimental procedure to obtain the formation constants and the limiting ionic molar conductivities of 18C6 complexes with alkali metal ions was just the same as that described in a previous paper.[2]

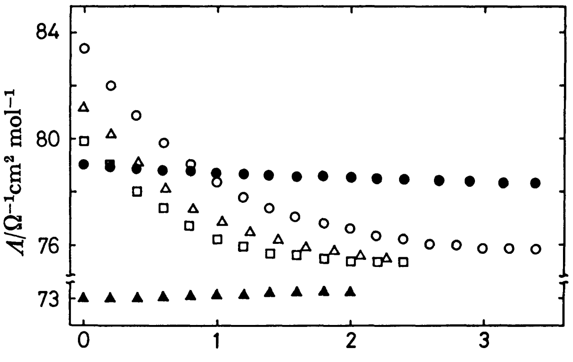

Fig. 1. Λ *vs.* $[L]_t/[M]_t$ curves for 18C6–alkali metal perchlorate systems in DMF at 25 °C.
▲: Li^+, ●: Na^+, □: K^+, △: Rb^+, ○: Cs^+, $[M]_t=5\times10^{-4}$ M.

Results

The molar conductivity, Λ, *vs.* $[L]_t/[M]_t$ plots in DMF at 25 °C are given in Fig. 1, where $[L]_t$ and $[M]_t$ are the total concentrations of 18C6 and the alkali metal ion respectively. The Λ *vs.* $[L]_t/[M]_t$ plots show a decrease in Λ with an increase in the 18C6 concentration, except for Li^+. In the case of Li^+, a very small increase in Λ is found with an increase in the 18C6 concentration. However, since the change in Λ is very small, the conductometric determination of the complex formation constant is impossible. It is assumed that the association between the cation and the perchlorate ion in DMF is negligible under these highly dilute experimental conditions and that, in this work, 18C6 forms the 1 : 1 complexes with the alkali metal ions in DMF. Since the 18C6 concentration was kept low ($<2.0\times10^{-3}$ M; 1 M=1 mol dm^{-3}) during these experiments, corrections for viscosity changes were neglected. The procedure for obtaining the complex-formation constant, K_{ML^+}, and the limiting ionic molar conductivity, λ°, of the alkali metal ion-18C6 complex was just the same as that described in a previous paper.[2] M^+ and L denote the alkali metal ion and 18C6 respectively. The log K_{ML^+} and the λ° values of the alkali metal ion–18C6 complexes are listed in Tables 1 and 2, together

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† 1 mmHg≈133.322 Pa.

Table 1. $\log (K_{\mathrm{ML}}^+/\mathrm{mol^{-1}\,dm^3})$ values at 25 °C and crystal ionic radii of alkali metals (Å)

		Na^+	K^+	Rb^+	Cs^+
Crystal ionic radius[14]		0.95	1.33	1.48	1.69
AN	18C6	4.5_5[5]	5.7_0[5]		>4[7]
	DB18C6	4.8_5[5] 5.0_0[15] 5.0[16]	4.8_1[5] 4.7_0[15] 4.8[16]	3.7_0[15]	3.5_9[5] 3.5_0[15]
PC	18C6	5.6_8[2] 5.2_5[5]	6.2_4[2] 6.3_2[5]	5.3_2[2]	4.4_8[2] 4.5_2[5] 4.2[7]
	DB18C6	5.2_0[5]	5.1_3[5]	3.9_1[5]	3.3_1[5]
H_2O	18C6	0.8_0[3] 0.8_2[17]	2.0_3[3] 2.04_7[17] 2.0_6[6]	1.5_6[3]	1.0[3] 0.9_8[17] 0.8[6]
	DB18C6	1.1_6[18] 1.1[5]	1.6_7[18] 1.6[5]	1.0_8[18]	0.8_3[18]
CH_3OH	18C6	4.3_2[6] 4.3_6[4]	6.1[6] 6.0_5[4]		4.6_2[6]
	DB18C6	4.3_6[6] 4.4[5] 4.5[10]	5.0_0[6] 5.0_5[5] 5.1[10] 4.6_0[15] 4.6[16]	4.2_3[5]	3.5_5[6]
DMF	18C6	2.4	4.3_1	3.9_8	3.6_7 3.9[7]
	DB18C6	2.4[5] 2.8_0[19]	2.8[5]	2.1[5]	1.5[7]
DMSO	18C6	1.4_3[5]	3.2_1[5]		3.0[7]
	DB18C6	1.9_3[5]	2.4_6[5] 2.5[20]	1.9[5]	1.3[7]

with the literature values and the $\lambda°$ values of the alkali metal and perchlorate ions in DMF at 25 °C respectively.

Discussion

As can be seen from Table 1, in the case of each crown ether-solvent system, except for Na^+, the more closely the alkali metal ion fits into the crown ether cavity (18C6 cavity radius: 1.3—1.6 Å[9]), the more stable is the alkali metal ion–crown ether complex. Of all the alkali metal ion–18C6 complexes in the same solvent, the $\log K_{\mathrm{ML}}^+$ value of the Na^+–18C6 complex is the second largest for acetonitrile (AN) and propylene carbonate (PC); however, it is the smallest for H_2O, CH_3OH, DMF, and DMSO. The $\log K_{\mathrm{ML}}^+$ value of the Na^+–dibenzo-18-crown-6 (DB18C6) complex is the largest for AN and PC, and the second largest for H_2O, CH_3OH, DMF, and DMSO. The difference in the $\log K_{\mathrm{ML}}^+$ values of Na^+ and K^+ with 18C6 about the same solvent is larger for H_2O, CH_3OH, DMF, and DMSO than for AN and PC. The difference in the $\log K_{\mathrm{ML}}^+$ values of Na^+ and Rb^+ with DB18C6 in relation to the same solvent is larger for AN and PC than for H_2O, CH_3OH, DMF, and DMSO; the same tendency is observed for the Na^+ and Cs^+ with the DB18C6 system. A possible interpretation for this is that, in every one of these solvents, Na^+ is the most strongly solvated of all the alkali metal ions (Na^+, K^+, Rb^+, and Cs^+), and that the differences in the free energies of the solvation of Na^+ and K^+, Na^+ and Rb^+, and Na^+ and Cs^+ are much smaller for AN and PC than for the others.[5]

The strength of the interaction of the alkali metal ion with the donor oxygen atoms of the crown ether is due to the basicity of the donor oxygen atoms. Since the aromatic ether oxygen atom is less basic than the aliphatic one, and since DB18C6 has four aromatic ether oxygen atoms, the stability of the DB18C6 complex with the same alkali metal ion may be lower than that of the 18C6 complex. For the same solvent, the $\log K_{\mathrm{ML}}^+$ value of the DB18C6 complex with the same alkali metal ion is smaller than that of the 18C6 complex except in the case of Na^+, which is consistent with this expectation; however, the $\log K_{\mathrm{ML}}^+$ value of the Na^+–DB18C6 complex is large for AN, H_2O, and DMSO, and nearly identical for PC, CH_3OH, and DMF, compared with 18C6 (Table 1). This result is unexpected. Because the charge density of Na^+ is the largest of all the alkali metal ions (Na^+, K^+, Rb^+, and Cs^+), Na^+ may attract the donor oxygen atoms of the crown ether much more strongly than the others. Thus, when a complexation reaction occurs between a flexible crown ether and the alkali metal ion, the greatest ligand-ring conformational change may be observed in the case of Na^+. Consequently, since 18C6 is more flexible than DB18C6, the 18C6 complex with Na^+ may be entropy destabilized much more than the DB18C6 complex, resulting in the small or nearly the same $\log K_{\mathrm{ML}}^+$ value of the Na^+–18C6 complex compared with DB18C6. This explanation may be supported by the following data. The values of the enthalpy ($\Delta H/\mathrm{kJ\,mol^{-1}}$) and entropy changes ($\Delta S/\mathrm{J\,K^{-1}\,mol^{-1}}$) in methanol are −35.0 and −34 for the Na^+–18C6 system,[4] −31.3 and −18.8 for the Na^+–DB18C6 system,[10] −56.13 and −72.4 for the K^+–18C6 system,[4] and −40.1 and −36.7 for the K^+–DB18C6 system[10] respectively. The reason why, in each case of Na^+ and K^+, the $-\Delta H$ value of DB18C6 is small and the $-\Delta S$ value of DB18C6 is very small compared with 18C6 may be largely due to the four aromatic ether oxygen atoms and the more rigid structure of DB18C6 respectively. Compared to DB18C6, the greater stability of the K^+–18C6 complex entirely depends on the much larger $-\Delta H$ value of the K^+–18C6 complex. However, in the case of Na^+, compared to DB18C6, the larger $-\Delta H$ value of 18C6 is greatly canceled by the much more unfavorable ΔS value of 18C6, resulting in the smaller $\log K_{\mathrm{ML}}^+$ value of 18C6. For H_2O, CH_3OH, DMF, and DMSO, the $\log K_{\mathrm{ML}}^+$ value of Na^+ with DB18C6 is the second largest; however, that with 18C6 is the smallest of all the alkali metal ions. Similarly, for AN and PC, that with DB18C6 is the largest; however, that with 18C6 is the second largest (Table 1). This may indicate that, from DB18C6 to 18C6, the Na^+ complex is much more entropy destabilized than the other alkali metal ion complexes because the structure of 18C6 is more flexible than that of DB18C6.

The solvation power sequences of the solvents for the same alkali metal ion are as follows:

Na^+: $PC<AN<CH_3OH<H_2O<DMF<DMSO$,
K^+: $CH_3OH<PC<AN<H_2O<DMF<DMSO$,
Rb^+: $CH_3OH<PC<AN<H_2O<DMF<DMSO$,

Cs^+: $CH_3OH < PC < AN < H_2O < DMF < DMSO$.[5]
The solvation power sequences of the aprotic solvents for the same alkali metal ion are $PC < AN \ll DMF < DMSO$,[5] while, for both 18C6 and DB18C6, the $\log K_{ML^+}$ value sequences of the aprotic solvents about the same alkali metal ion are completely the reverse except that, for the Cs^+–DB18C6 system, the $\log K_{ML^+}$ value of AN is larger than that of PC (Table 1). For the aprotic solvents, between the group of PC and AN, and that of DMF and DMSO, there is a very great difference in the solvation power for the same alkali metal ion, and also a large difference in the $\log K_{ML^+}$ value with regard to the same alkali metal ion in every system except for the Cs^+–18C6 system. These results indicate that, for the same alkali metal ion, the solvation power of the aprotic solvent is a very important factor in determining the K_{ML^+}-value sequences of the aprotic solvents for both 18C6 and DB18C6. For both 18C6 and DB18C6, the $\log K_{ML^+}$ value of CH_3OH about the same alkali metal ion gains in ranking in these solvents with an increase in the size of the alkali metal ion. This may reflect the fact that, of all the solvents, the solvation power of CH_3OH for Na^+ is the third smallest, while those for K^+, Rb^+, and Cs^+ are the smallest. It is interesting that, although the solvation power of H_2O for the same alkali metal ion is the third largest of all the solvents, the $\log K_{ML^+}$ value of H_2O is the smallest for every alkali metal ion–crown ether system (Table 1).

TABLE 2. ($\lambda^\circ/\Omega^{-1}\,cm^2\,mol^{-1}$) VALUES OF ALKALI METAL ION–18C6 COMPLEXES, ALKALI METAL IONS, AND A PERCHLORATE ION IN DMF AT 25 °C

Ion	$\lambda^\circ/\Omega^{-1}\,cm^2\,mol^{-1}$	
		M^+–18C6
Na^+	29.7_9	24
K^+	30.6_7	$24._6$
Rb^+	32.4_3	$24._3$
Cs^+	34.7_2	$23._4$
ClO_4^-	52.8_3	

Table 2 shows that the λ° value of the alkali metal ion-18C6 complex is much smaller than that of the corresponding alkali metal ion, indicating that the alkali metal ion–18C6 complex is much bulkier than the corresponding alkali metal ion in DMF. The λ° values of the 18C6 complexes with the alkali metal ions are approximately equal except for Cs^+ (Table 2). From the data, it appears that, in the cases of Na^+, K^+, and Rb^+, the charge of the alkali metal ion trapped in the 18C6 cavity is effectively screened by the 18C6 and that the 18C6 complexes with the alkali metal ions are nearly equal to each other in size in DMF. Since Cs^+, whose size is larger than the cavity size of 18C6, cannot get into the plane of the oxygen atoms of 18C6, Cs^+ may protrude from the plane of 18C6. Thus, the exposed part of Cs^+ in the 18C6 complex may strongly interact with the DMF molecules. This may be the reason why the λ° value of the Cs^+–18C6 complex is smaller than those of the others. Judging from the above observations, the ratio of the size of the alkali metal ion to that of the 18C6 cavity appears to be an important factor in determining the magnitude of λ° for alkali metal ion–18C6 complexes.

TABLE 3. STOKES' RADII, R_s, AND CRYSTAL IONIC RADII, R_c, OF ALKALI METAL ION–18C6 COMPLEXES (Å)

Cation	R_c/Å	R_s/Å	
		DMF	PC[2]
Na^+	4.8	4.3	3.8_0
K^+	4.9	4.1_8	3.6_3
Rb^+	4.9	4.2_3	3.6_5
Cs^+	4.9	4.4_0	3.6_9

The crystal ionic radii, $R_C(ML^+)$, of the alkali metal ion–18C6 complexes may be approximately evaluated from the crystal ionic radii, $R_C(M^+)$, of the alkali metal ions held in the 18C6 cavity and from the 18C6 volume, V:

$$R_c(ML^+) = \{R_c(M^+)^3 + 3V/4\pi\}^{1/3}.$$

V may be approximated by summing the van der Waals volumes of the atoms or groups forming 18C6. The $R_c(ML^+)$ values are given in Table 3, together with the Stokes' radii, $R_s(ML^+)$, of the alkali metal ion–18C6 complexes calculated from this equation: $R_s(ML^+) = 0.819/\eta_0\lambda^\circ$, where η_0 is the viscosity of the pure solvent. For the same alkali metal ion–18C6 complex, the R_s value of DMF, whose dielectric constant (36.71 at 25 °C[11]) is smaller than PC (64.4 at 25 °C[11]), is larger than that of PC. The crystal ionic radii of the alkali metal ion–18C6 complexes are nearly equal to that of a tetrabutylammonium ion (4.94 Å[12]) (Table 3). The λ° values of the alkali metal ion–18C6 complexes are, however, smaller than that of the tetrabutylammonium ion (26.9[13]) (Table 2). This is the same tendency as that found in the alkali metal ion–18C6 complex–PC system.[2] Since, in the case of the tetrabutylammonium ion, four butyl groups effectively shield the surface charge of the central nitrogen atom, while, in the case of the alkali metal ion–18C6 complex, solvent contacts with the alkali metal ion trapped in the 18C6 cavity are still possible in the direction perpendicular to the plane of 18C6, the alkali metal ion–18C6 complex would much more strongly undergo specific solvation than the tetrabutylammonium ion. This may be the reason why the λ° value of the alkali metal ion–18C6 complex is smaller than that of the tetrabutylammonium ion for both DMF and PC.

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