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Thermodynamic Study for Complexation Reactions of Dibenzo-24-crown-8 with Alkali Metal Ions in Acetonitrile

Yasuyuki TAKEDA,*Yasuki KUDŌ, and Shizuo FUJIWARA
Department of Chemistry, Faculty of Science, Chiba University, Yayoi-chō, Chiba 260

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Synopsis. Formation constants for 1:1 complexes of dibenzo-24-crown-8 with alkali metal ions in acetonitrile have been determined by conductometry at different temperatures. Enthalpy (ΔH°) and entropy changes (ΔS°) were calculated. All the ΔH° and ΔS° values are negative. The $-\Delta H^\circ$ and $-\Delta S^\circ$ sequences are $Na^+ > Cs^+ > Rb^+ > K^+$ and $Na^+ \geq Cs^+ > Rb^+ > K^+$, respectively.

In the previous papers,1,2) enthalpy (ΔH°) and entropy changes (ΔS°) of a 1:1 dibenzo-24-crown-8 (DB24C8) complex with an alkali metal ion in propylene carbonate and methanol, and transfer activity coefficients of the complex among nonaqueous solvents were determined. Behavior of the DB24C8–alkali metal ion complexes in nonaqueous solvents was discussed from a thermodynamic point of view. For further study on factors affecting stabilities of the DB24C8 complexes, more data on ΔH° and ΔS° are required. However, there are few data on ΔH° and ΔS° at present for complexation reactions between DB24C8 and alkali metal ions.3,4)

In the present work, formation constants for 1:1 complexes of DB24C8 with alkali metal ions in acetonitrile have been determined by conductometry at different temperatures in order to obtain ΔH° and ΔS° values. The results were compared with those of other solvents. Solvent effect were elucidated.

Experimental

Materials. Most of the reagents were the same as those described previously.1,2) Acetonitrile was allowed to stand in contact with molecular sieves for several days. The acetonitrile was then distilled twice. The middle 70% of the distillate was used. The water content of the purified acetonitrile, as determined by means of Karl Fischer titration, was less than 0.01%. The conductivity of the final product was less than $2 \times 10^{-7}\ \Omega^{-1}\,cm^{-1}$.

Apparatus and Procedure. Conductance measurements were conducted on a Fuso conductivity apparatus, model 362A, in a thermostated water bath 17, 21, 25, 29, 33, and 37±0.02 °C. Two cells were used with cell constants of 0.059701 and 0.093938 cm^{-1}. The experimental procedure to obtain formation constants of DB24C8-alkali metal ion complexes in acetonitrile was the same as those described in the previous paper.1)

Results

The molar conductivity (Λ) *vs.* $[L]_t/[M]_t$ plots for caesium perchlorate at 17, 21, 25, 29, 33, and 37 °C in acetonitrile are illustrated in Fig. 1, $[L]_t$ and $[M]_t$ being total concentrations of DB24C8 and alkali metal ion respectively. The Λ *vs.* $[L]_t/[M]_t$ plots show a monotonous decrease in Λ with an increase in the DB24C8 concentration. The Λ *vs.* $[L]_t/[M]_t$ plots for the other alkali metal perchlorates are similar to those for $CsClO_4$. In this work, it is assumed that the association between a cation and a perchlorate ion is negligible and that DB24C8 forms 1:1 complexes with the alkali metal ions. Corrections for viscosity changes caused by the addition of DB24C8 were neglected. The procedure for obtaining formation constant (K_{ML^+}) of a DB24C8–alkali metal ion complex was just the same as that mentioned in the previous paper,1) where $K_{ML^+} = [ML^+]/[M^+][L]$, and M^+ and L denote an alkali metal ion and DB24C8 respectively. For each alkali metal system, K_{ML^+} values decrease with an increase in temperature, and the log K_{ML^+} *vs.* T^{-1} plot shows a linear relationship. Values of ΔH° and ΔS° calculated from these results are listed in Table 1, together with log K_{ML^+} values at 25 °C. It is seen from Table 1 that, except for methanol, values of ΔH° and ΔS° for a DB24C8–Cs^+ complex obtained by us using conductometry are in good agreement with those by the NMR method.4)

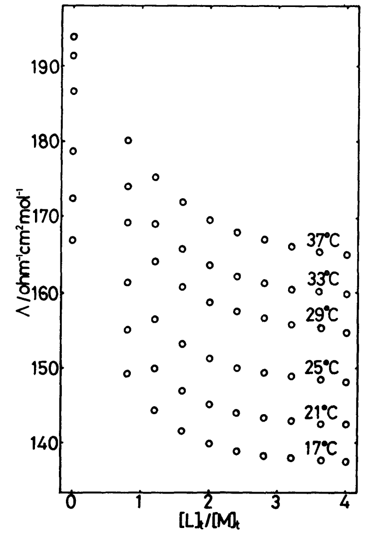

Fig. 1. Λ *vs.* $[L]_t/[M]_t$ plots for caesium perchlorate in acetonitrile at different temperatures. $[M]_t = 5 \times 10^{-4}$ M.

Discussion

Table 1 shows that all the ΔH° and ΔS° values for complexation reactions of DB24C8 with alkali metal ions in acetonitrile are negative as well as in propylene carbonate and methanol. Since DB24C8 is a large crown ether and has a great ligand-ring flexibility, the negative ΔS° values may be primarily due to large conformational changes when a complexation reaction occurs. For the DB24C8–acetonitrile system, the $-T\Delta S^\circ$ value is much smaller than the $-\Delta H^\circ$ value; thus, the magnitude of log K_{ML^+} value of the alkali metal ion complex is determined largely by the ΔH° value.

TABLE 1. log (K_{ML^+}/mol^{-1} dm^3), $\Delta H°$, AND $T\Delta S°$ VALUES FOR THE COMPLEXATION OF DB24C8 WITH ALKALI METAL IONS IN NONAQUEOUS SOLVENTS

Crown ether	Cation	Solvent	log K_{ML^+} (at 25 °C)	$-\Delta H°$ / kJ mol^{-1}	$-T\Delta S°$ / kJ mol^{-1} (at 25 °C)
DB24C8	Na^+	AN[a]	4.1_2	$34._9$	$11._4$
		PC[b, 1]	4.1_6	$37._7$	$13._7$
	K^+	AN[a]	3.8_4	$27._7$	$5._5$
		PC[b, 1]	3.7_3	$34._5$	$13._2$
		CH_3OH[1]	3.5_7	$35._3$	$14._7$
	Rb^+	AN[a]	3.8_0	$30._7$	$8._4$
		PC[b, 1]	3.5_5	$32._9$	$12._6$
		CH_3OH[1]	3.8_6	$39._4$	$17._2$
	Cs^+	AN[a]	3.9_5	$33._1$	$10._7$
				34.0[4]	10.8[4]
		PC[b]	3.4_6[1]	$32._3$[1]	$12._6$[1]
				33.9[4]	14.21[4]
		CH_3OH	3.8_4[1]	$36._8$[1]	$14._6$[1]
				41.3[4]	20.08[4]

a) Acetonitrile. b) Propylene carbonate.

For DB24C8 complexes, there is no large difference in both $\Delta H°$ and $\Delta S°$ among alkali metal ions except $\Delta S°$ value of a DB24C8-K^+ complex for acetonitrile. A sodium ion is the smallest and has the highest charge density of all the alkali metal ions (Na^+, K^+, Rb^+, Cs^+). If the sodium ion has the most suitable size for favorable arrangement of ether oxygen atoms of DB24C8 for the metal ion held in the cavity, the strongest interaction of the metal ion with the ether oxygen atoms and the largest ligand-ring conformational change would be observed for the Na^+-DB24C8 complex among all the alkali metal ion-DB24C8 complexes. The following data may support the above discussion. For acetonitrile and propylene carbonate, both $-\Delta H°$ and $-\Delta S°$ values of the Na^+-DB24C8 complex are the greatest of all the alkali metal ion complexes (Table 1), and also is $-\Delta S°$ value of the Na^+-DB24C8 complex for 70 wt% CH_3OH in H_2O.[3]

Generally, for a given DB24C8-alkali metal ion complex, both $\Delta H°$ and $\Delta S°$ values are somewhat dependent on the variation of solvent; unexpectedly, the $-\Delta H°$ value increases with an increase in the donicity of solvent (acetonitrile (14.1), propylene carbonate (15.1), methanol (19.0)[5]). For the same DB24C8-alkali metal ion complex, both $-\Delta H°$ and $-\Delta S°$ values of acetonitrile are the smallest of all the solvents except $-\Delta H°$ value of acetonitrile for a Cs^+ complex; although acetonitrile and propylene carbonate are non-structural solvents, the difference in $\Delta S°$ between the solvents is comparable to that between propylene carbonate and methanol, which has a hydrogen-bonded structure. This may be attributed to the specific interaction between uncomplexed DB24C8 and acetonitrile.[4,6] The reason why, for a given DB24C8-alkali metal ion complex, the $-\Delta H°$ value of methanol is the largest of all the solvents cannot be explained at the present time.

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