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Thermodynamic Study for Dibenzo-24-crown-8 Complexes with Alkali Metal Ions in Nonaqueous Solvents

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Complex-formation constants (K_{ML^+}) of dibenzo-24-crown-8 (DB24C8) with alkali metal ions in acetonitrile and the solubility of DB24C8 in methanol, acetonitrile, and propylene carbonate were determined conductometrically and spectrophotometrically at 25 °C, respectively. The K_{ML^+} value sequences of the alkali metal ions with DB24C8 are $Na^+ > Cs^+ > K^+ = Rb^+$. Dibenzo-24-crown-8 shows no remarkable selectivity for the alkali metal ions in acetonitrile. Transfer activity coefficients of the DB24C8 complexes with alkali metal ions were calculated from these data and literature values of transfer activity coefficients of alkali metal ions. For the same alkali metal ion, the bulky DB24C8–alkali metal ion complex is more soluble in the aprotic solvents acetonitrile and propylene carbonate than in the protic solvent methanol as compared with the case of the alkali metal ion itself. The transfer activity coefficient of the DB24C8–alkali metal ion complex from methanol to acetonitrile is somewhat sensitive to the variation of the alkali metal ion in the DB24C8 cavity, whereas the mobility of the DB24C8–alkali metal ion complex at the same concentration in the solvents is not sensitive.

Selectivity and complexing ability of dibenzo-24-crown-8 (DB24C8) for metal ions, which were studied by means of solvent extraction[1] and conductometry,[2,3] were reported in the previous papers. For both conductance and solvent extraction systems, DB24C8 shows no peak selectivity for any alkali metal ion. However, DB24C8 reveals the pronounced extraction-selectivity for Ba^{2+} among all the alkali and alkaline earth metal ions. Behavior of the DB24C8–alkali metal ion complexes in methanol and propylene carbonate was conductometrically investigated.[2,3] In each case of methanol and propylene carbonate, mobilities of the complexes at the same concentration are nearly equal to each other. Furthermore, DB24C8 was used for separation of Ba^{2+} from Sr^{2+} by means of solvent extraction.[4]

In the present work, complex-formation constants of DB24C8 with alkali metal ions in acetonitrile and the solubility of DB24C8 in methanol, acetonitrile, and propylene carbonate were conductometrically and spectrophotometrically determined at 25 °C, respectively. Transfer activity coefficients of the DB24C8 complexes with alkali metal ions were calculated from these data and literature values of transfer activity coefficients of alkali metal ions. The behavior of the DB24C8 complexes with alkali metal ions in solutions was discussed in terms of the transfer activity coefficients and the mobility of the complexes.

Experimental

Materials. Dibenzo-24-crown-8 (Nisso Co., Ltd.) was dissolved in hexane, and filtered while hot. Then it was recrystallized three times from hexane and, prior to use, dried at 50 °C in a vacuum oven. Sodium and potassium perchlorates were purchased commercially. The method of preparing rubidium and caesium perchlorates, as well as that of purifying alkali metal perchlorates was previously described.[2] The method of purification of methanol,[2] acetonitrile,[5] and propylene carbonate[2] was as has previously been reported. For these solvents, the middle 70% of the distillate was used. The water contents of the purified acetonitrile and propylene carbonate determined by means of the Karl Fischer titration were less than 0.01%, and, for methanol, less than 0.03%. The conductivity of the final product of acetonitrile was less than 1.5×10^{-7} Ω^{-1} cm^{-1}.

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. Two cells were used with cell constants of 0.05970_5 and 0.09393_4 cm^{-1}. The experimental procedure to obtain formation constants of DB24C8 complexes with alkali metal ions in acetonitrile was the same as those described in the previous paper.[2]

Dibenzo-24-crown-8 solubilities in methanol (225 nm), acetonitrile (275 nm), and propylene carbonate (275 nm) were determined spectrophotometrically at 25±0.02 °C. They are 6.5×10^{-3} M (1 M=1 mol dm^{-3}) in methanol, 1.0×10^{-1} M in acetonitrile, and 4.5×10^{-2} M in propylene carbonate.

Results and Discussion

From Fig. 1, the molar conductivity, Λ, *vs.* $[L]_t/[M]_t$ plots for each alkali metal system, where $[L]_t$ and $[M]_t$ denote the total concentrations of DB24C8 and an alkali metal ion respectively, show a monotonous decrease in Λ with an increase in the DB24C8 concentration. This indicates that the DB24C8 forms a complex with each alkali metal ion and the complexed cation is much less mobile than the corresponding alkali metal ion in

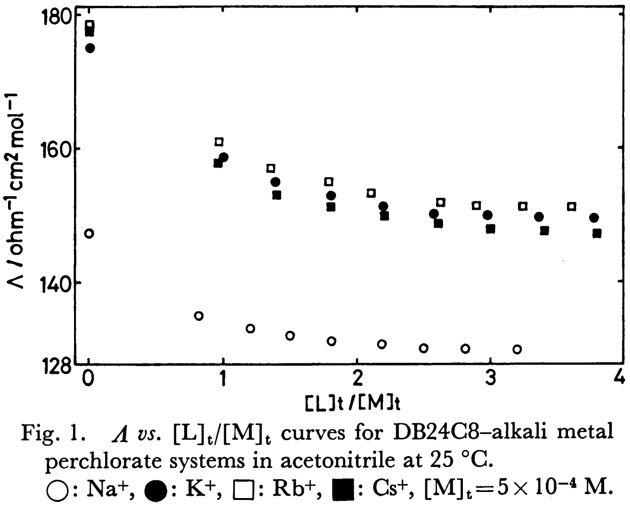

Fig. 1. Λ *vs.* $[L]_t/[M]_t$ curves for DB24C8–alkali metal perchlorate systems in acetonitrile at 25 °C.
○: Na^+, ●: K^+, □: Rb^+, ■: Cs^+, $[M]_t = 5 \times 10^{-4}$ M.

acetonitrile.

It is assumed that the association between the cation and the perchlorate ion in acetonitrile is negligible under these highly dilute experimental conditions ($[M]_t=5\times10^{-4}$ M) and that the DB24C8 forms the 1 : 1 complexes with the alkali metal ions in acetonitrile. The equilibrium equation is written as

$$\begin{array}{ccccc} M^+ & + & L & \rightleftarrows & ML^+ \\ \alpha[M]_t & & [L]_t-(1-\alpha)[M]_t & & (1-\alpha)[M]_t, \end{array} \tag{1}$$

where M^+, L, and α are the alkali metal ion, crown ether, and the fraction of free alkali metal ions. Thus, the complex-formation constant, K_{ML^+}, is defined by

$$\begin{aligned} K_{ML^+} &= [ML^+]/[M^+][L] \\ &= (1-\alpha)/\alpha[L]. \end{aligned} \tag{2}$$

The observed conductivity, κ, is given by

$$\kappa = \kappa_{MClO_4} + \kappa_{MLClO_4}, \tag{3}$$

where κ_{MClO_4} and κ_{MLClO_4} represent the conductivities of alkali metal perchlorate and alkali metal DB24C8 perchlorate, respectively. The molar conductivities are as follows

$$\begin{aligned} \Lambda_{MClO_4} &= \kappa_{MClO_4}/[M^+] \\ &= \kappa_{MClO_4}/\alpha[M]_t, \end{aligned} \tag{4}$$

$$\begin{aligned} \Lambda_{MLClO_4} &= \kappa_{MLClO_4}/[ML^+] \\ &= \kappa_{MLClO_4}/(1-\alpha)[M]_t, \end{aligned} \tag{5}$$

Λ_{MClO_4} and Λ_{MLClO_4} being the molar conductivities of alkali metal perchlorate and alkali metal DB24C8 perchlorate respectively. As a consequence of Eqs. 4 and 5, Eq. 3 can be transformed into

$$\begin{aligned} \Lambda &= \kappa/[M]_t \\ &= \alpha\Lambda_{MClO_4} + (1-\alpha)\Lambda_{MLClO_4}. \end{aligned} \tag{6}$$

Since the DB24C8 concentration was kept low during these experiments, corrections for viscosity changes were neglected. As a consequence of Eq. 6, Eq. 2 can be transformed into

$$K_{ML^+} = (\Lambda_{MClO_4}-\Lambda)/(\Lambda-\Lambda_{MLClO_4})[L], \tag{7}$$

where $[L]=[L]_t-[M]_t(\Lambda_{MClO_4}-\Lambda)/(\Lambda_{MClO_4}-\Lambda_{MLClO_4})$. The K_{ML^+} value can be obtained by the following procedure. The Λ_{MLClO_4} value is estimated from the Λ values at the points of large $[L]_t$ to $[M]_t$ ratios. Using this Λ_{MLClO_4} value, the K_{ML^+} value in Eq. 7 is calculated. The actual K_{ML^+} and Λ_{MLClO_4} values are calculated by a succesive approximation method. The $\log K_{ML^+}$ values are listed in Table 1.

TABLE 1. log (K_{ML^+}/mol^{-1} dm^3) VALUES OF DB24C8 WITH ALKALI METAL IONS AT 25 °C

	Na^+	K^+	Rb^+	Cs^+
Acetonitrile	4.1	3.8	3.8	4.0
Propylene carbonate[3]	4.1_6	3.7_3	3.5_5	3.4_6
Methanol[2]	—	3.5_7	3.8_6	3.8_4

Dibenzo-24-crown-8 shows no remarkable selectivity for the alkali metal ions in acetonitrile. For both acetonitrile and propylene carbonate, although Na^+ is most strongly solvated and its size is the least favorable to the DB24C8 cavity of all the alkali metal ions (Na^+, K^+, Rb^+, and Cs^+), DB24C8 forms the most stable complex with Na^+. The differences in the free energies of the solvation of Na^+ and K^+, Na^+ and Rb^+, and Na^+ and Cs^+ are much smaller for acetonitrile and propylene carbonate than for the solvents such as water, methanol, DMF, and DMSO.[6] The solvation power of propylene carbonate and acetonitrile for Na^+ is the smallest of all these solvents.[6] Judging from the large size and the flexibility of DB24C8, Na^+ seems to have a suitable size for the favorable arrangement of the ether oxygen atoms for the metal ion trapped in the cavity. This may be the reason why the DB24C8 complex with Na^+ is the most stable in both acetonitrile and propylene carbonate.

Table 1 shows that stability of the DB24C8 complex with the same alkali metal ion slightly varies with the solvent. In general, only for aprotic solvents (acetonitrile (DN=14.1[7]) and propylene carbonate (DN=15.1[7])), a reverse correlation exists between the stabilities of the DB24C8–alkali metal ion complexes and the donor number, DN, of the solvent.

Transfer Activity Coefficient. The transfer activity coefficient, $\log {}^{S_1}\gamma^{S_2}(ML^+)$, of the DB24C8–alkali metal ion complex between the solvent S_1 and the solvent S_2 is calculated by Eq. 8.

$$\log {}^{S_1}\gamma^{S_2}(ML^+) = (\log K_{ML^+})_{S_1} - (\log K_{ML^+})_{S_2} + \log {}^{S_1}\gamma^{S_2}(L) + \log {}^{S_1}\gamma^{S_2}(M^+) \tag{8}$$

These data are summarized in Table 2.

Dibenzo-24-crown-8 is much more soluble in the aprotic solvents acetonitrile and propylene carbonate than in the protic solvent methanol (Table 2). Both dibenzo-18-crown-6 (DB18C6) and dibenzo-30-crown-

TABLE 2. TRANSFER ACTIVITY COEFFICIENTS AT 25 °C

		S=AN[a]			S=PC[b]		
$\log^{MeOH\,[c]}\gamma^S(M^+)$[8]							
	K^+		-0.4			-0.1_6	
	Rb^+		-0.6			-0.4_8	
	Cs^+		-0.8			-0.6_6	
		DB18C6[8]	DB24C8	DB30C10[9]	DB18C6[8]	DB24C8	DB30C10[9]
$\log^{MeOH}\gamma^S(L)$		-1.6_5	-1.1_8	-1.4_0	-1.0_6	-0.8_4	-0.8_1
$\log^{MeOH}\gamma^S(ML^+)$							
	K^+	-1.9	-1.8_1	-1.3_3	-1.3_5	-1.1_6	-0.5_5
	Rb^+	-1.8	-1.7_2	—	-1.2_2	-1.0_1	—
	Cs^+	-2.5	-2.1_4	—	-1.4_8	-1.1_2	—

a) Acetonitrile. b) Propylene carbonate. c) Methanol.

10 (DB30C10) show the same tendency as DB24C8. From Table 2, for both DB24C8 and DB18C6, the log ${}^{\mathrm{MeOH}}\gamma^{\mathrm{S}}(\mathrm{L})$ value is larger than the log ${}^{\mathrm{MeOH}}\gamma^{\mathrm{S}}(\mathrm{ML}^+)$ value, and contrary holds for DB30C10, where S=AN and PC. This cannot clearly be explained at the present stage. However, possible reasons may be the difference in the strength of hydrogen bonds between CH_3OH-uncomplexed crown ether and CH_3OH-complexed crown ether, and the difference in the conformation between an uncomplexed crown ether and a complexed crown ether.

As can be seen from Table 2, for the same alkali metal ion, the bulky ML^+ is more soluble in an aprotic solvent than in a protic solvent as compared with the case of M^+.

In the case of DB24C8, log ${}^{\mathrm{MeOH}}\gamma^{\mathrm{PC}}(\mathrm{ML}^+)$ values of alkali metal ions are nearly equal to one another, whereas the log ${}^{\mathrm{MeOH}}\gamma^{\mathrm{AN}}(\mathrm{ML}^+)$ value of Cs^+ is relatively smaller than the others, and the log ${}^{\mathrm{PC}}\gamma^{\mathrm{AN}}(\mathrm{ML}^+)$ value varies with the alkali metal ion trapped in the DB24C8 cavity (Na^+: -0.9_3, K^+: -0.6_5, Rb^+: -0.7_1, Cs^+: -1.0_2). This indicates that, for the CH_3OH–propylene carbonate system, the charge of the alkali metal ion held in the DB24C8 cavity is effectively shielded, and that, for the CH_3OH–acetonitrile and propylene carbonate–acetonitrile systems, the charge is not effectively screened. The actual $\Lambda_{\mathrm{MLClO_4}}$ values of DB24C8–alkali metal perchlorate systems in acetonitrile at 25 °C obtained in this work are as follows.

	Na	K	Rb	Cs
$[\mathrm{MClO_4}]_t \times 10^{-4}/\mathrm{mol\ dm^{-3}}$	4.998	5.075	5.255	4.945
$\Lambda_{\mathrm{MLClO_4}}/\Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$	145.2	145.5	145.7	144.0

These data show that the alkali metal ion held in the DB24C8 cavity is effectively shielded by the DB24C8 from the solvent. The same tendency for DB24C8 complexes with alkali metal ions has been reported for methanol[2] and propylene carbonate.[3] It follows from the above discussion that the transfer activity coefficient of the DB24C8–alkali metal ion complex is somewhat sensitive to the variation of the alkali metal ion in the DB24C8 cavity, whereas the mobility of the DB24C8–alkali metal ion complex at the same concentration is not sensitive.

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