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A Conductance Study of the Complexation Reaction of Dibenzo-24-crown-8 with Alkali Metal Ions in Propylene Carbonate and Methanol

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The formation constants (K_{ML^+}) for 1:1 complexes of dibenzo-24-crown-8 (DB24C8) with alkali metal ions (Na^+, K^+, Rb^+, and Cs^+) in propylene carbonate (PC) and methanol have been determined conductometrically at different temperatures in order to obtain the values of the enthalpy (ΔH) and entropy changes (ΔS). The complexation reactions between DB24C8 and the alkali metal ions in PC and methanol are all exothermic, and the ΔS values of these systems are all negative. In the case of the PC system, there is no considerable difference in ΔS among the alkali metal ions (Na^+, K^+, Rb^+, and Cs^+); thus, the K_{ML^+} sequences depend entirely on the $-\Delta H$ sequences. Since, in methanol, the $-\Delta H$ and $-\Delta S$ values for K^+ are nearly equal to those for Cs^+, and since the largest $-\Delta H$ value for Rb^+ is balanced by the largest $-\Delta S$ value, DB24C8 shows no selectivity for the alkali metal ions (K^+, Rb^+, and Cs^+) in methanol.

The complexation reaction between dibenzo-24-crown-8 (DB24C8) and metal ions has been investigated by different methods, *e.g.*, calorimetry,1) conductometry,2) and solvent extraction.3) Moreover, solvent extraction with DB24C8 has been used in the separation of barium(II) from strontium(II).4)

DB24C8 forms stoichiometrically stable complexes with metal ions. They are mostly 1:1 complexes in solution. Since DB24C8, whose configuration is termed cylindrically symmetrical,5) is a flexible crown ether and has a large cavity size (4.5—5.0 Å6)), great conformational changes are required to fold around the metal ion on complexation. In the DB24C8 complex, the metal ion held in the cavity is partially wrapped around by DB24C8.7) The stability of the complexes depends largely on the solvent medium2) and the flexibility of the DB24C8 ring.1)

The present study was undertaken in order to understand in detail the thermodynamics of the complexations of DB24C8 with alkali metal ions in nonaqueous solvents. In this paper, the formation constants for 1:1 complexes of DB24C8 with alkali metal ions in propylene carbonate (PC) and methanol have been determined conductometrically at different temperatures in order to obtain the values of the enthalpy and entropy changes.

Experimental

Materials. The method of the purification of DB24C8 (Nisso Co., Ltd.) was as has previously been described.4) Lithium, sodium, and potassium perchlorates were obtained commercially. Rubidium and caesium perchlorates were prepared by adding an equimolar perchloric acid solution to an aqueous solution of rubidium bromide and caesium chloride respectively. All these perchlorates were recrystallized from water five times and, before use, dried at 150 °C in a vacuum oven. PC was distilled twice under nitrogen at about 12 mmHg. Methanol was allowed to stand in contact with molecular sieves for several days and then distilled twice. In each case of PC and methanol the middle 70% of the distillate was used. The water contents of the finally purified PC and methanol determined by the Karl Fischer titration were less than 0.01 and 0.03% respectively. The conductivities of the final products of PC and methanol were less than 5×10^{-8} and 1×10^{-7} ohm^{-1} cm^{-1} respectively.

Apparatus and Procedure. The conductance measurements were made on a Yanagimoto conductivity outfit, model MY-7, in a thermostated water bath at 10, 15, 20, 25, 30, and 35±0.02 °C. Two cells were used with cell constants of 0.09317 and 0.2046 cm^{-1}.

The experimental procedure to obtain formation constants of DB24C8 complexes with alkali metal ions is as follows; a solution of the alkali metal perchlorate (5×10^{-4} M; 1 M= 1 mol dm^{-3}) 200 cm^3 was placed in the cell (volume 300 cm^3) and the resistance of the solution was measured. Then a step-by-step increase in the DB24C8 concentration was effected by a quick transfer with a pipet from the solution of DB24C8 (PC: 1×10^{-2} M, methanol: 5×10^{-3} M) to the cell, until the total concentration of DB24C8 was about two-and-a-half (methanol) or four times (PC) as large as that of the alkali metal perchlorate. The resistance of the solution in the cell was remeasured after each transfer.

Results

The molar conductivity, Λ, *vs.* $[L]_t/[M]_t$ plots for caesium perchlorate at 10, 15, 20, 25, 30, and 35 °C in PC and in methanol are given in Figs. 1 and 2 respectively, where $[L]_t$ and $[M]_t$ are the total concen-

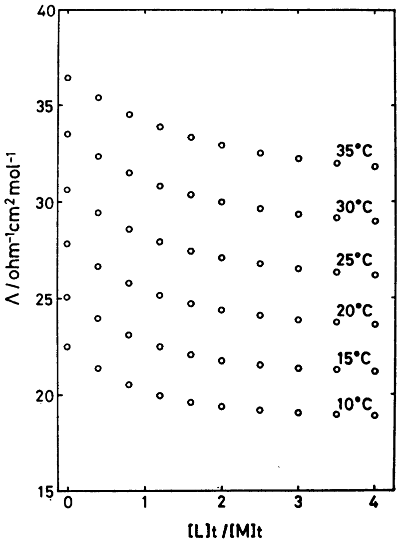

Fig. 1. Λ *vs.* $[L]_t/[M]_t$ plots for caesium perchlorate in PC at different temperatures.
$[M]_t=5\times10^{-4}$ M.

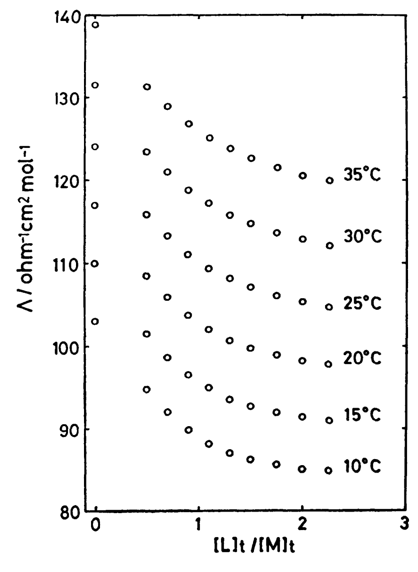

Fig. 2. Λ *vs.* $[L]_t/[M]_t$ plots for caesium perchlorate in methanol at different temperatures. $[M]_t = 5\times10^{-4}$ M.

trations of DB24C8 and the alkali metal ion respectively. The Λ *vs.* $[L]_t/[M]_t$ plots show a decrease in Λ with an increase in the DB24C8 concentration. The experimental plots of the other alkali metal perchlorates in PC and methanol are similar, and so have been omitted. In the cases of the Li^+–PC and methanol and the Na^+–methanol systems, since hardly any change in Λ is found in spite of an increase in the DB24C8 concentration, the conductometric determination of the complex formation constant is impossible. It is assumed that the association between the cation and the perchlorate ion in PC and methanol is negligible under these highly dilute experimental conditions and that, in this work, DB24C8 forms the 1: 1 complexes with the alkali metal ions in PC and methanol.

The equilibrium equation is given by:

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

where M^+, L, and α are the alkali metal ion, DB24C8, and the fraction of free alkali metal ions. Accordingly, the complex formation constant, K_{ML^+}, is defined by:

$$K_{ML^+} = [ML^+]/[M^+][L] = (1-\alpha)/\alpha[L]. \qquad (2)$$

The observed conductivity, κ, is written as:

$$\kappa = \kappa_{MClO_4} + \kappa_{MLClO_4}, \qquad (3)$$

where κ_{MClO_4} and κ_{MLClO_4} are the conductivities of alkali metal perchlorate and alkali metal DB24C8 perchlorate respectively. The molar conductivities are given by:

$$\Lambda_{MClO_4} = \kappa_{MClO_4}/[M^+] = \kappa_{MClO_4}/\alpha[M]_t, \qquad (4)$$

$$\Lambda_{MLClO_4} = \kappa_{MLClO_4}/[ML^+] = \kappa_{MLClO_4}/(1-\alpha)[M]_t, \qquad (5)$$

where Λ_{MClO_4} and Λ_{MLClO_4} are 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:

$$\Lambda = \kappa/[M]_t = \alpha\Lambda_{MClO_4} + (1-\alpha)\Lambda_{MLClO_4}. \qquad (6)$$

Since the DB24C8 concentration was kept low ($<2.5\times10^{-3}$ M) during these experiments, corrections for viscosity changes were neglected. As a consequence of Eq. 6, Eq. 2 can be transformed into:

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

where $[L] = [L]_t - [M]_t(\Lambda_{MClO_4}-\Lambda)/(\Lambda_{MClO_4}-\Lambda_{MLClO_4})$.

The procedure for obtaining the K_{ML^+} value is as follows. 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 nonlinear least-squares analysis.[8] In each system the K_{ML^+} values increase monotonously with a decrease in temperature. The $\log K_{ML^+}$ *vs.* T^{-1} plot shows a linear relationship for each system. By way of example, the $\log K_{ML^+}$ *vs.* T^{-1} plots for the caesium–PC and methanol systems are given in Fig. 3. The values of the enthalpy change, ΔH, and the entropy

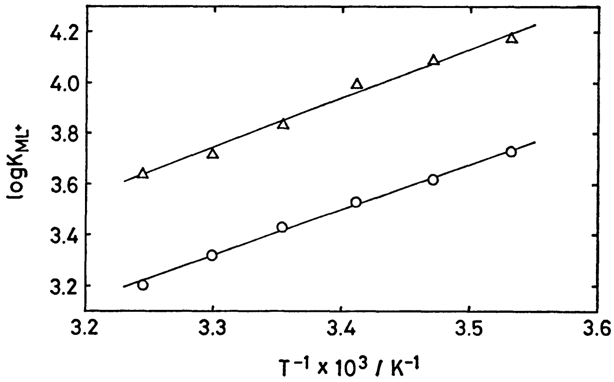

Fig. 3. $\log K_{ML^+}$ *vs.* T^{-1} plots for caesium–PC and methanol systems.
○: PC, △: methanol.

TABLE 1. $\log(K_{ML^+}/\text{mol}^{-1}\,\text{dm}^3)$, ΔH, AND ΔS VALUES FOR THE COMPLEXATION OF ALKALI METAL IONS WITH DB24C8 IN VARIOUS SOLVENTS

Crown ether	Cation	Solvent	$\log K_{ML^+}$ (at 25 °C)	$-\Delta H$ kJ mol⁻¹	$-\Delta S$ JK⁻¹ mol⁻¹
DB24C8	Na^+	PC	4.1_6	$37._7$	$46._0$
		70 wt% CH_3OH in H_2O[1]	1.54	32.4	79.1
	K^+	PC	3.7_3	$34._5$	$44._4$
		CH_3OH	3.5_7	$35._3$	$49._4$
		70 wt% CH_3OH in H_2O[1]	2.42	35.7	73.6
	Rb^+	PC	3.5_5	$32._9$	$42._3$
		CH_3OH	3.8_6	$39._4$	$57._7$
		70 wt% CH_3OH in H_2O[1]	2.55	36.5	73.6
	Cs^+	PC	3.4_6	$32._3$	$42._3$
		CH_3OH	3.8_4	$36._8$	$49._0$
		70 wt% CH_3OH in H_2O[1]	2.48	37.4	77.8
DB30C10[9]	Cs^+	CH_3OH		53.22	95.48

change, ΔS, calculated from these data are summarized in Table 1, together with the $\log K_{ML^+}$ values at 25 °C and the literature values.

Discussion

The complexation reactions between DB24C8 and the alkali metal ions in PC and methanol are all exothermic, and the ΔS values of these systems are all negative (Table 1). DB24C8 is a large crown ether and has a great ligand-ring flexibility. The uncomplexed DB24C8 may be more flexible than the complexed DB24C8. It thus appears that the negative ΔS values are largely attributable to the great conformational changes when a complexation reaction occurs. It may be seen from Table 1 that, in methanol, the ΔS value of Cs^+ for DB24C8, which is smaller than dibenzo-30-crown-10 (DB30C10), is much larger than that for DB-30C10. The $-\Delta H$ sequences of the alkali metal ions with DB24C8 in PC are $Na^+ > K^+ > Rb^+ \geq Cs^+$, while those in 70 wt% CH_3OH are completely the reverse. In the case of the DB24C8–PC system, there is no considerable difference in ΔS among the alkali metal ions; thus, the $\log K_{ML^+}$ sequences entirely depend on the $-\Delta H$ sequences (Table 1). Since, in methanol, the $-\Delta H$ and $-\Delta S$ values of DB24C8 for K^+ are nearly equal to those for Cs^+, and since the largest $-\Delta H$ value for Rb^+ is balanced by the largest $-\Delta S$ value, DB24C8 shows no selectivity for the alkali metal ions in methanol. In methanol, the ΔH value of Cs^+ for DB-24C8, which has smaller donor oxygen atoms than DB-30C10, is much larger than that for DB30C10.

Among the solvents, the $-\Delta S$-value series for the Na^+–, the K^+– and Cs^+–, and the Rb^+–DB24C8 systems are given in the order PC≪70 wt% CH_3OH, PC< methanol≪70 wt% CH_3OH, and PC<methanol<70 wt% CH_3OH, respectively (Table 1). It may be attributed chiefly to the solvent structural influences of methanol and water that, in the case of each alkali metal ion-DB24C8 system, the $-\Delta S$ value increases on moving from PC to 70 wt% CH_3OH. Moreover, in the cases of the K^+, Rb^+, and Cs^+–DB24C8 systems, the large increase in $-\Delta S$ on going from methanol to 70 wt% CH_3OH may be largely due to the stronger water structural influences compared to methanol. For the Na^+–DB24C8 system, the larger $-\Delta H$ and the much smaller $-\Delta S$ values of PC result in the much greater $\log K_{ML^+}$ value compared to 70 wt% CH_3OH. Although, in the cases of the K^+, Rb^+, and Cs^+–DB24C8 systems, there is no considerable difference in ΔH, the K_{ML^+} values in PC and methanol are as large as one order of magnitude larger than that in 70 wt% CH_3OH. This is largely attributed to the much smaller $-\Delta S$ values in PC and methanol compared to 70 wt% CH_3OH (Table 1). Since, in each case of the K^+ and Cs^+–DB24C8 systems, there are no significant differences in ΔH and ΔS between PC and methanol, the $\log K_{ML^+}$ values in PC and methanol are nearly equal. For the Rb^+–DB24C8 system, the larger $-\Delta H$ value in methanol is canceled by the larger $-\Delta S$ value compared to PC; thus, there is no considerable difference in $\log K_{ML^+}$ in PC and methanol.

TABLE 2. ($\Lambda_{MLClO_4}/\Omega^{-1}\ cm^2\ mol^{-1}$) VALUES IN METHANOL AT DIFFERENT TEMPERATURES

Temp/°C	Λ_{MLClO_4}		
	K^+	Rb^+	Cs^+
	$[M]_t = 5.054 \times 10^{-4}$ M	$[M]_t = 5.044 \times 10^{-4}$ M	$[M]_t = 5.041 \times 10^{-4}$ M
10	82.41	81.53	82.11
15	88.76	87.39	87.52
20	93.90	93.27	93.68
25	100.2	99.15	98.97
30	106.5	104.8	105.4
35	112.9	111.8	112.3

The Λ_{MLClO_4} values of K^+, Rb^+, and Cs^+ in methanol at different temperatures are given in Table 2. As can be seen from Table 2, the $[M]_t$ values of K^+, Rb^+, and Cs^+ are nearly equal to one another, and there is scarcely any difference in Λ_{MLClO_4} among K^+, Rb^+, and Cs^+ at the same temperature, suggesting that the charge of the alkali metal ion held in the DB24C8 cavity is effectively shielded by the DB24C8 and that the DB24C8 complexes with the alkali metal ions in methanol are approximately equal to each other in size.

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