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A Conductance Study of Alkali Metal Ion–Benzo-15-crown-5 Complexes in Propylene Carbonate

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The formation constants (K_{ML^+}) for 1:1 complexes of benzo-15-crown-5 (B15C5) with alkali metal ions at 25 °C, and the enthalpy (ΔH) and entropy changes (ΔS) of the K^+–B15C5 complex in propylene carbonate (PC) have been determined conductometrically. The K_{ML^+} series of B15C5 for the alkali metal ions are given in the order $Na^+ > Li^+ > K^+ > Rb^+ > Cs^+$. The selectivity tendency of B15C5 for the alkali metal ions is consistent with the size-fit concept, however, B15C5 shows poor selectivity. Both the ΔH and ΔS values for the complexation reaction of B15C5 with K^+ are negative. In the cases of Na^+, K^+, Rb^+, and Cs^+, the size of the moving entity in PC is larger for the B15C5 complex than for the corresponding alkali metal ion, while, in the case of Li^+, that is completely the reverse.

Benzo-15-crown-5 (B15C5) forms stoichiometric complexes with alkali metal ions. Most of them are 1:1 complexes, however, B15C5 also forms 2:1 complexes with K^+, Rb^+, and Cs^+ whose sizes are larger than the cavity size of the ligand.[1,2] In a water–methanol mixed solvent system,[1] B15C5 shows poor selectivity for alkali metal ions and the 1:1 complexes of B15C5 with alkali metal ions are not so much stable. In the present paper, the enthalpy and entropy changes of the K^+–B15C5 complex as well as the formation constants of the 1:1 complexes of B15C5 with alkali metal ions at 25 °C have been determined conductometrically in propylene carbonate (PC). The results have been compared with those of the corresponding 15-crown-5 (15C5) complexes with alkali metal ions in PC.

Experimental

Materials. Benzo-15-crown-5 (Merck Japan Ltd.) was dissolved in heptane, and filtered while hot. Then it was recrystallized from heptane three times and, prior to use, dried at 40 °C in a vacuum oven. Lithium, sodium, and potassium perchlorates were obtained commercially. The method of preparing rubidium and caesium perchlorates, as well as that of purifying alkali metal perchlorates were previously described.[3] Propylene carbonate was distilled twice under nitrogen atmosphere at 2.4 kPa. The water content of the finally purified PC determined by Karl Fischer titration was less than 0.02%. The conductivity of the final product was less than $4\times10^{-8}\,\Omega^{-1}\,cm^{-1}$.

Apparatus and Procedure. The apparatus and the experimental procedures were the same as those described in the previous paper.[3] For the K^+ system, the conductance measurements were performed at 5, 10, 15, 20, 25, 30, and 35±0.02 °C.

Results

The molar conductivity, Λ, *vs.* $[L]_t/[M]_t$ plots are given in Fig. 1, where $[L]_t$ and $[M]_t$ are the total concentrations of B15C5 and an alkali metal ion respectively. It is supposed that the association between a cation and perchlorate ion in PC is negligible under these highly dilute experimental conditions and that, in the present study, B15C5 forms 1:1 complexes with alkali metal ions in PC. Since the B15C5 concentration was kept below 3.0×10^{-3} M (1 M=1 mol dm^{-3}) during these experiments, corrections for viscosity changes were neglected. The procedure for obtaining complex-formation constant, K_{ML^+}, of an alkali metal ion–B15C5 complex was just the same as that described in the previous paper,[3] where M^+ and L denote an alkali metal ion and B15C5, respectively. The log K_{ML^+} *vs.* T^{-1} plots for the K^+–B15C5 system in PC are given in Fig. 2. The log K_{ML^+} *vs.* T^{-1} plots show a linear relationship. The log K_{ML^+} values, and the values of enthalpy and entropy changes are listed in Tables 1 and 2, together with the literature values, respectively.

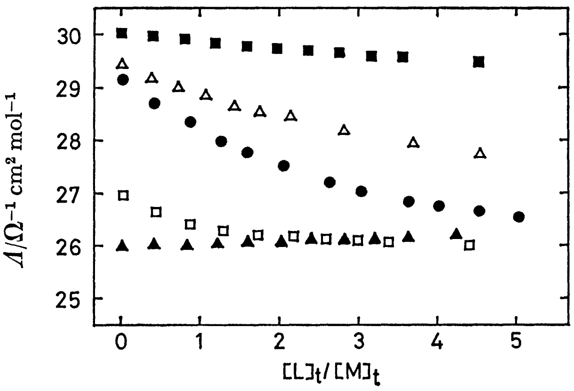

Fig. 1. Λ *vs.* $[L]_t/[M]_t$ curves for B15C5–alkali metal perchlorate systems in PC at 25 °C.
▲: Li^+, □: Na^+, ●: K^+, △: Rb^+, ■: Cs^+, $[M]_t=5\times10^{-4}$ M.

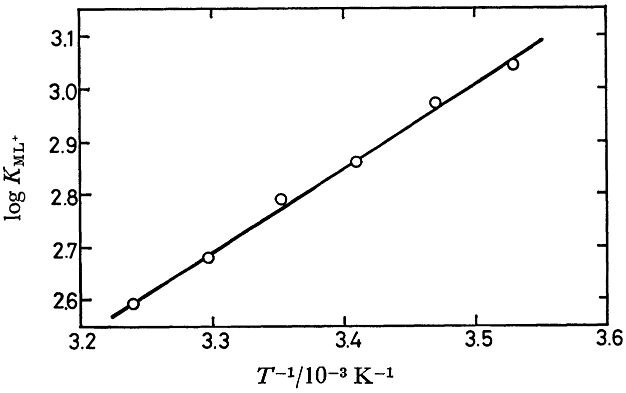

Fig. 2. log K_{ML^+} *vs.* T^{-1} plots for the K^+–B15C5 system in PC.

TABLE 1. log (K_{ML^+}/mol^{-1} dm^3) VALUES IN PC AT 25 °C

	15C5[4]	B15C5
Li^+	4.2_6	3.7_7
Na^+	3.7	4.3_5
K^+	3.4_1	2.7_8
Rb^+	3.0_4	2.3_8
Cs^+	2.6_9	2.0_3

TABLE 2. ΔH AND ΔS VALUES FOR THE COMPLEXATION OF THE POTASSIUM ION WITH CROWN ETHERS

Crown ether	Solvent	log K_{ML^+} (at 25 °C)	$-\Delta H$ / kJ mol^{-1}	$-\Delta S$ / J K^{-1} mol^{-1}
B15C5	PC	2.7_8	$26._4$	$35._4$
	H_2O[1]	0.38	9.75	26
DB24C8	PC[3]	3.7_3	$34._5$	$44._4$

Discussion

As can be seen from Table 1, the log K_{ML^+} series of B15C5 for alkali metal ions in PC are given in the order $Na^+ > Li^+ > K^+ > Rb^+ > Cs^+$. The selectivity tendency of B15C5 (cavity radius: 0.85—1.1 Å[5]) for the alkali metal ions is consistent with the size-fit concept, however, B15C5 shows poor selectivity. The B15C5 complex with the same alkali metal ion in PC is more unstable than the 15C5 complex except for the case of Na^+. This may be attributable to the fact that B15C5 has two aromatic ether oxygen atoms whose basicity is lower than that of the aliphatic ether oxygen atom. The value of enthalpy change (ΔH) of the 15C5 complex with Na^+ may be smaller than that of the B15C5 complex because of the two aromatic ether oxygen atoms. Thus, the reason why the 15C5 complex with Na^+ is more unstable than the B15C5 complex is presumably due to that the 15C5 complex may be much more entropy destabilized than the B15C5 complex.

Table 2 shows that the complexation reaction of B15C5 with K^+ in PC is exothermic and the ΔS value is negative. The smaller $-\Delta H$ and $-\Delta S$ (entropy change) values of B15C5 compared to dibenzo-24-crown-8 (DB24C8) may reflect the smaller number of donor oxygen atom and much more rigid structure of B15C5, respectively (Table 2). Very much greater $-\Delta H$ and slightly greater $-\Delta S$ values of B15C5 in PC result in the very much larger log K_{ML^+} value compared to water. The hydrogen bond between an ether oxygen atom of uncomplexed B15C5 and a water molecule may be the reason why the $-\Delta H$ value of PC is very much larger than that of water. In the previous paper,[6] it has been reported that, although the solvation power of water for the same alkali metal ion (Na^+, K^+, Rb^+, and Cs^+) is the third largest of all the solvents (acetonitrile, PC, water, methanol, DMF, and DMSO), the log K_{ML^+} value of water is the smallest for every alkali metal ion–crown ether (18-crown-6 and dibenzo-18-crown-6) system. This may also largely depend on the hydrogen bond between an ether oxygen atom of the uncomplexed crown ether and a water molecule. Since water is a three-dimensional structural solvent and PC is not, the $-\Delta S$ value of B15C5 in PC is expected to be smaller than that in water. On the contrary, Table 2 shows that $-\Delta S$ value of B15C5 in PC is larger than that in water. This fact seems to be related to that K^+ plays a net structure breaking role in water.

The Λ *vs.* $[L]_t/[M]_t$ plots in Fig. 1 show a decrease of Λ with an increase in the B15C5 concentration for Na^+, K^+, Rb^+, and Cs^+ systems, and on the contrary for the Li^+ system. This indicates that, in the cases of Na^+, K^+, Rb^+, and Cs^+, the size of the moving entity in PC is larger for the B15C5 complex than for the corresponding alkali metal ion, while, in the case of Li^+, that is completely the reverse. The Λ *vs.* $[L]_t/[M]_t$ plots for the 15C5 system in PC show the same tendency for the B15C5 system except for the case of Na^+.[4] The B15C5 complex with Na^+ is bulkier than the Na^+ ion in PC, and on the contrary for the case of 15C5.[4] Both B15C5 and 15C5 complexes with Na^+ may be scarcely solvated in a PC solution. It thus appears that the size of the moving entity of a Na^+ ion in PC is approximately equal to the size between that of the B15C5 complex with Na^+ and that of the 15C5 complex.

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