72 © *1980 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***53***, *72—76 (1980)* [Vol. 53, No. 1

A Conductance Study of Alkali Metal Ion-15-Crown-5, 18-Crown-6, and Dibenzo-24-crown-8 Complexes in Propylene Carbonate

Yasuyuki Takeda,* Hisao Yano, Masayuki Ishibashi, and Hiroshi Isozumi
Department of Chemistry, Faculty of Science, Chiba University, Yayoi-chō, Chiba 260

(Received July 23, 1979)

The formation constants, K_{ML^+}, for 1:1 complexes of 15-crown-5 (15C5), 18-crown-6 (18C6), and dibenzo-24-crown-8 (DB24C8) with alkali metal ions and the limiting ionic molar conductivities, λ°, of the complexed cations in propylene carbonate have been determined at 25 °C conductometrically. The K_{ML^+} value series about the same alkali metal ion among the crown ethers are given in the order 18C6$\gg$DB24C8$>$15C5. The K_{ML^+} sequences of the alkali metal ions with 15C5, 18C6, and DB24C8 are $\mathrm{Li}^+>\mathrm{Na}^+>\mathrm{K}^+>\mathrm{Rb}^+>\mathrm{Cs}^+$, $\mathrm{K}^+>\mathrm{Na}^+>\mathrm{Rb}^+\gg\mathrm{Cs}^+$, and $\mathrm{Na}^+>\mathrm{K}^+>\mathrm{Rb}^+\geq\mathrm{Cs}^+$, respectively. The indication is that the ability of the alkali metal ions to form complexes with the three crown ethers is not always affected primarily by the relative sizes of the alkali metal ions and the crown ether cavity. In each case of 18C6 and DB24C8 the λ° values of the alkali metal ions are nearly equal, while in the case of 15C5 there are considerably differences, suggesting that in the former case the charge of the alkali metal ion trapped in the crown ether cavity is effectively shielded. This is not true in the latter case.

It is known that crown ethers interact with certain cations, especially with alkali and alkaline earth metal ions, to form stable stoichiometric complexes. The stability of the complexes is governed by the solvent medium, the relative sizes of the cation and the crown ether cavity, the number of binding sites in the crown ether ring, and the flexibility of the crown ether.[1)] The crown ether complexes in the crystalline state have been investigated by X-ray crystallography[2)] and those in solution by spectroscopy[3)] and conductimetry.[1h,4)] The studies show that in many cases the cation is held in the crown ether cavity and surrounded by the oxygen atoms of the crown ether ring. The structure of the complex in solution is not always however the same as in the crystalline state.

The crown ethers used in this work are 15-crown-5 (15C5), 18-crown-6 (18C6), and dibenzo-24-crown-8 (DB24C8). The sizes, the cavity sizes, and the number of donor oxygen atoms of these three compounds are different from one another. Moreover, 15C5 and 18C6, whose oxygen atoms are coplanar and symmetrically distributed in the crown ether ring, are rigid crown ethers, while DB24C8, whose configuration is termed cylindrically symmetrical, is a flexible crown ether.[1a)] In this paper, the formation constants for 1:1 complexes of 15C5, 18C6, and DB24C8 with alkali metal ions and the limiting ionic molar conductivities of the complexed cations in propylene carbonate (PC) have been determined conductometrically in order to study the factors influencing complex formation between crown ethers and alkali metal ions and the behavior of the complexed cations in PC, respectively. PC has a high dielectric constant ($\varepsilon_r=64$ at 25 °C[5)]) and moderate Lewis base and weak Lewis acid properties.[6)] PC was used as the solvent since almost all univalent metal perchlorates are nearly completely dissociated in PC solution.[5,6b)]

Experimental

Materials. 15C5, 18C6, and DB24C8 were obtained from Nisso Co., Ltd. 15C5 was purified by distillation under vacuum (bp 115—129 °C, 1.5 mmHg). 18C6 was recrystallized from acetonitrile and, prior to use, dried at 70 °C in a vacuum oven. The method of purification of DB24C8 was previously described.[7)] Rubidium and caesium perchlorates were prepared by adding an equimolar perchloric acid solution to an aqueous solution of rubidium bromide and caesium hydroxide respectively. Lithium, sodium, and potassium perchlorates were purchased commercially. All perchlorates were recrystallized from water five times and, prior to use, dried at 150 °C in a vacuum oven. PC was distilled twice under nitrogen at approx. 12 mmHg. The middle 70% of the distillate was used. The water content of the finally purified PC determined by Karl Fischer titration was less than 0.01%. The conductivity of the final product was less than $5\times10^{-8}\,\Omega^{-1}\,\mathrm{cm}^{-1}$.

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. Two cells were used with cell constants of 0.09317_1 and $0.2046_7\,\mathrm{cm}^{-1}$.

The experimental procedure to obtain formation constants of crown ether complexes with alkali metal ions is as follows; a PC solution of the alkali metal perchlorate (4×10^{-4}—5×10^{-4} M, 200 cm^3) was placed in the cell (volume 300 cm^3) and the resistance of the solution measured. A step-by-step increase in the crown ether concentration was effected by a rapid transfer from the PC solution of the crown ether (5×10^{-3}—2×10^{-2} M) to the cell using a pipet, until the total concentration of the crown ether was approx. five times as large as that of the alkali metal perchlorate. The resistance of the solution in the cell was remeasured after each transfer.

The experimental procedure to obtain limiting ionic molar conductivities of the alkali metal ion–crown ether complexes was as follows; a PC solution of the crown ether (2×10^{-3} M, 200 cm^3) was placed in the cell and the resistance of the solution measured. Then a step-by-step increase in the alkali metal perchlorate concentration was effected by a rapid transfer from the PC solution of the alkali metal perchlorate (2×10^{-2} M) to the cell with a pipet, until the total concentration of the alkali metal perchlorate was approx. twice as large as that of the crown ether. The resistance of the solution in the cell was remeasured after each transfer.

Results

The molar conductivity, Λ, *vs.* $[\mathrm{L}]_t/[\mathrm{M}]_t$ plots in PC at 25 °C are given in Figs. 1—3, where $[\mathrm{L}]_t$ and $[\mathrm{M}]_t$ are the total concentrations of the crown ether

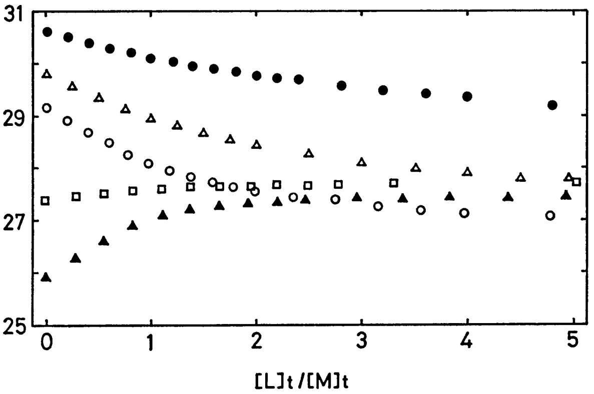

Fig. 1. Λ *vs.* $[L]_t/[M]_t$ curves for 15C5-alkali metal perchlorate systems in PC at 25 °C.
▲: Li$^+$, □: Na$^+$, ○: K$^+$, △: Rb$^+$, ●: Cs$^+$, $[M]_t = 5\times10^{-4}$ M.

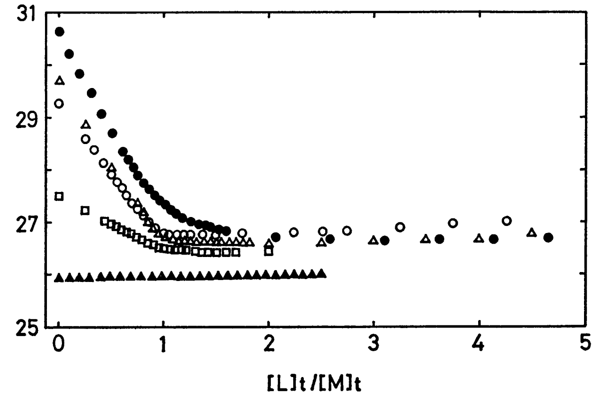

Fig. 2. Λ *vs.* $[L]_t/[M]_t$ curves for 18C6-alkali metal perchlorate systems in PC at 25 °C.
▲: Li$^+$, □: Na$^+$, ○: K$^+$, △: Rb$^+$, ●: Cs$^+$, $[M]_t = 5\times10^{-4}$ M.

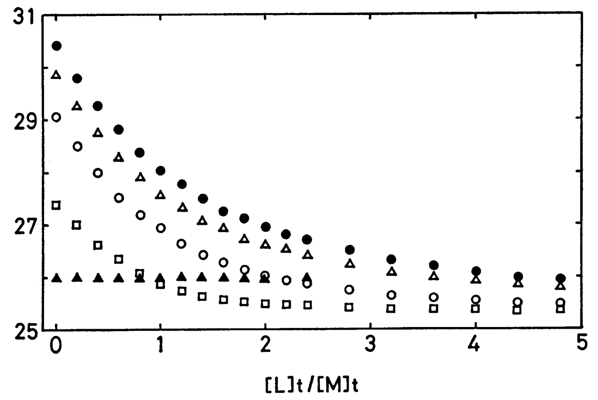

Fig. 3. Λ *vs.* $[L]_t/[M]_t$ curves for DB24C8-alkali metal perchlorate systems in PC at 25 °C.
▲: Li$^+$, □: Na$^+$, ○: K$^+$, △: Rb$^+$, ●: Cs$^+$, $[M]_t = 4\times10^{-4}$ M.

and the alkali metal ion respectively. Figures 1, 2, and 3 correspond to the cases of 15C5, 18C6, and DB24C8 respectively. The Λ *vs.* $[L]_t/[M]_t$ plots in Figs. 1—3 show a decrease of Λ with an increase in the crown ether concentration except for the 15C5-Li$^+$ and Na$^+$ and the Li$^+$–18C6 and DB24C8 systems. Those for the 15C5–Li$^+$ and Na$^+$ systems show an increase of Λ as the 15C5 concentration increases. In the Li$^+$–18C6 and DB24C8 systems, there is a negligible change in Λ in spite of an increase in the crown ether concentration, consequently the conductometric determination of the complex formation constant was impossible. The association between a cation, *i.e.*, an alkali metal ion and a tetraalkylammonium ion, and a perchlorate ion in PC is negligible,[5,6b] and therefore it is assumed on this basis that the association between the alkali metal ion–crown ether complex and the perchlorate ion in PC is also negligible under the highly dilute experimental conditions mentioned above. From Figs. 1—3, in the cases of the 15C5–Li$^+$ and Na$^+$, the 18C6–Na$^+$, K$^+$, Rb$^+$, and Cs$^+$, and the DB24C8–Na$^+$ systems, the slope of each curve changes sharply at the point when $[L]_t/[M]_t=1$, indicating that the crown ether forms a 1:1 complex with the alkali metal ion in PC under these experimental conditions.[8] For the 15C5 and DB24C8–K$^+$, Rb$^+$, and Cs$^+$ systems, no such clear breaking point was observed. From the literature[1b,1c,1f,1g] however, it is assumed that 15C5 and DB24C8 form 1:1 complexes with K$^+$, Rb$^+$, and Cs$^+$ in PC under these experimental conditions.

The equilibrium equation is given by

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

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

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

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 the alkali metal perchlorate and alkali metal crown ether perchlorate respectively. The molar conductivities are given by

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

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

where Λ_{MClO_4} and Λ_{MLClO_4} are the molar conductivities of the alkali metal perchlorate and alkali metal crown ether perchlorate respectively. Equation 3 may be transformed *via* Eqs. 4 and 5 to give

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

Since the crown ether concentration was kept low ($<2.5\times10^{-3}$ M), corrections for viscosity changes were neglected. Substituting from Eq. 6 into Eq. 2 gives

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

where

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

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

	15C5		18C6		DB24C8	
	PC	H_2O[1b)]	PC	H_2O[1b)]	PC	70 wt% CH_3OH in H_2O[1c)]
Li^+	4.2_6	—	—	—	—	—
Na^+	3.7	0.70	5.6_8	0.80	4.1_6	1.54
K^+	3.4_1	0.74	6.2_4	2.03	3.7_3	2.42
Rb^+	3.0_4	0.62	5.3_2	1.56	3.5_5	2.55
Cs^+	2.6_9	0.8	4.4_8	0.99	3.4_6	2.48

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^+} values in Eq. 7 is calculated. The actual K_{ML^+} and Λ_{MLClO_4} values are calculated by a nonlinear least-squares analysis.[1h)] The log K_{ML^+} values are listed in Table 1.

The procedure for obtaining the limiting ionic molar conductivity, $\lambda°$, of the alkali metal ion–crown ether complex is as follows. The mass balances are

$$[M]_t = [M^+] + [ML^+], \tag{8}$$

$$[L]_t = [L] + [ML^+]. \tag{9}$$

From Eqs. 2, 8, and 9, the following quadratic equation follows;

$$K_{ML^+}[ML^+]^2 - \{1+K_{ML^+}([M]_t+[L]_t)\}[ML^+] + K_{ML^+}[M]_t[L]_t = 0. \tag{10}$$

The $[M^+]$ value is obtained from Eq. 8 using the $[ML^+]$ value calculated from Eq. 10. The κ_{MClO_4} value in Eq. 3 at this $[M^+]$ point can be obtained from the previous $\Lambda_{MClO_4}-[MClO_4]^{1/2}$ plots in PC at 25 °C.[11)] Then, the Λ_{MLClO_4} value at this $[ML^+]$ point can be calculated from Eqs. 3 and 5 using this κ_{MClO_4} value. The limiting molar conductivity, $\Lambda°$, of the alkali metal crown ether perchlorate is determined by extrapolation of the calculated Λ_{MLClO_4} values from $\Lambda_{MLClO_4}-[MLClO_4]^{1/2}$ plots for ten-odd concentration points. From this $\Lambda°$ value, the $\lambda°$ value of the alkali metal ion–crown ether complex in PC at 25 °C is computed, using the $\lambda°$ value of the perchlorate ion, $\lambda° = 18.2_8$ Ω^{-1} cm^2 mol^{-1}.[5)] The $\lambda°$ values of the alkali metal ion–crown ether complexes are given in Table 2, together with the $\lambda°$ values of the alkali metal ions in PC at 25 °C.

Discussion

The log K_{ML^+} value series about the same alkali metal ion among the crown ethers in PC are from Table 1 in the order 18C6≫DB24C8>15C5. A complex is more stable the greater the number of oxygen atoms, provided the oxygens are coplanar and symmetrically distributed in the crown ether ring.[1a)] 15C5 and 18C6 structurally obey these criteria and the log K_{ML^+} values of 15C5 and 18C6 in both PC and aqueous solutions (Table 1) show the same tendency as stated above. The log K_{ML^+} values of DB24C8 in PC (Table 1) are smaller than expected based on the greater number of donor oxygen atoms (eight) compared to those of 15C5 and 18C6 (five and six respectively), as found in the calorimetric titration study of the DB24C8 complexes with cations.[1c)] This may be largely attributed to the entropy contribution due to the ring flexibility[1a)] of DB24C8.

TABLE 2. ($\lambda°$/Ω^{-1} cm^2 mol^{-1}) VALUES OF ALKALI METAL ION-CROWN ETHER COMPLEXES AND ALKALI METAL IONS IN PC AT 25 °C

		15C5	18C6	DB24C8
Li^+	8.5_5	9.2_7	—	—
Na^+	9.7_6	$10._1$	8.5_1	7.5_4
K^+	11.9_8	8.6_6	8.9_1	7.4_2
Rb^+	12.4_9	8.3_7	8.8_6	7.3
Cs^+	13.2_9	9.4_3	8.7_8	7.3

The log K_{ML^+} values of 15C5, 18C6, and DB24C8 for the alkali metal ions have been plotted as a function of the crystal ionic radius in Fig. 4. Figure 4 shows that the log K_{ML^+} values of these crown ethers for the same alkali metal ion are much larger for PC than for aqueous and 70 wt% CH_3OH solutions. This indicates that the alkali metal ions are more strongly solvated by water and methanol than PC. The data in Fig. 4 together with the fact that the dielectric constant, ε_r, value sequences of the three solvents are H_2O (ε_r=78 at 25 °C[1c)])>PC (ε_r=64 at 25 °C[5c)])> 70 wt% CH_3OH (ε_r=47 at 25 °C[1c)]) indicates that the dielectric constant of the solvent is not always a

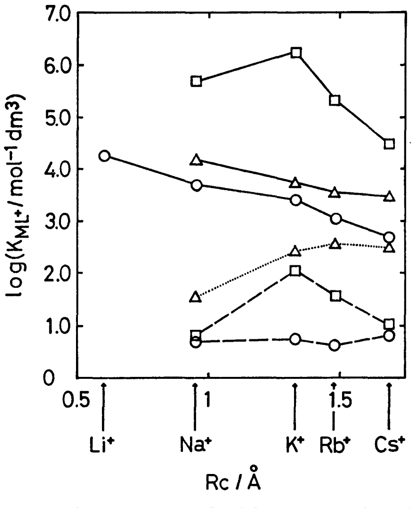

Fig. 4. Plots of log K_{ML^+} at 25 °C *vs*. crystal ionic radius, $R_c(M^+)$, of alkali metal.
○: 15C5, □: 18C6, △: DB24C8.
——: PC, present work, — —: H_2O, Ref. 1b,
----: 70 wt% CH_3OH in H_2O, Ref. 1c.

TABLE 3. CRYSTAL IONIC RADII OF ALKALI METALS AND CAVITY RADII OF CROWN ETHERS (Å)

Cation	Crystal ionic radius[9]	Crown ether	Cavity radius[10]
Li$^+$	0.60	15C5	0.85—1.1
Na$^+$	0.95	18C6	1.3—1.6
K$^+$	1.33	DB24C8	2.25—2.5
Rb$^+$	1.48		
Cs$^+$	1.69		

dominant factor in the alkali metal ion–crown ether complexing. The $\log K_{ML^+}$ series of 15C5 for the alkali metal ions in PC are in the order Li$^+$>Na$^+$>K$^+$>Rb$^+$>Cs$^+$ (Table 1), showing that the ability of the alkali metal ions to form complexes with 15C5 in PC is sensitive to the ratio of the ionic size to the cavity size except in the case of Li$^+$ (Table 3), while that in the aqueous solution is not (Fig. 4 and Table 3). The differences in the $\log K_{ML^+}$ values of 15C5 for the neighboring alkali metal ions increase from water to PC (Table 1). It is interesting that Li$^+$ forms a more stable complex with 15C5 than Na$^+$ in PC, although Li$^+$ is more strongly solvated by PC than Na$^+$[6a] and Na$^+$ fits more closely into the 15C5 cavity than Li$^+$ (Tables 1 and 3). From Table 1, the $\log K_{ML^+}$ sequences of the alkali metal ions with 18C6 in PC and aqueous solutions are K$^+$>Na$^+$>Rb$^+$≫Cs$^+$ and K$^+$>Rb$^+$>Cs$^+$>Na$^+$ respectively, indicating that the selectivity of 18C6 for the alkali metal ions in PC and aqueous solutions primarily depends on the ratio of the ionic size to the cavity size of 18C6 (Table 3) and that the $\log K_{ML^+}$ sequences of the complex in PC differ from those in the aqueous solution. The $\log K_{ML^+}$ series of DB24C8 for the alkali metal ions in PC are given in the order Na$^+$>K$^+$>Rb$^+$≥Cs$^+$, although the more the size of the alkali metal ion decreases, the more strongly it is solvated by PC[6a] and as the size of the alkali metal ion increases, the crystal radius approaches the cavity radius of DB24C8 (Tables 1 and 3). The $\log K_{ML^+}$ sequences of the complex with DB24C8 in PC entirely differ from those in the 70 wt% CH$_3$OH solvent. It may be seen from Table 1 that in the case of each crown ether system an increase in $\log K_{ML^+}$ in moving from aqueous and 70 wt% CH$_3$OH solutions to PC increases with a decrease in the size of the alkali metal ion. Based on the above observations, both the stabilities and selectivities on complexation appear to reflect the competition between ligand coordination and solvation.

As can be seen from Table 2, the λ° value of the alkali metal ion is much larger than that of the corresponding alkali metal ion–crown ether complex except for the cases of 15C5-Li$^+$ and Na$^+$ systems, indicating that the size of the moving entity in PC is much larger for the alkali metal ion–crown ether complex than for the corresponding alkali metal ion. On the contrary the Li$^+$ and Na$^+$ ions are bulkier than the complexes of 15C5 with these ions in PC respectively. The λ° values of the alkali metal ion–crown ether complexes are larger for 18C6 than for DB24C8 and the size of DB24C8 is larger than that of 18C6. It thus appears that the relative sizes of the two crown ethers are the main factor influencing the mobilities. The λ° values of the complexes of 15C5 with Na$^+$ and Cs$^+$ are larger than those of 18C6 with Na$^+$ and Cs$^+$ respectively, which is the same tendency as that found in the 18C6 and DB24C8 systems. Those of 15C5 with K$^+$ and Rb$^+$ are smaller than those of 18C6 with K$^+$ and Rb$^+$ respectively, although the size of 15C5 is smaller than that of 18C6.

In each case of 18C6 and DB24C8 the λ° values of the alkali metal ions are nearly equal (Table 2), suggesting that the charge of the alkali metal ion trapped in the crown ether cavity is effectively shielded by the crown ether and that in each case of 18C6 and DB24C8 the complexes with the alkali metal ions are approximately equal to each other in size. That the λ° values of 15C5 for the alkali metal ions are considerably different from each other is in remarkable contrast to the cases of the 18C6 and DB24C8 systems (Table 2). A possible explanation for this is that it may be impossible for 15C5 to effectively screen the surface charge of the alkali metal ion held in its cavity because of its smaller size compared to 18C6 and DB24C8 (Table 3). Thus the 15C5 complexes with the alkali metal ions would more strongly undergo specific solvation by PC molecules than would 18C6 and DB24C8. It is of interest to note that in the cases of the 15C5 and 18C6 systems the Na$^+$ and K$^+$ complexes, where Na$^+$ and K$^+$ most closely fit into the cavities of 15C5 and 18C6 respectively (Table 3), have the largest mobilities of all the alkali metal ion complexes respectively (Table 2).

According to Lehn[11] and Boileau *et al.*,[4] the crystal ionic radii, $R_c(ML^+)$, of the alkali metal ion–15C5 and 18C6 complexes have been approximately evaluated from the crystal ionic radii $R_c(M^+)$, of the cations located within the central molecular cavity and from the ligand volume V_L:

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

V_L may be approximated by summing the van der Waals volumes of the atoms or groups forming the ligand. Values of $R_c(ML^+)$ are given in Table 4 together with the calculated Stokes' radii, $R_s(ML^+)$, of the alkali metal ion-15C5 and 18C6 complexes from the equation $R_s(ML^+)=0.819/\eta_0\lambda^\circ$, where η_0 is the viscosity of the pure solvent. Table 4 shows that the $R_s(ML^+)$ value about the same alkali metal ion in PC is much smaller than the $R_c(ML^+)$ one for 15C5 and 18C6, which is the same and opposite trends

TABLE 4. STOKES' RADII, R_s, AND CRYSTAL IONIC RADII, R_c, OF ALKALI METAL ION–CROWN ETHER COMPLEXES (Å)

Cation	15C5		18C6	
	R_s	R_c	R_s	R_c
Li$^+$	3.4_9	4.5	—	—
Na$^+$	3.2_1	4.6	3.8_0	4.8
K$^+$	3.7_4	4.6	3.6_3	4.9
Rb$^+$	3.8_7	4.6	3.6_5	4.9
Cs$^+$	3.4_3	4.6	3.6_9	4.9

for tetraalkylammonium ($R_s \ll R_c$) and alkali metal ions ($R_s \gg R_c$) in PC respectively.⁵⁾ The crystal ionic radii of the alkali metal ion–15C5 and 18C6 complexes are nearly identical with those of tetrapropylammonium (4.52 Å¹²⁾) and tetrabutylammonium ions (4.94 Å¹²⁾) respectively (Table 4). The λ° values of the alkali metal ion–15C5 and 18C6 complexes are however smaller than those of tetrapropylammonium ($11.0_0$⁵⁾) and tetrabutylammonium ions ($9.32_5$⁵⁾) respectively (Table 2).

References

1) (a) C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967); (b) R. M. Izatt, R. E. Terry, B. L. Haymore, L. D. Hansen, N. K. Dalley, A. G. Avondet, and J. J. Christensen, *J. Am. Chem. Soc.*, **98**, 7620 (1976); (c) R. M. Izatt, R. E. Terry, D. P. Nelson, Y. Chan, D. J. Eatough, J. S. Bradshaw, L. D. Hansen, and J. J. Christensen, *J. Am. Chem. Soc.*, **98**, 7626 (1976); (d) H. K. Frensdorff, *J. Am. Chem. Soc.*, **93**, 600 (1971); (e) C. J. Pedersen, *Fed. Proc., Fed. Am. Soc. Exp. Biol.*, **27**, 1305 (1968); (f) Y. Takeda and H. Gotō, *Bull. Chem. Soc. Jpn.*, **52**, 1920 (1979); (g) Y. Takeda, *Bull. Chem. Soc. Jpn.*, **52**, 2501 (1979); (h) D. F. Evans, S. L. Wellington, J. A. Nadis, and E. L. Cussler, *J. Solution Chem.*, **1**, 499 (1972); (i) N. Matsuura, K. Umemoto, Y. Takeda, and A. Sasaki, *Bull. Chem. Soc. Jpn.*, **49**, 1246 (1976).

2) M. R. Truter and C. J. Pedersen, *Endeavour*, **30**, 142 (1971).

3) D. Live and S. I. Chan, *J. Am. Chem. Soc.*, **98**, 3769 (1976).

4) S. Boileau, P. Hemery, and J. C. Justice, *J. Solution Chem.*, **4**, 873 (1975).

5) N. Matsuura, K. Umemoto, and Y. Takeda, *Bull. Chem. Soc. Jpn.*, **48**, 2253 (1975).

6) (a) N. Matsuura, K. Umemoto, M. Waki, Z. Takeuchi, and M. Omoto, *Bull. Chem. Soc. Jpn.*, **47**, 806 (1974); (b) M. L. Jansen and H. L. Yeager, *J. Phys. Chem.*, **77**, 3089 (1973).

7) Y. Takeda, K. Oshio, and Y. Segawa, *Chem. Lett.*, **1979**, 601.

8) H. K. Frensdorff, *J. Am. Chem. Soc.*, **93**, 4684 (1971).

9) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell Univ. Press (1960).

10) C. J. Pedersen, *J. Am. Chem. Soc.*, **92**, 386 (1970).

11) J. M. Lehn, *Struct. Bonding*, **16**, 1 (1973).

12) D. E. Arrington and E. Griswold, *J. Phys. Chem.*, **74**, 123 (1970).