A Conductance Study of the Binding of Benzo-15-Crown-5 with Alkali Cations in Acetonitrile

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Abstract. The decrease in the molar electrolytic conductance of Na^+, K^+, Rb^+, and Cs^+ tetraphenylborates, caused by the addition of benzo-15-crown-5 in acetonitrile at constant ionic strength, is analyzed according to a model involving $1:1$ stoichiometry. The stability constant, K, and the limiting molar conductivity, Λ_c, for each $1:1$ complex are determined from the conductance measurements by using a nonlinear least squares curve fitting procedure. The stability sequence of the $1:1$ complexes, as deduced from data at 288, 293, 298, 303, and 308 K, has the order $Na^+ > K^+ > Rb^+ > Cs^+$. Values of ΔH^0, ΔS^0, and Λ_c at 298 K are reported and their significance is discussed.

Key words. Benzo-15-crown-5, alkali cations, electrolytic conductance, crown ethers.

1. Introduction

The binding of certain cations with 15-membered cyclic crown ethers results in the formation of $1:1$ and $1:2$ (cation:crown) complexes. Such $1:2$ complexes (usually referred to as sandwich complexes) were first isolated by Pedersen [1]. Benzo-15-crown-5 (B15C5, see Figure 1) has been reported to form sandwich complexes with Na^+ [2, 3], K^+ [4, 5, 6], and Rb^+ [6]. The formation of $1:2$ complexes has also been reported for the binding of cyclohexano-15-crown-5 with K^+ and Cs^+ [7] and for the binding of dibenzo-15-crown-5 with K^+ [8]. Most of these $1:2$ complexes were isolated from or detected in methanol or aqueous methanol solvents. The methods used in deducing the $1:2$ stoichiometry include crystal structure determination [3], potentiometry [7], calorimetry [6] and NMR [8]. The relative proportions of $1:1$ and $1:2$ complexes for a given cation–crown ether system seem to be solvent dependent. For example $1:2$ complexes of K^+ or Rb^+ with B15C5 were not detected for solvents having less than 70 wt.% methanol in water [6]. According to the compilation of formation constants reported by Izatt *et al.* [9], no mention of $1:2$ complexes has been made for the binding of the alkali cations with the 15-membered ring crown ethers in aprotic solvents. Only $1:1$ complexes were reported for the binding of the alkali cations with 15-crown-5 in acetonitrile [10] and with B15C5 in acetonitrile [11] and in propylene carbonate [12]. However, negligible amounts of $1:2$ complex had been reported for the binding of Na^+ with B15C5 in acetonitrile [13].

The purpose of the present work is to study the binding of the alkali cations with B15C5 in acetonitrile by using a conductometric method and to establish values for ΔH^0
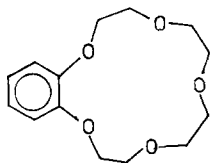
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Fig. 1. The structure of benzo-15-crown-5 (B15C5).

and ΔS^0 which are almost nonexistent for most of the 15-membered ring crown ether complexes in aprotic solvents. In order to avoid complications that might arise from ion pairs, dilute acetonitrile solutions of the alkali metal tetraphenylborates (MBPh$_4$) were used in the present study.

2. Experimental

Acetonitrile (HPLC grade) was obtained from Koch-Light Ltd. Its specific conductivity was less than 2×10^{-7} S cm^{-1} and its water content was $\sim 0.01\%$. It was used without further purification. Benzo-15-crown-5 was purchased from Merck and was used as received. Its solutions in acetonitrile gave the same specific conductivity as that of acetonitrile. Sodium tetraphenylborate (purum grade) was purchased from BDH. It was recrystallized from an acetone–toluene mixture [13]. The preparation and purification of K$^+$, Rb$^+$, and Cs$^+$ tetraphenylborates were carried out as reported in the literature [14]. The description of the conductometer and the details of the experimental procedure as well as the curve fitting procedure have been given previously [15].

3. Results and Discussion

The effect of temperature on the complexation reactions of B15C5 with Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ is shown in Figures 2 to 5. In these figures the quantities Λ, [LT], and [MT] represent the observed molar conductivity of a test solution and the total molar concentrations (mol dm^{-3}) of B15C5 and an alkali tetraphenylborate respectively. In all cases, Λ decreases monotonously as the mole ratio [LT]/[MT] is increased. Since dilute solutions of the alkali tetraphenylborates are strong electrolytes in acetonitrile [16], the decrease in Λ is considered as evidence for complex formation. The data of the Na$^+$ system, shown in Figure 2, indicate a significant change in the slope of the Λ vs. [LT]/[MT] plot at mole ratios close to unity. This observation is interpreted as an indication of the formation of a 1:1 complex between Na$^+$ and B15C5. On the other hand such an observation is not evident in the case of the K$^+$, Rb$^+$, and Cs$^+$ plots.

In order to analyze the conductivity data of the present study, the binding of an alkali cation, M$^+$, (M$^+$ = Na$^+$, K$^+$, Rb$^+$, or Cs$^+$) with B15C5, L, is assumed to be given by the following equilibrium:

$$M^+ + L \rightleftarrows LM^+. \tag{1}$$

With an equilibrium constant, K, given as follows:

$$K = [ML^+]/[M^+][L], \tag{2}$$

where [M$^+$], [L], and [ML$^+$] represent the equilibrium molar concentrations of the free
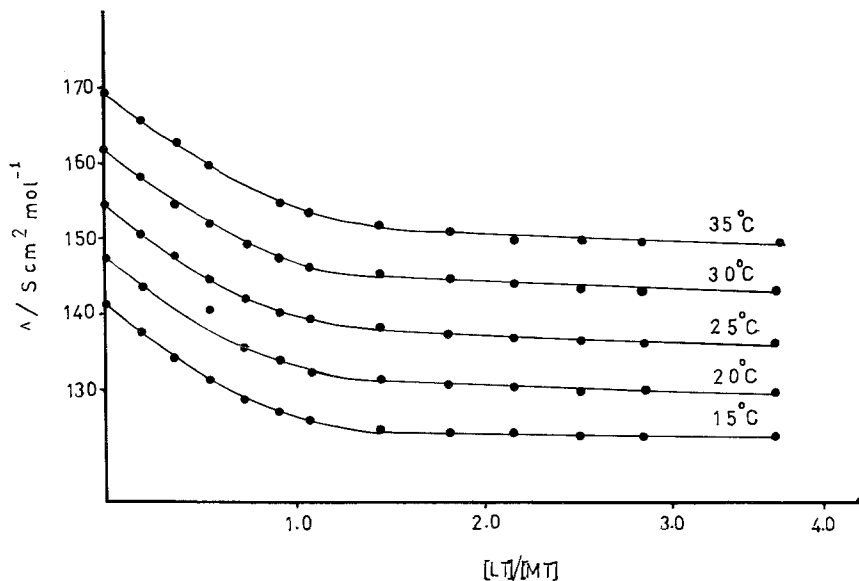
Fig. 2.   Plot of Λ vs. [LT]/[MT] for Na$^+$ binding with benzo-15-crown-5. Closed circles experimental, solid lines calculated data.

cation, free B15C5, and the 1:1 complex respectively. The complete mathematical treatment that relates K to Λ, Λ_0 (molar conductivity of the crown-free MBPh$_4$ solution), and Λ_c (molar conductivity of the 1:1 complex whose molar concentration is equal to [MT]) as well as the details of the curve fitting procedure are as reported previously [15]. Typical data showing the results of our curve fitting procedure for the 1:1 binding of B15C5 with Na$^+$ and K$^+$ at 25°C are given in Tables I and II, respectively. Table I shows that Λ assumes a constant value when the mole ratio exceeds 3. This constancy in Λ is very unlikely to happen if the two species NaL$^+$ and NaL$_2^+$ were to coexist in appreciable amounts in the reaction mixture, since their ionic mobilities are different and their concentration ratio [NaL$_2^+$]/[NaL$^+$] is directly proportional to [L]. Therefore the constancy in Λ is due to the presence of the species NaL$^+$. This conclusion was substantiated by direct calculation of K from Table I without using the nonlinear least squares procedure [15]. This calculation was made by assigning Λ_c a value of 135.82 S cm^2 mol^{-1} (see Table I) and using the following equations [15, 17]:

$$[L] = [LT] - [MT] \frac{(\Lambda_0 - \Lambda)}{(\Lambda_0 - \Lambda_c)}, \tag{3}$$

$$K = \frac{(\Lambda_0 - \Lambda)}{(\Lambda - \Lambda_c)} \frac{1}{[L]}. \tag{4}$$

The average calculated value of K for data points falling in the mole ratio range 0.732 to 2.513 in Table I was found to be within 1% of the value of K obtained by subjecting all the data in Table I to the curve fitting procedure. Such reasoning is not possible for the K$^+$, Rb$^+$, and Cs$^+$ data since the corresponding Λ does not assume a constant value at higher mole ratios. However, the excellent agreement between the observed and calculated values of Λ shown in Figures 3 to 5 implies the predominance of the 1:1 complexes
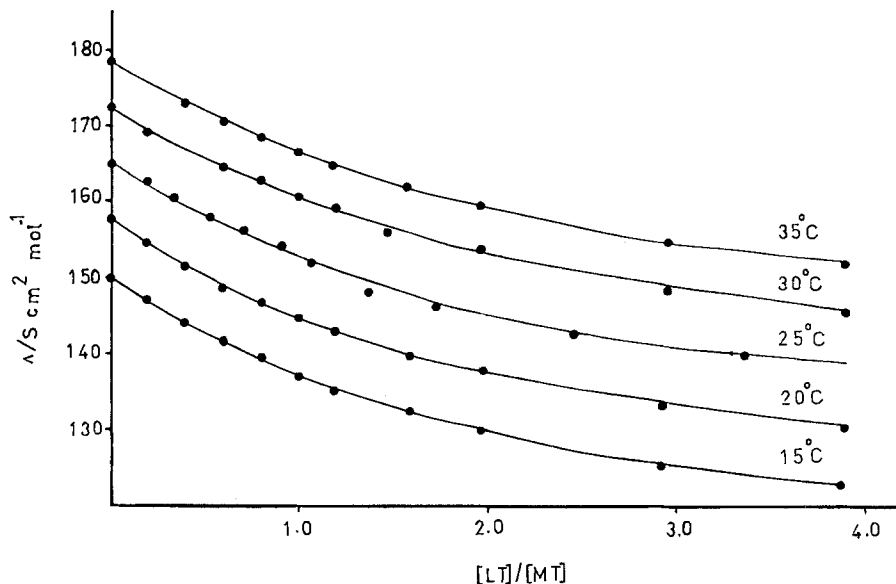
Fig. 3. Plot of Λ vs. [LT]/[MT] for K$^+$ binding with benzo-15-crown-5. Closed circles experimental, solid lines calculated data.

Table I. Observed molar conductivities, Λ, at various mole ratios, [LT]/[MT], for the binding of Na$^+$ with benzo-15-crown-5 at 298 K.

[LT]/[MT]	10^4 [LT]/mol dm^{-3}	Λ/S cm^2 mol^{-1}	Λcal/S cm^2 mol^{-1}
0.184	0.743	150.94	151.19
0.368	1.483	147.72	148.10
0.550	2.220	144.74	145.19
0.732	2.954	142.27	142.60
0.913	3.685	140.28	140.52
1.094	4.413	139.29	139.04
1.453	5.861	138.05	137.52
1.809	7.298	137.06	136.88
2.162	8.723	136.81	136.57
2.513	10.14	136.56	136.38
2.860	11.54	136.07	136.26
3.548	14.32	135.82	136.11
5.222	21.07	135.82	135.95
6.833	27.57	135.82	135.88
8.386	33.84	135.82	135.84
9.884	39.88	135.82	135.81
11.33	45.71	135.82	135.80
12.72	51.34	135.82	135.78
14.07	56.78	135.82	135.77
15.38	62.03	135.82	135.77

[MT] $= 4.035 \times 10^{-4}$ mol dm^{-3}; $\Lambda_0 = 154.41$ S cm^2 mol^{-1};
$\Lambda_c = 135.69$ S cm^2 mol^{-1}; $K = 4.165 \times 10^4$ mol^{-1} dm^3.
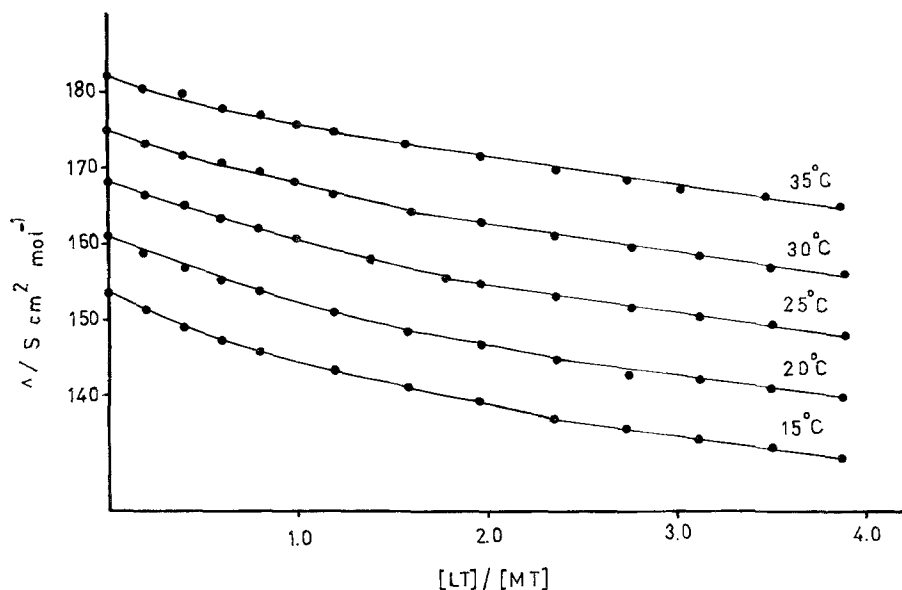
Fig. 4. Plot of Λ vs. [LT]/[MT] for Rb^+ binding with benzo-15-crown-5. Closed circles experimental, solid lines calculated data.

in the binding of B15C5 with K^+, Rb^+, and Cs^+. No attempt has been made to include 1:2 complexes in analyzing the conductance measurements of cation–crown ether complexes.

An important feature of the graphs shown in Figures 2 to 5 is that the degree of curvature of the graph of Λ vs. [LT]/[MT] has the order: $Na^+ > K^+ > Rb^+ > Cs^+$. This

Table II. Observed molar conductivities, Λ, at various mole ratios, [LT]/[MT], for the binding of K^+ with benzo-15-crown-5 at 298 K.

[LT]/[MT]	10^4 [LT]/mol dm^{-3}	Λ/S cm^2 mol^{-1}	Λ cal/S cm^2 mol^{-1}
0.175	0.799	159.11	159.20
0.348	1.595	156.05	156.35
0.522	2.387	153.64	153.85
0.694	3.177	151.68	151.60
0.866	3.963	149.49	149.57
1.037	4.746	147.97	147.76
1.378	6.303	144.68	144.67
1.715	7.848	142.28	142.18
3.364	15.39	135.06	134.96
4.952	22.65	131.57	131.72
6.480	29.65	129.82	129.93
7.952	36.38	128.73	128.81
9.372	42.88	128.07	128.05
12.07	55.21	127.20	127.08
14.44	66.06	126.54	126.51

$[MT] = 4.00 \times 10^{-4}$ mol dm^{-3}; $\Lambda_0 = 162.00$ S cm^2 mol^{-1}; $\Lambda_c = 123.57$ S cm^2 mol^{-1}; $K = 1.962 \times 10^3$ mol^{-1} dm^3.
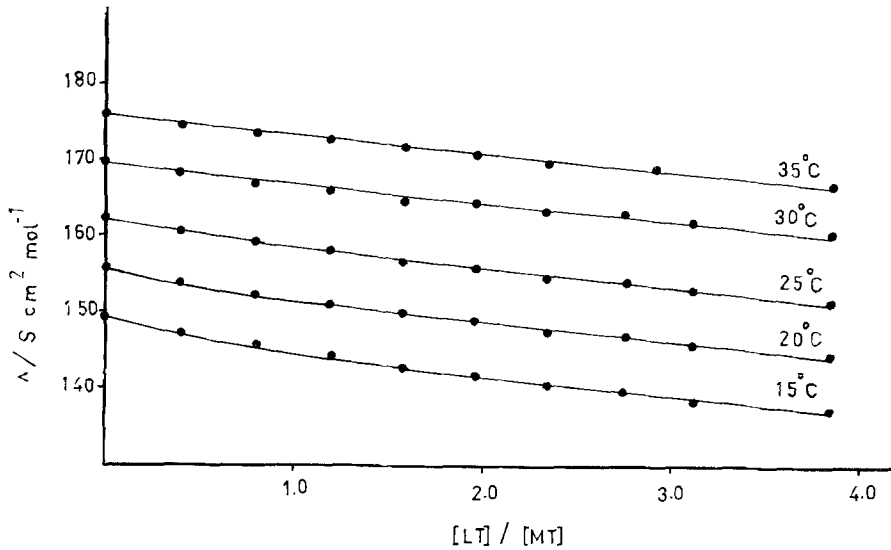
Fig. 5. Plot of Λ vs. [LT]/[MT] for Cs^+ binding with benzo-15-crown-5. Closed circles experimental, solid lines calculated data.

observation is in agreement with our result for the binding sequence (complex stability sequence) that is obtained by comparing $\log K$ at 25°C for the complexes of B15C5 with the alkali cations as given in Table III. However, Hopkins and Norman [10] have reported plots of Λ vs. [LT]/[MT] that show a kink at a mole ratio of about 0.5 for the binding of Na^+ and K^+ with 15-crown-5. The effect of temperature, T, on the binding of the alkali cations with B15C5 in acetonitrile is shown in Figure 6. In all cases K decreases as T is increased. Values of ΔH^0 and ΔS^0 are obtained from the slope and

Table III. Stability constants and thermodynamic quantities of the 1 : 1 complexes of benzo-15-crown-5 with alkali metal cations at 25°C.

Cation	Anion	Solvent[a]	Log K^b	$-\Delta H^{0c}$	$-\Delta S^{0d}$	$\Delta H^0/T\Delta S^0$	Method	Ref.
Na^+	BPh_4^-	AN	4.61	36.0	32.8	3.7	Cond.[e]	This work
	ClO_4^-	AN	4.55	–	–	–	polg.[f]	[11]
	BPh_4^-	AN	>4	–	–	–	NMR	[13]
	ClO_4^-	PC	4.35	–	–	–	Cond.	[12]
K^+	BPh_4^-	AN	3.24	24.5	20.0	4.1	Cond.	This work
	ClO_4^-	AN	3.40	–	–	–	polg.	[11]
	ClO_4^-	PC	2.78	26.4	35.4	2.5	Cond.	[12]
Rb^+	BPh_4^-	AN	2.82	29.7	46.0	2.2	Cond.	This work
	ClO_4^-	AN	2.90	–	–	–	polg.	[11]
	ClO_4^-	PC	2.38	-	–	–	Cond.	[12]
Cs^+	BPh_4^-	AN	2.46	32.9	63.7	1.7	Cond.	This work
	ClO_4^-	AN	3.10	–	–	–	polg.	[11]
	ClO_4^-	PC	2.03	–	...	–	Cond.	[12]

[a] AN = acetonitrile; PC = propylene carbonate;   [b] K in $dm^3 \, mol^{-1}$;   [c] ΔH^0 in $kJ \, mol^{-1}$;   [d] ΔS^0 in $J \, K^{-1} \, mol^{-1}$;   [e] conductivity;   [f] polarography; – information unavailable.
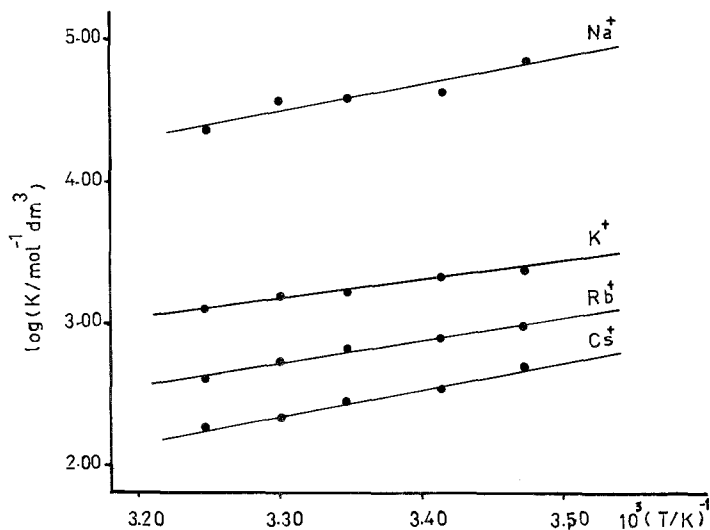
Fig. 6. Plot of log K vs. $(T)^{-1}$ for the 1:1 binding of Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ with benzo-15-crown-5.

intercept of the corresponding log K vs. $(T)^{-1}$ plot, respectively. These values are included in Table III. The literature information concerning ΔH^0 and ΔS^0 values for the binding of B15C5 with all of the alkali cations is very limited. The values reported by Takeda [12] for the binding of K$^+$ with B15C5 in propylene carbonate are in fair agreement with our study in acetonitrile (see Table III). On the other hand Izatt et al. [6] have reported lower $|\Delta H^0|$ values for Na$^+$ and Cs$^+$ complexes with B15C5 in aqueous methanol. This difference is due to the greater desolvation energy of these cations in aqueous methanol as compared to that in acetonitrile. Despite the lack of any correlation between the ΔH^0 or ΔS^0 sequence and the stability sequence (as deduced from log K at 25°C in Table III), our study shows that both ΔH^0 and ΔS^0 affect the overall stability of a complex. It is worth noting that the ratio $\Delta H^0/T\Delta S^0$ at 25°C is smallest for the Cs$^+$ complex. This can be attributed to the larger size of Cs$^+$ when compared to the cavity size of B15C5. Consequently, the Cs$^+$ complex is entropy destabilized. The crystal ionic diameters of Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ are 1.90, 2.66, 2.96, and 3.34 Å respectively [18]. The cavity diameter of B15C5 can be assumed to be similar to that of 15-crown-5 which is given as 1.70 Å [19]. Among these cations, the ionic radius of Na$^+$ most closely corresponds to the cavity radius of B15C5, consequently Na$^+$ forms the most stable complex as predicted by the hole-size rule. The 1:1 binding order for K$^+$, Rb$^+$, and Cs$^+$ is in accord with this rule. However, Hofmanova et al. [11] have reported the 1:1 binding sequence Na$^+$ > K$^+$ > Cs$^+$ > Rb$^+$ in acetonitrile, while Takeda [12] has reported the sequence Na$^+$ > K$^+$ > Rb$^+$ > Cs$^+$ in propylene carbonate which is in agreement with our study. It is interesting to note that B15C5 selectively binds Na$^+$ in all studies reported in Table III. The same observation holds for 15-crown-5 complexes in propylene carbonate [17].

Some of our preliminary experiments were focused on measuring Λ_0 for equal molar concentrations ($\sim 4 \times 10^{-4}$ mol dm^{-3}) of MBPh$_4$ solutions in acetonitrile. The sequence we found for Λ_0 at 25°C is: Λ_0 (NaBPh$_4$) < Λ_0 (KBPh$_4$) < Λ_0 (RbBPh$_4$) < Λ_0 (CsBPh$_4$) as in Table IV. On the other hand, the limiting molar conductivities, Λ_c, at 25°C for the completely complexed cations at about the same molar concentration are 135.5, 123.6,

Table IV. Average values[a] of Λ_0, Λ_c, K and their standard deviations(s) for the 1:1 complexes of benzo-15-crown-5 with Na$^+$, K$^+$, Rb$^+$, and Cs$^+$. Λ_0 and Λ_c are in S cm^2 mol^{-1} and K in dm^3 mol^{-1}.

Temp./K	Parameter	Cation			
		Na$^+$	K$^+$	Rb$^+$	Cs$^+$
288	$\Lambda_0 \pm s$	137.90 ± 2.40	149.00 ± 1.60	151.20 ± 2.60	152.00 ± 2.70
288	$\Lambda_c \pm s$	123.36 ± 0·01	117.07 ± 2.74	114.58 ± 1.00	117.89 ± 1.18
288	$K \pm s$	73662 ± 2498	2427 ± 66	935 ± 31	439 ± 17
293	$\Lambda_0 \pm s$	145.00 ± 2.80	155.60 ± 2.20	158.70 ± 3.00	158.50 ± 2.80
293	$\Lambda_c \pm s$	129.21 ± 0.01	120.26 ± 0.83	119.01 ± 0.50	121.56 ± 1.20
293	$K \pm s$	42986 ± 2406	2212 ± 100	775 ± 34	345 ± 11
298	$\Lambda_0 \pm s$	152.50 ± 2.80	162.60 ± 1.60	165.40 ± 2.90	164.70 ± 2.60
298	$\Lambda_c \pm s$	135.52 ± 0.17	123.57 ± 0.62	125.68 ± 0.20	127.81 ± 0.33
298	$K \pm s$	40286 ± 1366	1732 ± 230	666 ± 20	288 ± 14
303	$\Lambda_0 \pm s$	160.00 ± 3.50	170.00 ± 2.00	171.90 ± 2.80	172.70 ± 3.20
303	$\Lambda_c \pm s$	142.37 ± 0.05	132.34 ± 0.38	130.04 ± 1.30	130.78 ± 2.00
303	$K \pm s$	39051 ± 882	1580 ± 4	532 ± 11	212 ± 13
308	$\Lambda_0 \pm s$	166.70 ± 3.10	176.90 ± 1.80	179.60 ± 3.50	179.30 ± 2.90
308	$\Lambda_c \pm s$	148.30 ± 0.06	136.95 ± 1.86	134.65 ± 1.80	136.20 ± 2.32
308	$K \pm s$	2273 ± 464	1252 ± 5	412 ± 8	184 ± 3

[a] Average values of Λ_0 were obtained from 5 determinations in the concentration range (3.93 to 4.09) × 10^{-4} mol dm^{-3}, while those of K and Λ_c were obtained from 3 determinations in the same concentration range.

125.7, and 127.8 S cm^2 mol^{-1} for the Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ 1:1 complexes with B15C5 respectively. Since the counter ion, BPh$_4^-$ is assumed to have the same molar conductivity whether it is a counter ion for M$^+$ or the ML$^+$, the decrease in molar conductivity is due to the formation of the less mobile macrocation, ML$^+$. The trend in Λ_c for K$^+$, Rb$^+$, and Cs$^+$ complexes is nearly the same as that of Λ_0 for the crown ether-free solutions. This means that the charge of any of these cations is not fully shielded by B15C5 which makes room for the solvent molecules to interact with the cation. On the other hand, Λ_c for the Na$^+$ complex is the highest in the series which indicates that the Na$^+$ complex is the most mobile one. This might indicate that the charge of Na$^+$ is effectively shielded by B15C5 with little involvement of solvent molecules. It has been observed [17] that cations having a close fit to a crown ether cavity form the most stable complexes with higher mobilities. Our result for the Na$^+$ complex with B15C5 is in agreement with such an observation. The uncertainties of the ΔH^0 values were calculated according to [20]. These are 8.5, 2.3, 2.0, and 1.8 kJ mol^{-1} for the Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ complexes, respectively.

Acknowledgements

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