# Conductance Study of Binding of Some Rb<sup>+</sup> and Cs<sup>+</sup> Ions by Macrocyclic Polyethers in Acetonitrile Solution

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A conductance study of the interaction between  $Rb^+$  and  $Cs^+$  ions and 18-crown-6 (18C6), dicyclohexyl-18-crown-6 (DC18C6), dibenzo-18-crown-6 (DB18C6), dibenzo-24-crown-8 (DB24C8), and dibenzo-30-crown-10 (DB30C10) in acetonitrile solution has been carried out at various temperatures. The formation constants of the resulting 1:1 complexes were determined from the molar conductance-mole ratio data and found to vary in the order

$$DC18C6 > 18C6 > DB30C10 > DB18C6 \sim DB24C8$$

for Rb<sup>+</sup> ion and

 $DC18C6 > 18C6 > DB30C10 \sim DB24C8 > DB18C6$ 

for  $Cs^+$  ion. The enthalpy and entropy of complexation were determined from the temperature dependence of the formation constants. The complexes with the 18-crowns are both enthalpy and entropy stabilized while, in the case of large crown ethers, the corresponding complexes are enthalpy stabilized but entropy destabilized.

**KEY WORDS:** Rb<sup>+</sup> and Cs<sup>+</sup> complexes; 18, 24, and 30 crown ethers; conductance; stability constants; enthalpy; entropy; acetonitrile.

## **1. INTRODUCTION**

The several factors that influence the formation of crown ether complexes of metal ions in solution are well known.<sup>(1–3)</sup> The most emphasized factor is the crown's cavity size–cation diameter ratio, although its importance has

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been questioned in the case of large crown ethers.<sup>(1,2)</sup> Actually, large crown ethers (*i.e.*, larger than 18-crown-6) possess highly flexible geometries in solution and adapt their conformations for optimum complexation of guest cations. Thus, evidence for the formation of tridimensional "wrap-around" complexes between large crown ethers and some alkali metal ions both in solid state<sup>(4,5)</sup> and solution<sup>(6–9)</sup> have been reported in the literature. Other important factors include the number and the nature of heteroatoms participating in cation binding, the nature of substituted groups on the macrocyclic ring, and, especially, the solvent properties.<sup>(1)</sup> The nature of solvent has found to strongly influence the stoichiometry, selectivity, thermodynamic stability, and exchange kinetics of metal ion–crown ether complexes.<sup>(1-3,7,9)</sup>

In recent years, we have employed different spectroscopic and electrochemical methods to investigate the influence of macrocyclic structure and solvent properties on the stoichiometry, stability, thermodynamics<sup>(10–15)</sup> and kinetics<sup>(7–20)</sup> of different metal ion–crown ether complexes. In this work, we study the thermodynamics of complexation of Rb<sup>+</sup> and Cs<sup>+</sup> ions with 18crown-6 (18C6), dicyclohexyl-18-crown-6 (DC18C6), and dibenzo-18crown-6 (DB18C6) and larger crowns dibenzo-24-crown-8 (DB24C8) and dibenzo-30-crown-10 (DB30C10) in acetonitrile solution conductometrically. Structures of the ligands are shown in Fig. 1. It should be noted that both cations have small sizes compared to the cavity of the large crown ethers used here. On the other hand, while Rb<sup>+</sup> ion with an ionic diameter of 3.02 Å<sup>(21)</sup> conveniently matches the cavity of 18-membered crown ethers (with a cavity size 2.8–3.2 Å);<sup>(22)</sup> Cs<sup>+</sup> ion possesses a somewhat larger size than the 18-crowns cavity (*i.e.*, 3.34 Å).<sup>(21)</sup>

#### 2. EXPERIMENTAL

Reagent-grade nitrate salts of rubidium and cesium (both from Aldrich) were of the highest purity available and used without any further purification except for vacuum drying over P<sub>2</sub>O<sub>5</sub>. Crown ethers 18C6, DB18C6, DC18C6, DB24C8 (all from Merck), and DB30C10 (Aldrich) were purified and dried as described elsewhere.<sup>(10,12,14)</sup> Reagent-grade acetonitrile was purified and dried by the previously described method.<sup>(23)</sup> The conductivity of the solvent was less than  $1.0 \times 10^{-7}$  S-cm<sup>-1</sup>.

Conductance measurements were carried out with a Metrohm 712 conductometer. A dip-type conductivity cell made of platinum black was used. The cell constant at the different temperatures used was determined by measuring the conductivity of a 0.010 mol-dm<sup>-3</sup> solution of analytical-grade KCl (Merck) in triply distilled deionized water. The specific conductance of this solution at various temperatures have been reported in the literature.<sup>(24)</sup> In



Fig. 1. Structure of macrocyclic ligands.

all measurements, the cell was thermostated at the desired temperature  $\pm 0.03$  °C using a HAAKE D1 thermostated circulator water bath.

In a typical experiment, 15 cm<sup>3</sup> of a metal nitrate solution  $(5.0 \times 10^{-5} \text{ mol-dm}^{-3})$  was placed in a water-jacketed cell equipped with a magnetic stirrer and connected to the thermostated circulating water at the desired temperature. In order to keep the electrolyte concentration constant during the titration, both the starting solution and the titrant had the same metal ion concentration. The conductance of the initial solution was measured after thermal equilibrium had been reached. A known amount of the macrocycle solution was then added in a stepwise manner using a calibrated micropipette. The conductance of the solution was measured after each addition. Addition of the ligand was continued until the desired ligand-to-cation mole ratio was achieved.

# 3. RESULTS AND DISCUSSION

The molar conductance  $\Lambda$  of nitrate salts of Rb<sup>+</sup> and Cs<sup>+</sup> was monitored as a function of crown ether to metal ion mole ratio in acetonitrile solution at various temperatures. The resulting molar conductance vs. crown/cation mole ratio plots at 15.0, 25.0, 35.0, and 45.0°C are shown in Figs. 2–5, respectively. In every case, there is a gradual decrease in the molar conductance with an increase in the crown ether concentration. This behavior indicates that the complexed metal ions are less mobile than the corresponding solvated M<sup>+</sup> ions.

As can be seen from Figs. 2–5, in the case of 18C6 and DC18C6, addition of the ligand to both metal solutions causes a continuous decrease in the molar conductance, which begins to level off at mole ratios greater than one. The slope of the corresponding mole ratio plots changes more dramatically as it goes through a ligand to metal ion mole ratio of one, indicating predominant formation of a relatively stable 1:1 complex. However, in the case of other crown ethers used, the relatively large decrease in molar



**Fig. 2.** Molar conductance *vs.*  $C_{\text{crown}}/C_{\text{M}}$  plots at 15°C for Rb<sup>+</sup> (A) and Cs<sup>+</sup> (B) complexes with different crown ethers in acetonitrile solution: (1) 18C6, (2) DC18C6, (3) DB18C6, (4) DB24C8, (5) DB30C10.



**Fig. 3.** Molar conductance vs.  $C_{\text{crown}}/C_{\text{M}}$  plots at 25°C for Rb<sup>+</sup> (A) and Cs<sup>+</sup> (B) complexes with different crown ethers in acetonitrile solution: (1) 18C6, (2) DC18C6, (3) DB18C6, (4) DB24C8, (5) DB30C10.

conductance of the metal nitrate solutions upon addition of the macrocycles exhibits neither considerable change in the slope at the mole ratio of about one, nor any tendency for leveling off, even at a mole ratio of 4, emphasizing the formation of weaker complexes.

By comparison of the molar conductance-mole ratio plots for all  $Rb^+$ -crown and  $Cs^+$ -crown systems obtained at different temperatures (Figs. 2–5), two trends are observed that deserve attention. First, as expected, the corresponding molar conductances increase rapidly with temperature, because of the decreased viscosity of the solvent and, consequently, the enhanced mobility of the charged species present. Second, for each cation used, the curvature of the corresponding mole ratio plot decreases with increasing temperature, indicating the formation of weaker complexes at elevated temperatures.

The 1:1 binding of both metal ions,  $M^+$ , with the crown ethers used, C, can be expressed by the following equilibrium:

$$\mathbf{M}^{+} + \mathbf{C} \stackrel{K_{f}}{\leftrightarrows} \mathbf{M}\mathbf{C}^{+} \tag{1}$$

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**Fig. 4.** Molar conductance *vs.*  $C_{\text{crown}}/C_{\text{M}}$  plots at 35°C for Rb<sup>+</sup> (A) and Cs<sup>+</sup> (B) complexes with different crown ethers in acetonitrile solution: (1) 18C6, (2) DC18C6, (3) DB18C6, (4) DB24C8, (5) DB30C10.

The corresponding equilibrium constant,  $K_{\rm f}$ , is given by

$$K_{\rm f} = \frac{[\rm MC^+]}{[\rm M^+][\rm C]} \times \frac{f(\rm MC^+)}{f(\rm M^+)f(\rm C)}$$
(2)

where [MC<sup>+</sup>], [M<sup>+</sup>], [C], and *f* represent the equilibrium molar concentrations of complex, free cation, free ligand, and the activity coefficients of the species indicated, respectively. Under the dilute conditions used, the activity coefficient of uncharged macrocycle, f(C), can be reasonably assumed as unity.<sup>(25,26)</sup> The use of Debye–Hückel limiting law<sup>(27)</sup> leads to the conclusion that  $f(M^+) \approx f(MC^+)$ , so the activity coefficients in Eq. (2) cancel.

The complex formation constant in terms of the molar conductances,  $\Lambda$ , can be expressed as<sup>(28,29)</sup>

$$K_{\rm f} = \frac{[\rm MC^+]}{[\rm M^+][\rm C]} = \frac{(\Lambda_{\rm M} - \Lambda_{\rm obs})}{(\Lambda_{\rm obs} - \Lambda_{\rm MC})[\rm C]}$$
(3)

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**Fig. 5.** Molar conductance vs.  $C_{\text{crown}}/C_{\text{M}}$  plots at 45°C for Rb<sup>+</sup> (A) and Cs<sup>+</sup> (B) complexes with different crown ethers in acetonitrile solution: (1) 18C6, (2) DC18C6, (3) DB18C6, (4) DB24C8, (5) DB30C10.

where

$$[C] = C_{C} - \frac{C_{M}(\Lambda_{M} - \Lambda_{obs})}{(\Lambda_{M} - \Lambda_{MC})}$$
(4)

Here,  $\Lambda_{\rm M}$  is the molar conductance of the metal ion before addition of ligand,  $\Lambda_{\rm MC}$  the molar conductance of the complexed ion,  $\Lambda_{\rm obs}$  the molar conductance of the solution during titration, C<sub>C</sub> the analytical concentration of the macrocycle added, and C<sub>M</sub> the analytical concentration of the salt. The complex formation constant,  $K_{\rm f}$ , and the molar conductance of the complex,  $\Lambda_{\rm MC}$ , were evaluated by computer fitting of Eq. (3) and (4) to the molar conductancemole ratio data using a nonlinear least-squares program KINFIT.<sup>(30)</sup> It should be noted that, in acetonitrile as a solvent of intermediate donor number (DN = 14.1) and relative permittivity ( $\varepsilon = 38.0$ ), it was assumed that the association into ion pairs is negligible under the highly dilute experimental conditions used.<sup>(10,31)</sup> Sample computer fit of the mole ratio data for Cs<sup>+</sup>-18C6 and Rb<sup>+</sup>-DB30C10 systems are shown in Fig. 6. Our assumption of 1:1 stoichiometry for the resulting complexes of both Rb<sup>+</sup> and Cs<sup>+</sup> ions was further supported by excellent agreement between the observed and calculated



**Fig. 6.** Computer fit of the molar conductance–mole ratio data for Cs<sup>+</sup>-18C6 at 35°C (A) and Rb<sup>+</sup>–DB30C10 at 45°C (B) in acetonitrile: ( $\times$ ) experimental point; (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plot.

molar conductances in the process of computer fitting of the mole ratio data. It should noted that although there are some reported evidences for the formation of both 1:1 and 2:1 (ligand-to-metal) complexes between Cs<sup>+</sup> and 18C6 in solution by NMR,<sup>(15,32,33)</sup> no clear-cut evidence for the existence of such complexes was observed during the conductance measurements. In fact, the reported K<sub>2</sub> value for the Cs<sup>+</sup>–(18C6)<sub>2</sub> complex in acetonitrile solution is very low (*i.e.*,  $K_2 = 3.7$ ).<sup>(31)</sup> Thus, at very low metal ion concentrations used here (i.e.,  $5.0 \times 10^{-5}$  mol-dm<sup>-3</sup>), the ratio [Cs<sup>+</sup>–(18C6)<sub>2</sub>]/[Cs<sup>+</sup>–18C6] =  $K_2$ [18C6] is expected to be very small. All calculated formation constants are listed in Table I.

In order to have a better understanding of the thermodynamics of complexation reactions of  $Rb^+$  and  $Cs^+$  ion with the crown ethers used, it is useful to consider the enthalpic and entropic contributions to these reactions. The

		$\log K_f$				$\Delta H^{\circ}$	$\Delta S^{o}$
Cation	Crown	15°C	25°C	35°C	45°C	$(kJ-mol^{-1})$	$(J-mol^{-1}-K^{-1})$
$Rb^+$	18C6	>5.5	>5.5	5.32±0.04	5.18±0.06	-24	23
	DC18C6	>5.5	>5.5	$5.39{\pm}0.06$	$5.29{\pm}0.06$	-17	46
	DB18C6	$4.17\!\pm\!0.02$	$4.10{\pm}0.02$	$4.07 \pm 0.04$	$4.02 \pm 0.04$	$-8 \pm 1$	50±2
	DB24C8	$4.11 \pm 0.03$	$3.98 \pm 0.02$	$3.83 \pm 0.04$	$3.72 \pm 0.06$	$-23\pm1$	$-2\pm1$
	DB30C10	$4.83 \pm 0.03$	$4.64 \pm 0.08$	$4.50 \pm 0.04$	$4.25 \pm 0.02$	$-33\pm3$	$-21\pm7$
$Cs^+$	18C6	$4.57 \pm 0.02$	$4.49 \pm 0.08$	$4.37 \pm 0.03$	$4.31 \pm 0.04$	$-16\pm1$	33±3
	DC18C6	>5.5	>5.5	$5.11 \pm 0.03$	$5.00 \pm 0.03$	-19	35
	DB18C6	$3.41 \pm 0.07$	$3.34 \pm 0.04$	$3.22 \pm 0.08$	$3.17 \pm 0.07$	$-15\pm1$	14±3
	DB24C8	$4.24 \pm 0.02$	$4.08 \pm 0.02$	$4.05 \pm 0.02$	$3.73 \pm 0.03$	$-27\pm3$	$-13\pm9$
	DB30C8	$4.33 {\pm} 0.04$	$4.20{\pm}0.03$	$4.08 {\pm} 0.03$	$3.63 \pm 0.04$	$-38 \pm 5$	$-49 \pm 12$

 
 Table I.
 Formation Constants Enthalpies and Entropies for Different M<sup>+</sup>-Crown Ether Complexes in Acetonitrile

 $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  values for the complexation reactions were evaluated from the corresponding log  $K_{\rm f}$  and temperature data by applying a linear least-squares analysis according to the equation

2.303 log 
$$K_{\rm f} = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$
 (5)

Plots of log  $K_f$  vs. 1/T for different M<sup>+</sup>-macrocycle systems were close to linear for all cases studied (Fig. 7). The enthalpies and entropies of complexation were determined in the usual manner from the slopes and intercepts of the plots and the results are also included in Table I.

From the data given in Table I, it is immediately obvious that, in the case of all macrocyclic ligands used, Rb<sup>+</sup> ion forms more stable complexes than Cs<sup>+</sup> ion. The increased stability of 18-crowns (*i.e.*, 18C6, DC18C6, and DB18C6) with Rb<sup>+</sup> over that with Cs<sup>+</sup> ion is mainly due to more convenient fitting of rubidium ion (with anionic size of 3.02 Å)<sup>(21)</sup> inside the macrocyclic cavity (2.8-3.2 Å).<sup>(22)</sup> While the ionic size of cesium (3.34 Å) is too large for the cavity size. On the other hand, for large crown ethers such as DB30C10 and DB24C8, which are capable of forming tridimensional "wrap around" complexes with metal ions, the size of the cation is expected to strongly influence the extent of complexation reaction.<sup>(4-9)</sup> According to the observed stability order, and that reported in the literature,<sup>(7,34,35)</sup> Rb<sup>+</sup> ion seems to be of proper size to fit conveniently inside the cavity formed by twisting of the large molecules, with all donating ether oxygens of the ring participating in the bond formation with the central cation.<sup>(4,5)</sup> In the case of the larger Cs<sup>+</sup> ion, the complete tridimensional structure cannot be formed and only some

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Fig. 7. Van't Hoff plots for Rb<sup>+</sup> (A) and Cs<sup>+</sup> (B) complexes with different crown ethers in acetonitrile: (1) 18C6, (2) DC18C6, (3) DB18C6, (4) DB24C8, (5) DB30C10.

of the oxygen atoms have the opportunity of bond formation with cation; consequently a weaker complex results.

From Table I, it is also seen that the stability order of the 1:1  $Rb^+$  and  $Cs^+$  complexes with the crown ethers vary in the order:

 $Rb^+: DC18C6 > 18C6 > DB30C10 > DB18C6 \sim DB24C8$ 

Cs<sup>+</sup>: DC18C6 > 18C6 > DB30C10 ~ DB24C8 > DB18C6

As it is seen, it the case of both cations, among three 18-membered crown ethers used, where the ring frame remains the same, the stabilities of the resulting complexes fall in the order DC18C6 > 18C6 > DB18C6. The presence of two cyclohexyl groups in DC18C6 can pump electrons into the ligand ring and thus increase the basicity oxygens, while the flexibility of

the macrocycle remains more or less the same as 18C6. Thus, it is not unexpected to observe the highest stability for DC18C6 complexes among the 18-crowns used. On the other hand, the addition of two benzo groups to 18C6 markedly lowers the stability of the  $Rb^+$  and  $Cs^+$  complexes. This behavior may be attributed to some combination of the electron-withdrawing property of the benzo groups, which weakens the electron-donor ability of the oxygen atoms of the ring and reduces flexibility of the ligand, which prevents the macrocyclic molecule from wrapping itself around the cation. The net result is a weaker cation–ligand interaction.

It is interesting to note that, while Cs<sup>+</sup> ion forms 1:1 complexes of about the same stability with the large crown ethers DB30C10 and DB24C8, the Rb<sup>+</sup>-DB30C10 is more stable than the Rb<sup>+</sup>-DB24C8 complex. It has been shown that Rb<sup>+</sup> ion is a more convenient size for the formation "wrap-around" tridimensional complex with DB30C10<sup>(35)</sup> and, thus, forms a more stable complex than it does with the smaller DB24C8 molecule. On the other hand, the Cs<sup>+</sup> ion with a larger ionic size cannot form a complete "wrap-around" structure with neither DB30C10 nor DB24C8<sup>(7,4,34)</sup> so that both of the ligands result in Rb<sup>+</sup> and Cs<sup>+</sup> complexes of about the same stability.

The thermodynamic data given in Table I reveal that, in the case of all  $M^+$ –18-crown systems studied, the resulting 1:1 complexes are both enthalpy and entropy stabilized. Here, the desolvation of solvated  $M^+$  cations [and possibly that of the 18-crown ligands used<sup>(36,37)</sup>] seems to be mainly responsible for the positive  $\Delta S^{\circ}$  values in acetonitrile solution.<sup>(1,2)</sup> While, in the case both Rb<sup>+</sup> and Cs<sup>+</sup> ion complexes with large crown ethers DB24C8 and DB30C10, the complexes are enthalpy stabilized but entropy destabilized. It is noteworthy that, in the complexation reactions of large crown ethers, the conformational change of the macrocyclic crown ethers from a rather flexible structure in the free state to a rigid conformation in the complexed form, results in the decreased entropy of the system.<sup>(7,9,34)</sup>

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