

Conductometric Determination of the Stability Constants of the Inclusion Complexes of Alkali Cations with [22-DD] Diaza Crown Ether, [211] and [221] Cryptands in Acetonitrile

KHALID M. TAWARAH*, MOHAMMAD A. KHASAWNEH and SHEHADEH A. MIZYED

Department of Chemistry, Yarmouk University, Irbid, Jordan

(Received: 9 December 2003; in final form: 9 February 2005)

Key words: alkali metal cations, azacrown ethers, conductivity, cryptands, macrocyclic compounds, stability constants

Abstract

An equilibrium study concerning the association of Na^+ , K^+ , Rb^+ and Cs^+ with 4, 7, 13, 18-tetraoxa-1,10-diazabicyclo [8, 5, 5]-eicosane [211], 4, 7, 13, 16, 21-pentaoxa-1, 10-diazabicyclo [8, 8, 5]-tricosane [221] and 4, 13-didecyl-1, 7, 10, 16-tetraoxa-4, 13-diazacyclooctadecane [22-DD] in acetonitrile has been carried out at 25 °C by using a conductometric technique. The observed molar conductivity, Λ , of a test solution was found to decrease significantly for mole ratios less than 1:1 upon the addition of the complexing ligand. A model based on 1:1 stoichiometry has been used to analyze the conductivity data. The data have been fitted according to a non-linear least-squares analysis that provides the stability constant, K , and the molar conductivity, Λ_c , for each cation – ligand inclusion complex. The binding sequences were found to follow the order: $\text{Na}^+ > \text{K}^+ > \text{Rb}^+ \gg \text{Cs}^+$ ($K \approx 0$) for [211], $\text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ for [221] and $\text{K}^+ > \text{Na}^+ > \text{Rb}^+ > \text{Cs}^+$ for [22-DD] complexes. Trends in ionic conductivities of complexed ions are also discussed.

Introduction

The interaction of macrocyclic compounds with alkali metal cations has been the subject of numerous research articles as revealed by the large compilation of data in several major review articles [1–4]. The stability constants, which refer to the overall macrocycle–cation reaction, constitute the major part of such data. The experimental techniques used for determining the values of the stability constants are mostly calorimetry, potentiometry and less frequently conductometry. Due to differences in the experimental conditions, most of these values are only correct for the specified conditions [2]. In a previous publication [5], the conductometric method was applied for the evaluation of the stability constant of the $\text{K}^+/\text{[22-DD]}$ system in acetonitrile at several temperatures. In the present study we report the values of the stability constants of Na^+ , Rb^+ and Cs^+ complexes with [22-DD] macrocycle in acetonitrile at 25 °C since such data are not available in the literature. The binding of K^+ was included in the present study for comparison purposes. The binding of these alkali cations with cryptands [211] and [221] was previously studied in acetonitrile by using a combination of calo-

rimetric, potentiometric and ion selective electrode techniques [6]. Since the conductometric method avoids the need for relatively high values of ionic strength, we believe that a reinvestigation of these systems is advantageous especially when using high dilution conditions and a non-coordinating anion as the tetraphenylborate anion. The excellent agreement between values of stability constants obtained by the conductometric method and values obtained by other workers for the K^+ complexes with 18-crown-6 and 1,10-dibenzo-18-crown-6 was previously reported [5].

The structural formulae of the investigated macrocycles are shown in Figure 1. Their nominal cavity radii are 1.4, 1.1 and 0.8 Å for [22-DD], [221] and [211], respectively [7]. The radii of Na^+ , K^+ , Rb^+ and Cs^+ are 1.02, 1.38, 1.49 and 1.70 Å, respectively [8].

Experimental

The macrocycles were purchased from Merck. The cryptands [211] and [221] are liquids and were used without further purification, while the diaza crown ether [22-DD] was recrystallized from acetone followed by drying under vacuum. Acetonitrile (BDH, M and B Laboratory Chemicals) was purified by treatment with

* Author for correspondence.

E-mail: khalidtawarah@hotmail.com

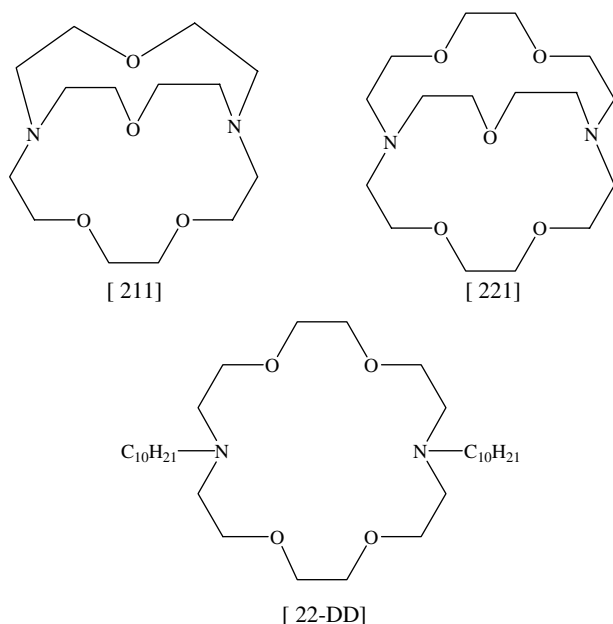


Figure 1. Molecular structures of [211], [221] and [22-DD] macrocycles.

molecular sieves and distillation over CaH_2 [9, 10]. The middle 70% of the distillate was used with electrolytic conductivity less than $1.0 \times 10^{-7} \text{ S cm}^{-1}$ (the detection limit of the conductometer). Sodium tetraphenyl borate, NaBPh_4 (fluka), was recrystallized from acetone-toluene mixture as described in the literature [11]. KBPh_4 , RbBPh_4 and CsBPh_4 were prepared by mixing a dilute aqueous solution of NaBPh_4 with an equivalent amount of the corresponding alkali metal chloride (Fisher Scientific) and were recrystallized from acetone as described in the literature [12].

Acetonitrile solutions of NaBPh_4 , KBPh_4 , RbBPh_4 and CsBPh_4 with concentration of ca. 2 to $8 \times 10^{-4} \text{ mol dm}^{-3}$ were used. Similar solutions having the same total salt concentration were used as solvents for preparing the macrocycles solutions with total macrocycle concentration of ca. $8 \times 10^{-3} \text{ mol dm}^{-3}$. In such dilute solutions the ionic strength is kept constant and the essence of the procedure amounts to a conductometric titration. The temperature was controlled at $25 \pm 0.02 \text{ }^\circ\text{C}$. Three runs were used for the calculation of a certain K value. The stability constants were evaluated by using a computer program [13] based on the simplex algorithm of Nedler and Mead [14]. Other details concerning equipment and techniques are similar to those reported previously [5].

Results and discussion

Model equations

The stoichiometry of the binding of alkali cations with macrocycles of the type studied in the present work is 1:1 in dilute solutions [2]. Consequently, the binding of

an alkali cation, M^+ , by a macrocycle, L , can be represented by the following equilibrium



with

$$K = \{[\text{ML}^+]/[\text{M}^+][\text{L}]\} \cdot \{f[\text{ML}^+]/f[\text{M}^+]f[\text{L}]\} \quad (2)$$

where $[\text{ML}^+]$, $[\text{M}^+]$, $[\text{L}]$ and f stand for the equilibrium concentrations (mol dm^{-3}) of the 1:1 complex, uncomplexed cation, uncomplexed macrocycle and the activity coefficient of the species indicated, respectively. Under the experimental conditions used in the present study, it was argued [5] that the factor involving the activity coefficients in Equation (2) is almost unity. Therefore the stability constants reported in the present study are essentially thermodynamic constants.

The usual practice [15] followed in dealing with systems similar to the present study is to define Λ , the measured molar conductance of the test solution under the assumption of complete dissociation of the uncomplexed and complexed salts, as

$$\Lambda = \alpha\Lambda_m + (1 - \alpha)\Lambda_c \quad (3)$$

where α represents the degree of dissociation of the macrocycle complex and is given as the ratio $[\text{M}^+]/[\text{M}_t^+]$, where $[\text{M}_t^+]$ is the total concentration of the alkali tetraphenyl borate. Λ_m and Λ_c are the molar conductivities of the uncomplexed (MBPh_4) and complexed (MLBPh_4) salts, respectively. Equation (3) is an approximate expression which states that Λ is calculated by the simple additivity rule applied to two electrolytes (complexed and uncomplexed salt) with a common anion at a constant ionic strength. In Equation (3), Λ is treated as a calculated quantity in the simplex program [5, 13] while K and Λ_c are adjustable parameters. The reported values of K and Λ_c correspond to the condition $\Sigma (\Lambda - \Lambda_{\text{cal}})^2$ is a minimum, at which the program terminates. Other details were reported previously [16].

Complexes of [211]

Figure 2 illustrates the behavior of Λ as a function of the ratio $[\text{L}_t]/[\text{M}_t^+]$, where $[\text{L}_t]$ denotes the total molar concentration of a macrocycle in the test solution, for acetonitrile solutions of [211] and the tetraphenyl borates of Na^+ , K^+ and Rb^+ at $25 \text{ }^\circ\text{C}$. The observed molar conductivity of NaBPh_4 /[211] solution changes significantly and levels off shortly after 1:1 mole ratio. On the other hand the K^+ and Rb^+ solutions show gradual decrease in Λ as the mole ratio is increased. However, the change in Λ is more significant for the K^+ solutions. No measurable change in Λ was found in the case of CsBPh_4 /[211] solutions. Factors related to the precision and accuracy of the conductometer as

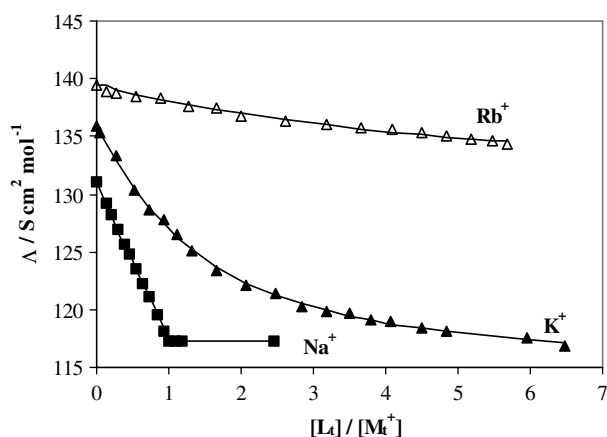


Figure 2. Plot of the molar conductivity, Λ , vs. mole ratio $[L_t]/[M_t^+]$ for the binding of Na^+ , K^+ and Rb^+ by [211] in acetonitrile at 25 °C.

well as the detection of possible changes in the viscosity of the test solution caused by the presence of a macrocycle were discussed previously [5] and were found to be of no major concern. Therefore the observation concerning the Cs^+ solutions can be explained either by assuming that the conductivity of the solvated Cs^+ ion is the same as that of the complexed Cs^+ ion or by assuming that the [211] macrocycle does not bind the Cs^+ ion.

The binding of alkali metal cations and other divalent cations by the [211], [221] and [222] cryptands has been discussed by Cox *et al.* [17] in several protic and aprotic solvents. These authors concluded that the donicity of the solvent plays a major role in determining the stability of the cryptand complex while the dielectric constant is of little importance. Table 1 shows that our result for $\log K$ of the $\text{Na}^+ / [211]$

complex is lower by at least one $\log K$ unit from literature data given in the table. This might be due to differences in the actual nature of the reaction medium. No conductometric determination is available in the literature for comparison. Compared with the complexes of K^+ , Rb^+ and Cs^+ , the $\text{Na}^+ / [211]$ complex is the most stable in the series which is in accord with the fact that the Na^+ cation has the nearest match for the dimensions of the [211] cage. The value of $\log K$ for the $\text{K}^+ / [211]$ complex in acetonitrile is in good agreement with the value reported by Buschmann [6] but a little higher than the value reported by Cox *et al.* [17]. The value of $\log K$ for the $\text{Rb}^+ / [211]$ complex is significantly lower than that reported by Buschmann [6]. No other literature data are available in acetonitrile for further comparison. However, the value reported in the present study is close to the literature values in propylene carbonate (≤ 2.2 [20], 2.69 [21]) and reasonably higher than literature values in methanol (1.9 [22], 2.5 [23]). This is consistent with expectations based on the solvating ability of a solvent [17]. Since no measurable change in the conductivity was observed, the stability constant of the binding of Cs^+ by [211] can not be determined. The literature information on this system indicates that no detectable heat was produced during the calorimetric titration of the $\text{Cs}^+ / [211]$ system which meant that either $\log K$ is very small or the enthalpy of the reaction is zero [6]. In this regard our conductometric result is a confirmation of the calorimetric result implying the immeasurability of the $\text{Cs}^+ / [211]$ interaction at least by these two techniques. It is interesting to note that other workers have reported $\log K$ values in propylene carbonate [21] and methanol [22, 23] for the $\text{Cs}^+ / [211]$ system by using calorimetry. These findings seem paradoxical on the basis that the donor numbers of acetonitrile and propylene carbonate are quite comparable, which is also true for the dielectric constants of acetonitrile and methanol.

By reference to Table 1, the values of $\log K$ reported in the present study imply the following stability sequence for the [211] complexes in acetonitrile: $\text{Na}^+ > \text{K}^+ > \text{Rb}^+ \gg \text{Cs}^+$ (K immeasurable). Other sequences in acetonitrile are: $\text{Na}^+ > \text{Rb}^+ > \text{K}^+ \gg \text{Cs}^+$ (K immeasurable) [6] and $\text{Na}^+ > \text{K}^+$ [17]. Unfortunately, there are no other literature reports that simultaneously include data on the [211] binding with K^+ and Rb^+ in acetonitrile which could help in resolving the discrepancy concerning the relative stabilities of the complexes of K^+ and Rb^+ with [211] as reported here and previously by Buschmann [6]. However, inspection of literature data in methanol [23] and in propylene carbonate [20] shows that the stability sequence found in the present study is similar to those reported in such studies.

Complexes of [221]

In the case of the [221] macrocycle, the behavior of Λ vs. $[L_t]/[M_t^+]$ is shown in Figure 3. The data of this figure indicate that a significant change in Λ is initially ob-

Table 1. Values of $\log K$ for the 1:1 complexes of Na^+ , K^+ , Rb^+ and Cs^+ with [211] cryptand at 25 °C in acetonitrile

Cation	Medium	Method	$\log K$	Reference
Na^+	MeCN ^a	Cond. ^b	8.02 ± 0.07	This work
	MeCN	$\text{Ag}^+ / \text{ISE}^c$	>9	[17]
	MeCN	Pot. ^d	9.09	[20]
	MeCN, 0.1 M	Pot.	9.8	[21]
	MeCN, 0.05 M	ISE	8.74	[6]
K^+	MeCN	Cond.	3.41 ± 0.06	This work
	MeCN	Cal. ^e	3.5	[6]
	MeCN, 0.10 M	Pot.	2.84	[17]
	MeCN, 0.10 M	Pot.	2.84	[17]
Rb^+	MeCN	Cond.	2.64 ± 0.11	This work
	MeCN	Cal.	3.9	[6]
Cs^+	MeCN	Cond.	Im. ^f	This work
	MeCN	Cal.	Im.	[6]

^a Acetonitrile, ^b conductivity, ^c ion selective electrode, ^d potentiometry, ^e calorimetry, ^f immeasurable.

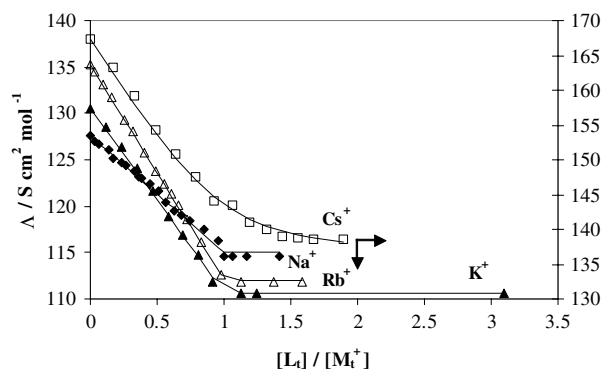


Figure 3. Plot of the molar conductivity, Λ , vs. mole ratio $[L_1]/[M_1^+]$ for the binding of Na^+ , K^+ , Rb^+ and Cs^+ by [221] in acetonitrile at 25 °C.

served then the value of Λ begins to level off shortly after 1:1 mole ratios for Na^+ , K^+ and Rb^+ solutions. However, a gradual decrease in Λ persists for Cs^+ solutions of mole ratios exceeding 1:1. The values of $\log K$ obtained in the present study are given in Table 2 together with literature information in acetonitrile. The value of $\log K$ for the $\text{Na}^+/[221]$ complex as reported here is in reasonable agreement with those reported by Buschmann [6] and by Schmidt *et al.* [24] in acetonitrile but significantly lower than those reported by Lejaille *et al.* [19] and by D'aprano *et al.* [25]. The conductometric results reported in ref. [25] were based on a model that takes into account the ion pair formation. The value of $\log K$ for the $\text{K}^+/[221]$ is in fair agreement with the values reported by Buschmann [6] and by Schmidt *et al.* [24] in acetonitrile, but is significantly higher than the value reported by D'aprano *et al.* [25]. The $\log K$ values obtained in the present study for the Rb^+ and

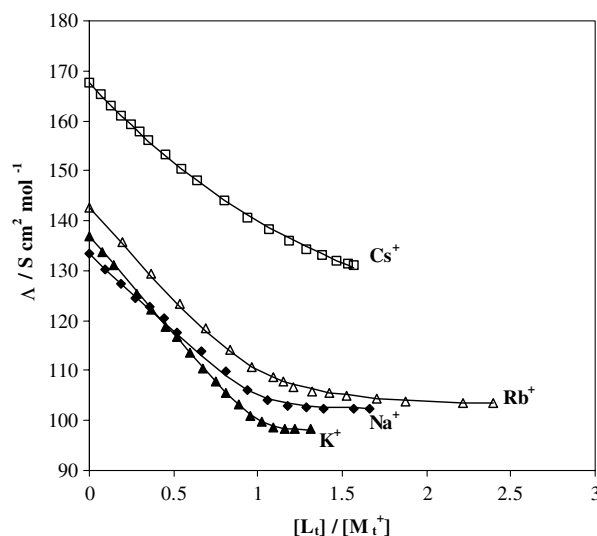


Figure 4. Plot of the molar conductivity, Λ , vs. mole ratio $[L_1]/[M_1^+]$ for the binding of Na^+ , K^+ , Rb^+ and Cs^+ by [22-DD] in acetonitrile at 25 °C.

Cs^+ complexes with [221] are in good agreement with the literature values reported in acetonitrile [6].

According to our results, the stability sequence of the [221] complexes is: $\text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$. This trend is in accord with literature results in acetonitrile [6], methanol [23] and propylene carbonate [20]. Consideration of the literature value $\log K = 10.3$ for the $\text{Li}^+/[221]$ complex in acetonitrile [17] and the data of Table 2 indicates that the most stable complex of the cryptand [221] is with Na^+ . This high stability reflects the fact that the size of Na^+ is the best match to the cage of the [221] cryptand.

Our data given in Tables 1 and 2 indicate that the stability of a given complex is enhanced as the cryptand size is increased on going from [211] to [221]. This is in

Table 2. Values of $\log K$ for the 1:1 complexes of Na^+ , K^+ , Rb^+ and Cs^+ with [221] cryptand at 25 °C in acetonitrile

Cation	^a Medium	^b Method	$\log K$	Reference
Na^+	MeCN	Cond.	10.53 ± 0.07	This work
	MeCN, 0.1 M Bu_4NClO_4	Pot.	12.4	[19]
	MeCN	Cal.	11.2	[24]
	MeCN, 0.05 M Et_4NClO_4	ISE	10.97	[6]
	MeCN	Cond.	>12	[25]
K^+	MeCN	Cond.	8.71 ± 0.09	This work
	MeCN	Cal.	9.46	[24]
	MeCN, 0.05 M Et_4NClO_4	ISE	9.10	[6]
	MeCN	Cond.	7.63	[25]
Rb^+	MeCN	Cond.	6.92 ± 0.21	This work
	MeCN	Pot.	6.74	[6]
Cs^+	MeCN	Cond.	4.35 ± 0.04	This work
	MeCN	Cal.	4.68	[6]

^{a,b} Abbreviations are as given in Table 1.

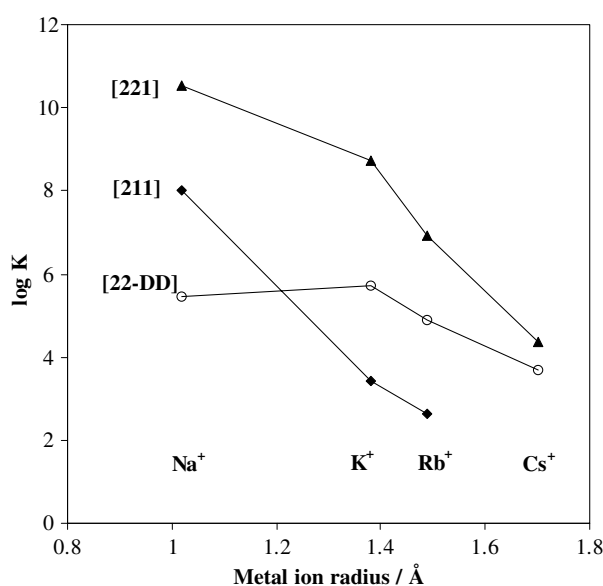


Figure 5. Plot of $\log K$ as function of alkali metal ion radius.

Table 3. Limiting molar ionic conductivities and apparent solvodynamic radii of Na⁺, K⁺, Rb⁺, Cs⁺ and their 1:1 complexes with [211], [221] and [22-DD] macrocycles in acetonitrile at 25 °C

	CH ₃ CN		[211]		[221]		[22-DD]	
Cation	λ_i^0	a_i	λ_c^0	a_c	λ_c^0	a_c	λ_c^0	a_c
Na ⁺	77.3	0.31	61.9	0.39	59.7	0.40	45.6	0.52
K ⁺	83.7	0.29	59.0	0.41	54.4	0.44	41.7	0.57
Rb ⁺	85.7	0.28	73.9	0.32	56.5	0.42	45.8	0.52
Cs ⁺	87.3	0.27	–	–	80.8	0.30	42.5	0.56

Units: λ_i^0 and λ_c^0 , S cm² mol⁻¹, a_i and a_c , nm. Values of λ_i^0 in acetonitrile, CH₃CN, are from ref.[26].

accord with literature data in acetonitrile [6] methanol [23] and propylene carbonate [20].

Complexes of [22-DD]

A plot of a typical data showing the behavior of Λ as a function of the ratio $[L_d]/[M^+]$ is given in Figure 4 for the binding of Na⁺, K⁺, Rb⁺ and Cs⁺ with 1,10-*N,N'*-dicyclodiazia-18-crown-6, [22-DD]. In these plots, Λ decreases continuously even for mole ratios exceeding 1:1, especially for Rb⁺ and Cs⁺ solutions. The calculated values of log K for the 1:1 complexes of this diaza crown ether with Na⁺, K⁺, Rb⁺ and Cs⁺ are: 5.47 ± 0.06 , 5.72 ± 0.06 , 4.89 ± 0.06 and 3.68 ± 0.28 , respectively. Because of the limited literature data on the [22-DD] complexes in acetonitrile, quantitative comparison is not possible in this solvent except for one report on K⁺/[22-DD] with log $K = 5.52 \pm 0.06$ [5], which is in reasonable agreement with the present value. The presence of long alkyl chains in the [22-DD] macrocycle favors the endo–endo conformation [23]. Its cavity radius of 1.4 Å matches the radius of the K⁺ cation; hence the 1:1 complex of K⁺ is expected to have the highest stability. The literature values of log K for the complexes of the diaza crown ether [22] (the two alkyl groups of [22-DD] are replaced by two hydrogen atoms) with alkali metal cations in acetonitrile are 3.92, 4.13, 3.32 and 2.69 for Na⁺, K⁺, Rb⁺ and Cs⁺ complexes, respectively [6]. By comparing our data on the [22-DD] complexes with these values of the [22] complexes, we arrive at the same conclusion drawn from the data in methanol [23] regarding the relative stabilities of the complexes of [22] and [22-DD] macrocycles. Differences in the conformations of these macrocycles and their relevance to the stabilities of their complexes were discussed in the literature [23].

The relation between log K and the radius of the metal ion for the systems reported in our study is presented in Figure 5. It is evident that [22-DD] is not a discriminating ligand for the alkali metal cations.

Limiting molar conductivities

The limiting molar conductivities of NaBPh₄, KBPh₄, RbBPh₄ and CsBPh₄ as well as the limiting molar ionic conductivities, λ_i^0 , of Na⁺, K⁺, Rb⁺ and Cs⁺ in ace-

tonitrile at 25 °C were reported by Kay *et al.* [26]. We have attempted the calculation of the limiting molar ionic conductivities of the complexed alkali cations, λ_c^0 . The results of such calculations are reported in Table 3. The calculations were based on Kohlrausch's law of independent migration of ions and on the Debye–Hückel–Onsager equation $\Lambda = \Lambda^0 - (a + b\Lambda^0)\sqrt{c}$, c is the total salt concentration in mol dm⁻³, with $a = 22.9$ S cm² mol⁻¹/(mol dm⁻³)^{1/2} and $b = 0.716$ /(mol dm⁻³)^{1/2} for a symmetrical electrolyte in acetonitrile at 25 °C [27]. Included in Table 3 are the calculated apparent solvodynamic radii (Stokes radii) of the solvated alkali cations, a_i , and those of their corresponding complexes, a_c . The calculations are based on Equation 4 [28]

$$a_{\text{ion}} = (z^2 F^2 / 6\pi L)(1/\eta)(1/\lambda_{\text{ion}}), \quad (4)$$

which reduces to $a_{\text{ion}} = 23.93 / \lambda_{\text{ion}}$, where a_{ion} is given in nm and λ_{ion} in S cm² mol⁻¹. The viscosity, η , of acetonitrile at 25 °C is 3.426×10^{-4} kg m⁻¹ s⁻¹ [10]. Inspection of the data of Table 3 reveals that each solvated alkali cation, M⁺, and its 1:1 complex with a macrocycle, ML⁺, satisfy the following trend in their ionic conductivities, λ_+^0 :

$$\lambda_+^0(\text{M}^+) > \lambda_+^0(\text{M}[211])^+ > \lambda_+^0(\text{M}[221])^+ > \lambda_+^0(\text{M}[22-\text{DD}])^+$$

The inverse of this trend holds for their apparent solvodynamic radii. This result seems consistent with the increase in the size of a macrocycle as we move from [211] to [22-DD]. The regular pattern observed in Table 3 for the limiting molar ionic conductivities of the solvated uncomplexed cations, where the ionic conductivity increases with ionic radius, is not maintained for their complexed counterparts. Such irregular trend is also evident in the data of a closely related study [25]. This observation may be rationalized on the basis that cation complexation, which is dependent on both cation and macrocycle, does not completely eliminate the solvent molecules from the ion atmosphere.

Acknowledgements

This work was supported by Yarmouk University. The authors are grateful to Mr. F. Rawagah for his help in updating the computer program.

References

1. J.J. Christensen, D.J. Eatough, and R.M. Izatt: *Chem. Rev.* **74**, 315 (1974).
2. R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen, and D. Sen: *Chem. Rev.* **85**, 271 (1985).
3. R.M. Izatt, K. Pawlak, J.S. Bradshaw, and R.L. Bruening: *Chem. Rev.* **91**, 1721 (1991).
4. R.M. Izatt, K. Pawlak, J.S. Bradshaw, and R.L. Bruening: *Chem. Rev.* **95**, 2529 (1995).
5. K.M. Tawarah and F.A. Ababneh: *J. Incl. Phenom. Mol. Rec. Chem.* **29**, 15 (1997).
6. H.J. Buschmann: *Inorg. Chim. Acta.* **120**, 125 (1986).
7. J.M. Lehn: *Struct. Bonding. (Berlin)* **16**, 1 (1973).
8. R.D. Shanon and C.T. Prewitt: *Acta. Crystallog.* **B25**, 925 (1969).
9. Y. Takeda: *Bull. Chem. Soc. Jpn.* **56**, 866 (1983).
10. J. Barthel, L. Ibert, J. Rossmairer, H.J. Gores, and B. Kaukal: *J. Solution. Chem.* **19**, 321 (1990).
11. E. Mei, A.I. Popov, and J.L. Dye: *J. Phys. Chem.* **81**, 1677 (1977).
12. E. Mei, A.I. Popov, and J.L. Dye: *J. Am. Chem. Soc.* **99**, 6532 (1977).
13. M.A. Khasawneh: M. Sc. Thesis, Yarmouk University (1994).
14. J.A. Nedler and R. Mead: *Comput. J.* **7**, 308 (1965).
15. Y. Takeda and H. Yano: *Bull. Chem. Soc. Jpn.* **53**, 1720 (1980).
16. K.M. Tawarah and S.A. Mizyed: *J. Solution Chem.* **18**, 387 (1989).
17. B.G. Cox, J. Garcia-Rosas, and H. Schneider: *J. Am. Chem. Soc.* **103**, 1384 (1981).
18. T. Nakamura, Y. Yumoto, and K. Izutsu: *Bull. Chem. Soc. Jpn.* **55**, 1850 (1982).
19. M.F. Lejaille, M.H. Livertoux, C. Guidon, and J. Bessiere: *Bull. Soc. Chim. Fr.* 1373: (1978)..
20. B.G. Cox, J. Garcia-Rosas, and H. Schneider: *J. Phys. Chem.* **84**, 3178 (1980).
21. H.J. Buschmann: *J. Incl. Phenom. Mol. Recognit. Chem.* **7**, 581 (1989).
22. J.M. Lehn and J.P. Sauvage: *J. Am. Chem. Soc.* **97**, 6700 (1975).
23. H.J. Buschmann: *Inorg. Chim. Acta.* **125**, 31 (1986).
24. E. Schmidt, J.M. Tremilon, J.P. Kintzinger, and A.I. Popov: *J. Am. Chem. Soc.* **105**, 7563 (1983).
25. A. D'aprano, B. Sesta, V. Mauro, and M. Salomon: *J. Incl. Phenom. Mac. Chem.* **35**, 451 (1999).
26. R.L. Kay, B.J. Hales, and G.P. Cunningham: *J. Phys. Chem.* **71**, 3925 (1967).
27. P.W. Atkins: *Physical Chemistry*, 5th ed., Oxford University Press, Oxford (1994), pp. 846.
28. Ibid pp. 849–850.