

A Thermodynamic Study of the Association of Alkali Metal Cations with Dicyclohexano-18-crown-6

KHALID M. TAWARAH* and SHEHADEH A. MIZYED
Department of Chemistry, Yarmouk University, Irbid, Jordan

(Received: 20 October 1987; In final form: 3 May 1988)

Abstract. A thermodynamic study of the association of Na^+ , K^+ , Rb^+ , and Cs^+ with dicyclohexano-18-crown-6 in acetonitrile has been carried out at 308, 303, 298, 293, and 288 K using a conductometric technique. The observed molar conductivities, Λ , were found to decrease significantly for mole ratios less than unity. A model involving 1 : 1 stoichiometry has been used to analyze the conductivity data. The stability constant, K , and the limiting molar conductivity, Λ_∞ , for each 1 : 1 complex were determined from the conductivity data by using a nonlinear least squares curve fitting procedure. The binding sequence, based on the value of $\log K$ at 298 K, as derived from this study is $\text{K}^+ > \text{Na}^+ > \text{Rb}^+ > \text{Cs}^+$. Values of ΔH° and ΔS° are reported and their significance is discussed.

Key words. Dicyclohexano-18-crown-6, alkali cations, thermodynamic study, crown ethers.

1. Introduction

Dicyclohexano-18-crown-6 (DCH18C6) has five possible configurational diastereoisomers designated as (*cis, syn, cis*), (*cis, anti, cis*), (*trans, syn, trans*), (*trans, anti, trans*), and (*trans, cis*) [1]. The first two isomers are usually referred to as the A and B isomers respectively. There is very little information regarding the association of the alkali metal cations with the isomers of DCH18C6 [2]. A few single-isomer studies have been made in the protic solvents methanol [1, 3] and water [4, 5]. It has been noted [1] that the alkali metal cations form more stable complexes with the *cis*-isomers as compared with the *trans*-isomers. Also within each pair of isomers, the *syn*-isomers form stronger complexes than the *anti*-isomers. These observations suggest that the isomers of DCH18C6 have different binding abilities towards the alkali metal cations. In protic solvents, the isomers exhibit selectivity for binding K^+ . Studies dealing with the association of alkali metal cations with DCH18C6 (as a mixture of isomers) have been limited to the aprotic solvent acetonitrile. Evans *et al.* [6] have reported the binding sequence $\text{K}^+ > \text{Na}^+ > \text{Cs}^+$ and Hofmanova *et al.* [7] have reported the binding sequence $\text{K}^+ > \text{Rb}^+ > \text{Cs}^+$. The scarcity of thermodynamic data on the association of Na^+ , K^+ , Rb^+ , and Cs^+ with DCH18C6 has motivated us to carry out a thermodynamic study on this system. Since high dilution conditions and the use of a non-coordinating anion, such as tetraphenylborate (BPh_4^-), can be deliberately chosen to study the formation of 1 : 1 cation–crown ether complexes [2], the conductometric method seems to us to be an appropriate method for the present study. Several approaches [6, 8, 9, 10] have been applied to tackle the problem of determining the formation constant, K , of the 1 : 1 complexes from the conductivity data. To the best of our knowledge, there is only one report that contains conductivity data in

* Author for correspondence.

tabular form [10]. The lack of such data eliminates the possibility of making a comparison among these approaches. In this article we provide such data and report on the use of the Simplex program [11] for analyzing conductometric measurements of the systems reported in this study.

2. Experimental

DCH18C6 was obtained from Merck as a mixture of isomers. It gave a residual conductivity in acetonitrile (most likely due to a salt impurity) which amounted to about 2% or less of the conductivity of a test solution. The residual conductivity was subtracted from that of a test solution. No attempt to purify the sample was made. Acetonitrile (HPLC grade) was obtained from Koch-Light Ltd. Its specific conductivity was less than $2 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$. It was used without further purification. Sodium tetraphenylborate (purum grade) was purchased from BDH. It was recrystallized from an acetone-toluene mixture as suggested in the literature [12]. The tetraphenylborates of K^+ , Rb^+ , and Cs^+ were prepared by reacting sodium tetraphenylborate with the corresponding metal chloride in water. Filtration of the aqueous mixture was followed by recrystallization from acetone as described in the literature [13]. The conductivity measurements were carried out by using a Metrohm-E 518 conductometer. A conductivity cell (Metrohm-EA 608 C), with cell constant of 0.1533cm^{-1} , was used. This value was determined by using standard aqueous KCl solutions [14]. The required reaction temperature was attained by using a thermostating unit. The unit is provided with a cooling facility and can be controlled to $\pm 0.1^\circ\text{C}$. Specific conductivities as small as $2 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$ were easily detected by the conductometer we used. Acetonitrile solutions of alkali metal tetraphenylborates having concentrations of about $4 \times 10^{-4} \text{mol dm}^{-3}$ were used. Similar solutions, with the same total salt concentration, were also used as solvents for preparing the DCH18C6 solutions. In a typical experiment 50cm^3 of a given MBPh_4 ($\text{M} = \text{Na}^+, \text{K}^+, \text{Rb}^+$ or Cs^+) solution was placed in a 100-cm^3 Erlenmeyer flask, brought to the required temperature in a thermostat, then the specific conductivity of the DCH18C6-free solution was measured. Increments (0.10cm^3) of the DCH18C6 solution ($\sim 8 \times 10^{-3} \text{mol dm}^{-3}$), having the same salt concentration as that of the initial metal salt solution, were delivered by means of a pipette and the specific conductivity of the resulting mixture was measured. Addition of DCH18C6 solution was continued until the required total amount of DCH18C6 was achieved. The conductivity data were analyzed according to a nonlinear least squares curve fitting procedure. This was achieved by using a superbrain (64K) computer facility. Linear least squares analysis of $\log K$ vs. $1/T$ data was carried out using a programmable calculator.

3. Results and Discussion

The 1 : 1 binding of an alkali metal cation, M^+ , ($\text{M}^+ = \text{Na}^+, \text{K}^+, \text{Rb}^+$, or Cs^+), with dicyclohexano-18-crown-6, L, is represented by the following equilibrium



the corresponding equilibrium constant, K , expressed in terms of concentrations is given by the equation

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

If α is taken as the fraction of total metal remaining as free solvated cation, the following equations result

$$[M^+] = \alpha[MT] \quad (3)$$

$$[ML^+] = (1 - \alpha)[MT] \quad (4)$$

$$[L] = [LT] - (1 - \alpha)[MT] \quad (5)$$

where $[MT]$, $[LT]$, $[M^+]$, $[ML^+]$ and $[L]$ represent the concentrations (mol dm^{-3}) of total cation, total crown, free solvated cation, the complex, and free solvated crown, respectively. After the addition of the crown ether, the measured specific conductivity of the resulting solution, k , is assumed to be given as follows

$$k = k_0 + k_c \quad (6)$$

k_0 accounts for the contribution of the free alkali metal salt, while k_c accounts for that of the complexed alkali metal salt. Ion pair formation is known to be negligible [15] and corrections for viscosity changes can be neglected under the dilute conditions used. The observed molar conductivity, Λ , of the resulting solution is calculated by using the equation

$$\Lambda = 10^3 k / [MT] \quad \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \quad (7)$$

Λ can also be related to α by the equation

$$\Lambda = \alpha\Lambda_0 + (1 - \alpha)\Lambda_c \quad (8)$$

where Λ_0 and Λ_c represent the molar conductivities of the crown-free alkali metal salt solution and the completely complexed cation salt solution respectively. Equation (8) is an approximate expression which states that Λ is calculated by the simple additivity rule. However solutions containing free M^+ and ML^+ with the common anion, BPh_4^- , can be viewed as mixtures of two electrolytes with a common anion at a constant ionic strength such as $KCl-LiCl$ mixtures. For such systems Kell and Gordon [16] have shown that the deficit in the molar conductance of the mixture, Λ , as compared with that calculated by the simple additivity rule is negligibly small when compared to experimental error. Formation constants obtained from the analysis of conductivity data, based on Equation (8), were in good agreement with those obtained by other methods [17]. Substitution of Equations (3) and (4) into Equation (2) yields

$$K = (1 - \alpha) / \alpha[L] \quad (9)$$

It can be shown that the manipulation of Equation (8), followed by substitution into Equations (5) and (9) generates the following two equations

$$[L] = [LT] - [MT](\Lambda_0 - \Lambda) / (\Lambda_0 - \Lambda_c) \quad (10)$$

$$K = (\Lambda_0 - \Lambda) / [L](\Lambda - \Lambda_c) \quad (11)$$

Equations (1) to (11) are essentially the same as those given by Takeda and Yano [9]. Substitution of Equation (10) into Equation (11) gives

$$K = a_1 a_2 / (a_2 a_3 [LT] - a_1 a_3 [MT]) \quad (12)$$

where

$$a_1 = \Lambda_0 - \Lambda \quad (13)$$

$$a_2 = \Lambda_0 - \Lambda_c \quad (14)$$

$$a_3 = \Lambda - \Lambda_c \quad (15)$$

In order to be in a form suitable for nonlinear least squares analysis, Equation (12) can be rearranged to give a quadratic equation in Λ having the following form

$$a\Lambda^2 + b\Lambda + c = 0 \quad (16)$$

where

$$a = K[\text{MT}] \quad (17)$$

$$b = a_2(K[\text{LT}] + 1) - [\text{MT}]K(\Lambda_0 + \Lambda_c) \quad (18)$$

$$c = [\text{MT}]K\Lambda_0\Lambda_c - a_2([\text{LT}]K\Lambda_c + \Lambda_0) \quad (19)$$

In Equation (16) Λ is treated as a calculated quantity in the Simplex program with the understanding that the physically significant solution of Equation (16) has the form

$$\Lambda_{\text{cal}} = -b/2a + (b^2 - 4ac)^{1/2}/2a \quad (20)$$

while K and Λ_c are the adjustable parameters which are needed to evaluate a , b , and c . The procedure followed in calculating K from the conductivity data involved the use of an approximate value for Λ_c taken from the corresponding Λ vs. $[\text{LT}]/[\text{MT}]$ graph. This value, together with the known quantities $[\text{LT}]$, $[\text{MT}]$, Λ_0 and Λ provide a value for $[\text{L}]$ as given by Equation (10). A subroutine is then used to calculate an approximate average value of K for a given series. These approximate values of K and Λ_c are then used as reasonable starting guesses in the program to solve for Λ_{cal} as given by Equation (20). 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 exits.

Typical data showing the results of our curve fitting procedure for the binding of DCH18C6 with Rb^+ are shown in Table I. The temperature effect on the complexation reaction for the various combinations of dicyclohexano-18-crown-6 with Na^+ , K^+ , Rb^+ , and Cs^+ are shown in Figures 1–4 at five different temperatures. In every case the

Table I. Observed molar conductivities, Λ , at various mole ratios for the system Rb^+ /dicyclohexano-18-crown-6 at 25°C. $[\text{MT}] = 4.09 \times 10^{-4} \text{ mol dm}^{-3}$ and $\Lambda_0 = 161.00 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Program exits at $K = 4.658 \times 10^4 \text{ mol}^{-1} \text{ dm}^3$ and $\Lambda_c = 121.00 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

$[\text{LT}]/[\text{MT}]$	$10^4 [\text{LT}]/\text{mol dm}^{-3}$	$\Lambda/\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	$\Lambda_{\text{cal}}/\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
0.098	0.401	157.33	157.29
0.198	0.808	154.15	153.57
0.293	1.199	150.97	150.06
0.390	1.595	147.30	146.57
0.487	1.990	144.12	143.21
0.583	2.383	140.69	139.10
0.775	3.165	134.33	134.26
0.964	3.941	129.56	129.84
1.153	4.710	126.47	126.94
1.340	5.475	125.03	125.22
1.525	6.233	123.81	124.20
1.892	7.731	123.12	123.11
2.342	9.571	122.46	122.47
2.784	11.38	122.14	122.13
3.643	14.89	121.70	121.78
4.471	18.27	121.36	121.60

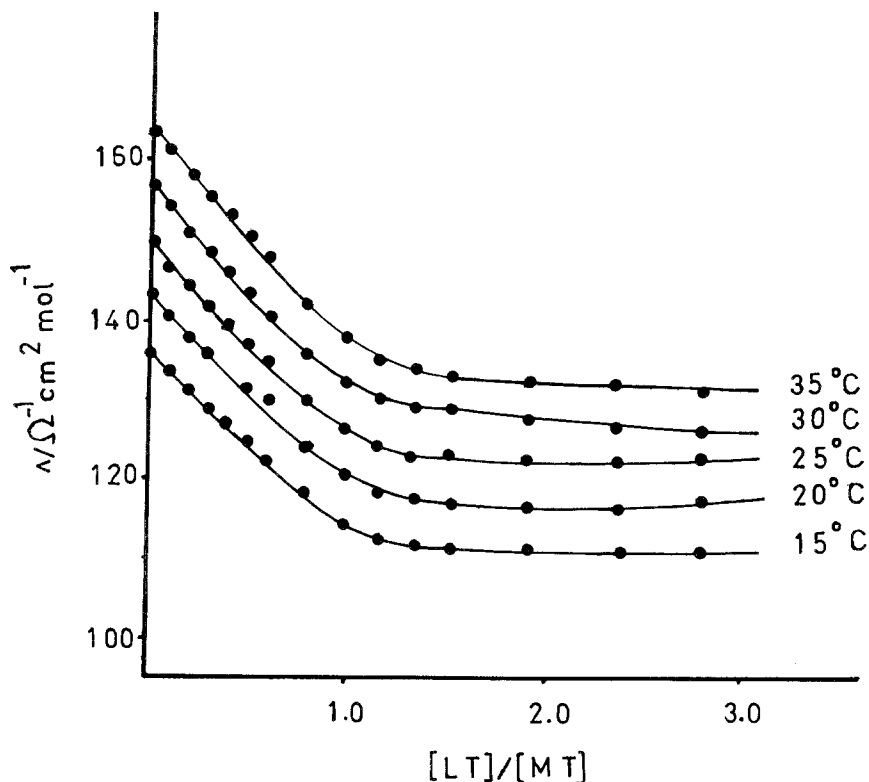


Fig. 1. Λ vs. $[LT]/[MT]$ for the system Na^+ /dicyclohexano-18-crown-6. Closed circles represent experimental, and solid lines calculated data. $[MT] = 4.02 \times 10^{-4} \text{ mol dm}^{-3}$.

observed molar conductivity, Λ , decreases monotonously with the mole ratio $[LT]/[MT]$ and starts to level off at mole ratios ≥ 1 . The decrease in Λ is considered as evidence for complex formation. As can be seen from Figures 1–4, a significant change in the slope of Λ vs. $[LT]/[MT]$ plots occurs at a mole ratio close to unity, indicating the formation of 1 : 1 complexes. The selectivity of dicyclohexano-18-crown-6 for K^+ is signified by an appreciable curvature in the Λ vs. $[LT]/[MT]$ ratio as indicated in Figure 2. Our model of 1 : 1 stoichiometry seems justifiable, since the experimental points are in good agreement with the calculated ones (solid lines) as indicated in Figures 1 to 4. However, Evans *et al.* [6] have speculated on the formation of 2 : 1 (crown : cation) complexes when the ratio $[LT]/[MT]$ exceeds 2. Their concentration range, $[MT]$, is an order of magnitude higher than that of our study.

The effect of temperature on the stability constant, K , as deduced from Figures 1 to 4 is that K decreases as the temperature is increased. This indicates that the binding of Na^+ , K^+ , Rb^+ and Cs^+ with dicyclohexano-18-crown-6 is an exothermic process. The thermodynamic quantities ΔH^0 and ΔS^0 were calculated from the corresponding $\log K$ and T data by applying a linear least squares analysis according to the equation

$$2.303 \log K = -(\Delta H^0/R)(1/T) + \Delta S^0/R \quad (21)$$

Duplicated data (with at least 10% agreement of their average) were used in this analysis.

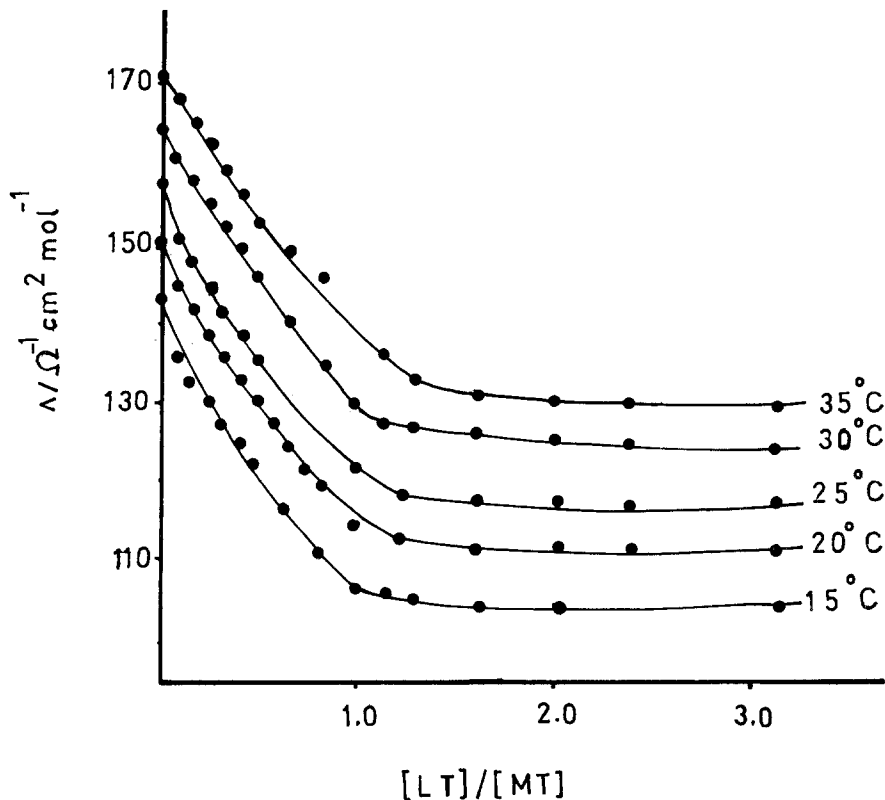


Fig. 2. Λ vs. $[LT]/[MT]$ for the system K^+ /dicyclohexano-18-crown-6. Closed circles represent experimental, and solid lines calculated data. $[MT] = 4.56 \times 10^{-4} \text{ mol dm}^{-3}$.

Table II. Stability constants and thermodynamic quantities of the 1 : 1 complexes of dicyclohexano-18-crown-6 with alkali metal cations in acetonitrile at 25°C.

Cation	Anion	Log K^a	$-\Delta H^{0b}$	$-\Delta S^{0c}$	$\Delta H^0/T\Delta S^0$	Method	[Ref.]
Na^+	BPh_4^-	4.93	51.7	78.9	2.2	Cond. ^d	This work
	BPh_4^-	5.20	—	—	—	Cond.	[6]
K^+	BPh_4^-	5.53	66.8	122.8	1.8	Cond.	This work
	BPh_4^-	5.63	—	—	—	Cond.	[6]
	SCN^-	6.60*	—	—	—	polg. ^e	[7]
Rb^+	BPh_4^-	4.67	47.7	71.4	2.2	Cond.	This work
	ClO_4^-	5.40*	—	—	—	polg.	[7]
Cs^+	BPh_4^-	4.06	50.1	89.7	1.9	Cond.	This work
	BPh_4^-	4.26	—	—	—	Cond.	[6]
	ClO_4^-	5.10*	—	—	—	polg.	[7]
	BPh_4^-	>4	—	—	—	NMR	[12]

^a K in $\text{dm}^3 \text{ mol}^{-1}$, ^b ΔH^0 in kJ mol^{-1} , ^c ΔS^0 in $\text{J mol}^{-1} \text{ K}^{-1}$, ^d conductivity, ^e polarography, * temperature = 22°C, — information unavailable.

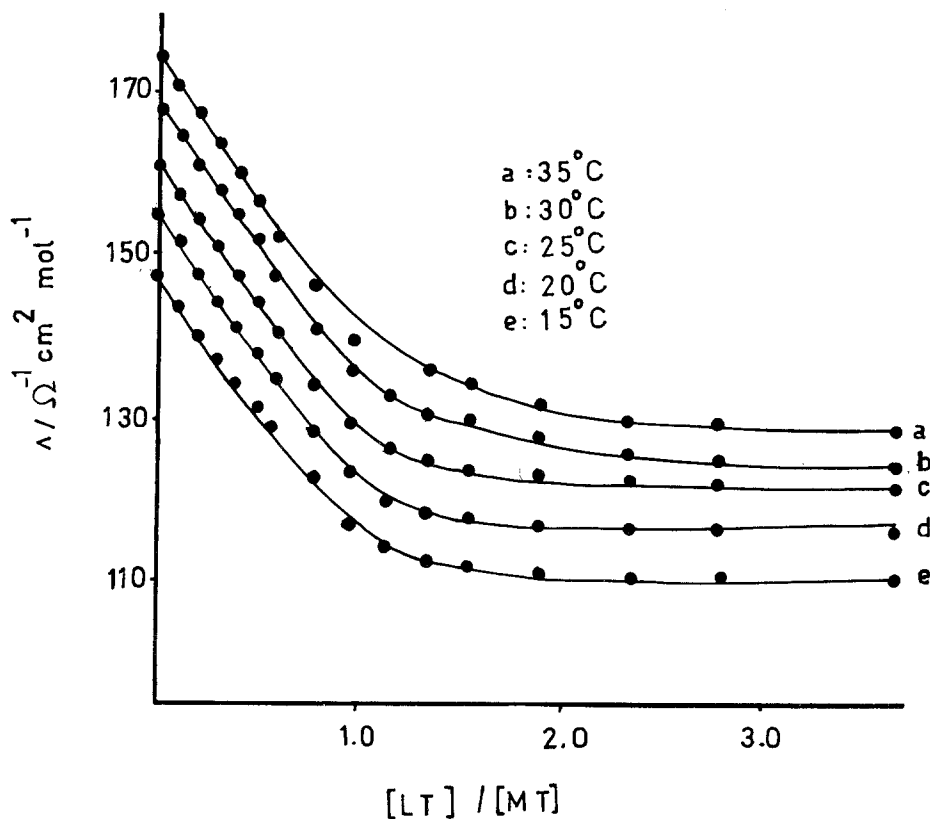


Fig. 3. Λ vs. $[LT]/[MT]$ for the system Rb^+ /dicyclohexano-18-crown-6. Closed circles represent experimental, and solid lines calculated data. $[MT] = 4.09 \times 10^{-4} \text{ mol dm}^{-3}$

The data of each cation were in accord with the linearity suggested by Equation (21). The correlation coefficients were ≥ 0.96 . The estimated uncertainty in $\log K$ for all cases reported here is ± 0.02 to ± 0.04 . The values of ΔH^0 and ΔS^0 are shown in Table II.

Due to the lack of thermodynamic data on the association of alkali metal cations with dicyclohexano-18-crown-6 (as a mixture of isomers) in aprotic solvents, a direct comparison of our data with literature values is not feasible. However, a comparison between our results and literature data on single-isomer complexes has been attempted. The following trends were obtained:

$$|\Delta H^0|(\text{AN}) > |\Delta H^0|(\text{H}_2\text{O}) \text{ for } \text{Na}^+ \text{ complex with isomer A [4],}$$

$$|\Delta H^0|(\text{AN}) > |\Delta H^0|(\text{H}_2\text{O}) \text{ for } \text{K}^+ \text{ complexes with isomers A and B [5],}$$

$$|\Delta H^0|(\text{AN}) > |\Delta H^0|(\text{H}_2\text{O}) \text{ for } \text{Rb}^+ \text{ complexes with isomers A and B [5], and}$$

$$|\Delta H^0|(\text{AN}) > |\Delta H^0|(\text{H}_2\text{O}) \text{ for } \text{Cs}^+ \text{ complex with isomer A [5]}$$

where $|\Delta H^0|(\text{AN})$ represents our data on the isomer mixture of dicyclohexano-18-crown-6 in acetonitrile. The above trends indicate that the complexation reactions are more

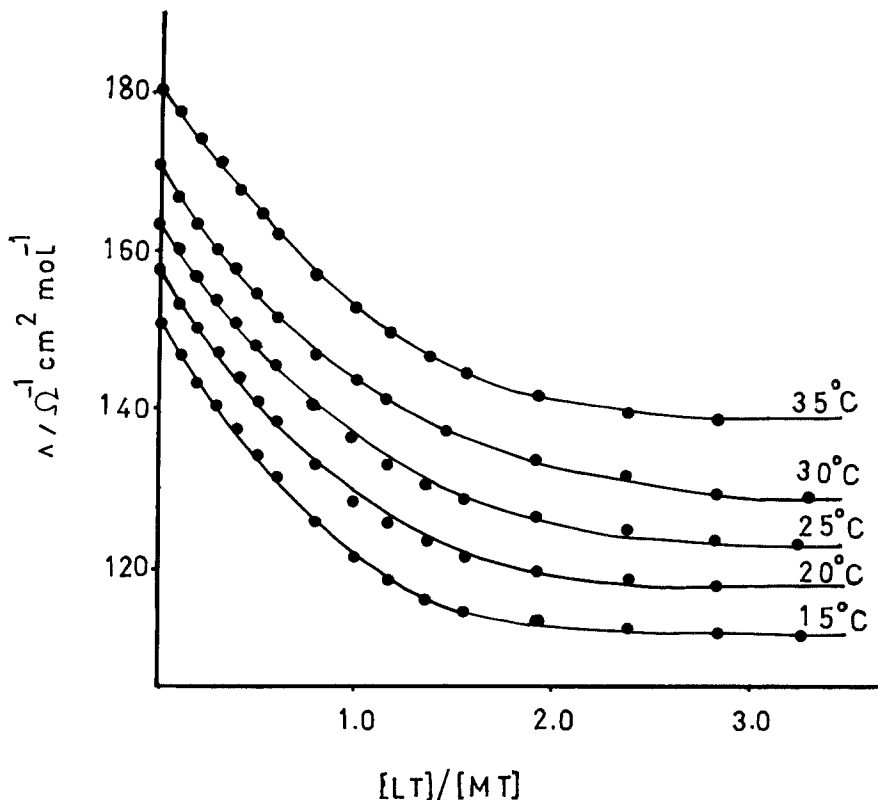


Fig. 4. Λ vs. $[LT]/[MT]$ for the system Cs^+ /dicyclohexano-18-crown-6. Closed circles represent experimental, and solid lines calculated data. $[MT] = 4.05 \times 10^{-4} \text{ mol dm}^{-3}$.

exothermic in acetonitrile than in water. This is an indication that the solvent competes with the crown ether for the alkali metal cation and the latter is more solvated in water than in acetonitrile. The exothermicity pattern shown above is in accord with the solvation power sequence reported by Kolthoff and Chantooni [18]. Our ΔH^0 values, shown in Table II, suggest the following complex stability sequence $K^+ > Na^+ \cong Cs^+ \cong Rb^+$, which is practically in accord with the stability sequence obtained from values of $\log K$ at $25^\circ C$. On the other hand the ΔS^0 sequence does not correlate with the stability sequence obtained from $\log K$ values. It is worth noting that the K^+ complex has the highest $|\Delta S^0|$ value. The ratio $\Delta H^0/T\Delta S^0$ at $25^\circ C$ (see Table II) is almost the same for the Na^+ , Rb^+ , and Cs^+ complex with dicyclohexano-18-crown-6, while its value for the K^+ complex is the smallest in the series. This shows that the K^+ complex is entropy destabilized. However, the large value of $|\Delta H^0|$ compensates for this destabilization. The cavity diameter of 18-crown-6 is reported to be 2.6 to 3.2 Å [19]. No information is available on the cavity diameter of dicyclohexano-18-crown-6. However, Mei *et al.* [12] have argued that attaching two benzo groups or two dicyclohexano groups to the 18-crown-6 cavity should lead to a reduction in the cavity diameter. The binding sequence of Cs^+ with 18-crown-6 (18C6), dicyclohexano-18-crown-6 (DCH18C6), and dibenzo-18-crown-6 (DB18C6) in several nonaqueous solvents has the

form 18C6 \gtrsim DCH18C6 \gg DB18C6 [12]. This trend in binding ability was assumed to reflect changes in cavity size and in the donor ability of the ether oxygens [12]. Consideration of these factors might explain the selectivity of dibenzo-18-crown-6 for Na⁺ as reported by Evans *et al.* [6] and Hofmanova *et al.* [7]. Our results for dicyclohexano-18-crown-6 complexes have shown that the selectivity for K⁺ as well as the complex stability pattern are the same as those of the unsubstituted 18-crown-6 [20]. This finding suggests that attaching two cyclohexano groups to the cavity of 18-crown-6 has no dramatic effect on the cavity size/or donicity of the ether oxygens.

The molar conductivities, at 25°C, of the dicyclohexano-18-crown-6 complexes with Na⁺, K⁺, Rb⁺ and Cs⁺ were found to be 122.30, 121.38, 121.00 and 118.93 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ respectively. These values are about 20% higher than the corresponding values reported by Evans *et al.* [6]. The higher values obtained from our study are due to our use of more dilute metal salt solutions. Inspection of Figures 1, 2, 3, and 4 shows that values of Λ_0 at 25°C for the alkali cations, M⁺, in acetonitrile follow the order Na⁺ < K⁺ < Rb⁺ < Cs⁺ at nearly the same concentration ($\sim 4 \times 10^{-4} \text{ mol dm}^{-3}$). However, the corresponding values of Λ_{∞} , which are nearly equal, indicate that the complexed alkali cations, ML⁺, are of similar ionic mobility. This might suggest that the complexed cations are of similar size due to an approximately equal shielding of their charge by the crown ether.

Smetana and Popov [21] have studied the influence of ionic strength on the equilibrium constant of an ion-molecule reaction, e.g., the reaction defined by Equation (1). These authors have reported that the concentration formation constant, *K*, for the 18-crown-6 complex with Na⁺ in anhydrous methanol remained reasonably constant for ionic strength $\leq 0.05 \text{ mol dm}^{-3}$. In our study the total metal salt concentration is about $4 \times 10^{-4} \text{ mol dm}^{-3}$ and the total crown ether concentration is 1.2×10^{-3} to $6.2 \times 10^{-3} \text{ mol dm}^{-3}$. Under these dilute conditions the activity coefficient of the neutral crown ether is essentially 1. In this case the application of the Debye–Huckel limiting law of 1 : 1 electrolytes leads to the conclusion that the equilibrium constants reported in this study are essentially thermodynamic equilibrium constants.

Acknowledgement

The authors thank Dr. D. Marji for his interest in initiating this work, Dr. D. Bloor for providing the Simplex Programme, and Mr. M. Barood for his assistance in setting up the Simplex Programme. This work is supported by Yarmouk University (Project number 26/86).

References

1. I. J. Burden, A. C. Coxon, J. F. Stoddart, and C. M. Wheatley: *J. Chem. Soc. Perkin Trans. 1* 220 (1977).
2. R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, and J. J. Christensen: *Chem. Rev.* **85**, 271 (1985).
3. H. K. Frensdorff: *J. Am. Chem. Soc.* **93**, 600 (1971).
4. 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).
5. R. M. Izatt, D. P. Nelson, J. H. Rytting, B. L. Haymore, and J. J. Christensen: *J. Am. Chem. Soc.* **93**, 1619 (1971).
6. D. F. Evans, S. L. Wellington, J. A. Nadis, and E. L. Cussler: *J. Solution Chem.* **1**, 499 (1972).
7. A. Hofmanova, J. Koryta, M. Brezina, and M. L. Mittal: *Inorg. Chim. Acta* **28**, 73 (1978).
8. Y. Takeda, Y. Kudo, and S. Fujiwara: *Bull. Chem. Soc. Jpn.* **58**, 1315 (1985).

9. Y. Takeda and H. Yano: *Bull. Chem. Soc. Jpn.* **53**, 1720 (1980).
10. H. P. Hopkins and A. B. Norman: *J. Phys. Chem.* **84**, 309 (1980).
11. J. A. Nedler and R. Mead: *Comput. J.* **7**, 308 (1965).
12. E. Mei, A. I. Popov, and J. L. Dye: *J. Phys. Chem.* **81**, 1677 (1977).
13. E. Mei, A. I. Popov, and J. L. Dye: *J. Am. Chem. Soc.* **99**, 6532 (1977).
14. S. Kulstad and L. A. Malmsten: *J. Inorg. Nucl. Chem.* **43**, 1299 (1981).
15. R. L. Kay, B. J. Hales, and G. P. Cunningham: *J. Phys. Chem.* **71**, 3925 (1967).
16. G. S. Kell, and A. R. Gordon: *J. Am. Chem. Soc.* **81**, 3207 (1959).
17. H. J. Buschmann: *J. Solution Chem.* **16**, 181 (1987).
18. I. M. Kolthoff and M. K. Chantooni: *Anal. Chem.* **52**, 1039 (1980).
19. C. J. Pedersen: *J. Am. Chem. Soc.* **92**, 386 (1970).
20. Y. Takeda, H. Yano, M. Ishibashi, and H. Isozumi: *Bull. Chem. Soc. Jpn.* **53**, 72 (1980).
21. A. J. Smetana, and A. I. Popov: *J. Chem. Thermodynamics* **11**, 1145 (1979).