

Conductance Study of the Binding of K^+ by Dibenzo-pyridino-18-crown-6 and 1,10-*N,N'*-didecyl-diaza-18-crown-6 in Acetonitrile

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Abstract. The binding of K^+ by dibenzo-pyridino-18-crown-6 (B₂-py-18-C-6) and 1,10-*N,N'*-didecyl-diaza-18-crown-6 (22-DD) has been studied conductometrically at 10, 15, 20 and 25 °C in acetonitrile. The complexes formed were assumed to have 1 : 1 stoichiometry. The complexes of K^+ with 18-crown-6 (18-C-6) and dibenzo-18-crown-6 (B₂-18-C-6) were also studied for comparison purposes. The stability constant, K , of a given complex and its molar conductance, Λ_c , were obtained by subjecting the conductance data to a non-linear least-squares curve fitting procedure. The values of the enthalpy change, ΔH , the entropy change, ΔS and the Gibbs free energy, ΔG , associated with the formation of the 1 : 1 complexes were derived and compared with relevant literature data. The values of ΔG at 25 °C indicate that the binding capacity of the four macrocycles follows the order 18-C-6 > 22-DD > B₂-18-C-6 > B₂-py-18-C-6. The difference between the molar ionic conductance of the free K^+ cation and that of the bound cation, KL^+ , was estimated and the trend in such differences correlates with the molecular size of the macrocycle, L .

Key words: Inclusion complexes, stability constants, crown ethers, aza crown ethers, potassium ion.

1. Introduction

Extensive thermodynamic and kinetic data concerning cation–macrocycle interactions have been tabulated in several review articles [1–3]. The most numerous thermodynamic data included in these reviews are the stability constants of cation–macrocycle complexes which were determined under a variety of experimental conditions. The major parameters involved in ion–macrocycle interactions have been discussed and specific examples are given in Refs. [1–5].

The purpose of the present study is to derive the values of ΔH and ΔS for the complexes of K^+ with less popular macrocycles of the 18-crown-6-type structure, namely dibenzo-pyridino-18-crown-6 and 1,10-*N,N'*-didecyl-diaza-18-crown-6, whose structural formulae are given in Figure 1. 18-Crown-6 and 1,10-dibenzo-18-crown-6 were included in the present study for comparison purposes.

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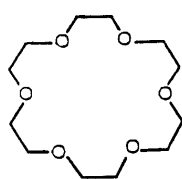
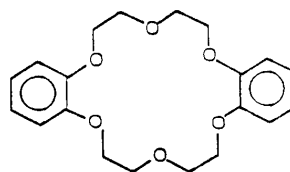
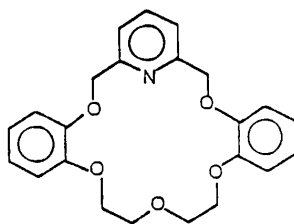
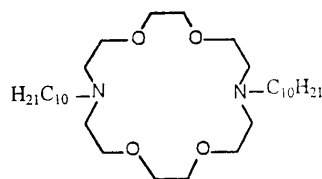
**18-C-6****B₂-18-C-6****B₂-py-18-C-6****22-DD**

Figure 1. Structural formulae of macrocycles. 18-crown-6 (18-C-6), 1,10-dibenzo-18-C-6 (B₂-18-C-6), 1,10-dibenzo-pyridino-18-crown-6 (B₂-py-18-C-6) and 1,10-*N,N'*-didecyl-diaza-18-crown-6 (22-DD).

2. Experimental

The macrocycles were purchased from Merck. 18-Crown-6 was purified by forming a solid addition compound with acetonitrile, followed by freeing from acetonitrile under vacuum [6]. Dibenzo-18-crown-6 was recrystallized from acetonitrile and then dried in an oven at 100 °C. Its melting point was found to be 163–164 °C (lit. [7], 164 °C). Dibenzo-pyridino-18-crown-6 and didecyl-diaza-18-crown-6 were recrystallized from acetonitrile. In the case of the diaza crown ether the traces of acetonitrile were removed by drying under vacuum, while the dibenzo-pyridino crown ether was dried at 100 °C in an oven for 24 h before use.

Sodium tetraphenylborate, NaBPh₄, (Fluka) was recrystallized from an acetone–toluene mixture, as described in the literature [8]. Potassium tetraphenylborate, KBPh₄ was prepared by mixing a dilute aqueous solution of NaBPh₄, with an equivalent amount of KCl (Fisher Scientific) and was recrystallized from acetone as described in the literature [6]. KClO₄ (Fluka) was recrystallized from deionized water and dried at 120 °C before use. Acetonitrile (BDH, M & B Laboratory Chemicals) was dried by treatment with molecular sieves and distillation over CaH₂ [9, 10]. The middle 70% of the distillate was used with specific conductance less than 1.0×10^{-7} S cm⁻¹ (the detection limit of the conductometer).

A Metrohm E518 conductometer and a Metrohm EA645 conductance cell (cell constant 2.140 cm^{-1}) were used for measuring the specific conductance of the solution. The stoppered cell was kept in a thermostating unit with temperature controlled to $\pm 0.02 \text{ }^\circ\text{C}$. A Cordata PC was used for the least-squares analysis of the conductance data. Microburettes of 10 mL capacity and $\pm 0.01 \text{ mL}$ sensitivity were used for volume measurements.

Acetonitrile solutions of KBPh_4 with concentrations of ca. 4 to $6 \times 10^{-4} \text{ mol dm}^{-3}$ were used. Similar solutions, having the same total KBPh_4 concentration, were also used as solvents for preparing the macrocycle solutions. In a typical run, 25.00 mL of KBPh_4 solution was placed in the conductance cell, thermostated to the required temperature and the reading of the specific conductance of the salt solution was then recorded. The cell was removed from the thermostat and the first increment (ca. 0.10 mL, macrocycle concentration ca. $8 \times 10^{-3} \text{ mol dm}^{-3}$) of the macrocycle solution was added. After stirring for a few minutes, the cell was replaced in the thermostat and the steady reading of the specific conductance was recorded. Addition of the increments of the macrocycle solution was continued until the change in the specific conductance was negligible.

NaCl was used for checking the precision of the conductometer and for detecting the effect of viscosity changes (caused by the addition of macrocycles) on the conductance measurements in a manner similar to that reported previously [11]. It was concluded that the precision of the conductometer amounts to ca. 1% and any variation in the molar conductance caused by the effect of macrocycles on the viscosity of the medium was not detected by the conductometer.

3. Results and Discussion

The stoichiometry of the binding of alkali cations with macrocycles of the type studied in the present work is 1 : 1 in dilute solutions [1, 2]. Consequently, the binding of K^+ by the macrocycles, L, can be given by the following equilibrium



with

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

where $[\text{KL}^+]$, $[\text{K}^+]$, $[\text{L}]$ and f represent the molar concentrations (mol dm^{-3}) of the K^+ complex, uncomplexed cation, uncomplexed macrocycle and the activity coefficient of the species indicated, respectively. Since the solutions are dilute, the activity coefficient $f(\text{L})$ is essentially unity. On the basis of the Debye–Hückel limiting law, the ratio $f(\text{KL}^+)/f(\text{K}^+)$ is also unity [12]. Therefore the activity coefficients cancel out in Equation 2 and the equilibrium constants reported in the present study are essentially thermodynamic constants.

The usual practice [13] 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 KBPh_4 and KLBPh_4 , as

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

where α represents the degree of dissociation of the complex, Λ_m and Λ_c are the molar conductances of the uncomplexed and the complexed salt, respectively. α is given as the ratio $[\text{K}^+]/[\text{K}_t^+]$, where $[\text{K}_t^+]$ is the total concentration of the potassium salt. Equation 3 is an approximate expression which states that Λ is calculated by the simple additivity rule. However, solutions containing K^+ and KL^+ 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 mixtures of KCl and LiCl . For such systems Kell and Gordon [14] have shown that the deficit in the molar conductance of the mixture as compared with that calculated by using the simple additivity rule is negligibly small.

In Equation (3) Λ is treated as a calculated quantity in the Simplex program [15, 16] while K and Λ_c are adjustable parameters. The reported values for K and Λ_c correspond to the condition that $\sum(\Lambda - \Lambda_{\text{cal}})^2$ is a minimum, at which the program terminates. For each data set the computational procedure was repeated several times by changing the program variables in order to get the K and Λ_c values as the average of the best agreeing program outputs. For each K^+ /macrocycle system, three trials were carried out to find K and Λ_c at a given temperature. The details of the computational procedure were reported previously [12].

Table I summarises our results as obtained by the non-linear least-squares method at 10, 15, 20 and 25 °C. Figure 2 illustrates the behavior of Λ as a function of the ratio $[\text{L}]/[\text{K}_t^+]$ at 25 °C. The figure indicates that the observed molar conductances decrease significantly for mole ratios less than unity. The value of $\log K$ for the 1 : 1 complex of K^+ with 18-crown-6 as determined in the present study at 25 °C in acetonitrile is 5.72 and is in good agreement with the literature values of 5.70, 5.72 and 5.72 given in Refs. [7], [9] and [17], respectively under the same conditions. The corresponding $\log K$ value determined for the K^+ /1,10-dibenzo-18-crown-6 complex is 4.77 which is in reasonable agreement with the literature values of 4.81 [7], 4.83 [9] and 4.78 [17]. The value of $\log K$ for the K^+ complex with dibenzo-pyridino-18-crown-6 determined in the present study at 25 °C is 4.06. To the best of our knowledge, no literature data are available on this system. On the other hand the value of $\log K$ determined in this study for the K^+ complex with 1,10-*N,N'*-didecyl-diaza-18-crown-6 is 5.52. The literature value for the same system in methanol is 4.00 [18] and no literature value is reported in acetonitrile.

The values of ΔH and ΔS of the 1 : 1 complexes of K^+ with the macrocycles shown in Figure 1 were determined from the values of the stability constants given

Table I. The molar conductances, Λ_m and Λ_c , and the stability constants of the macrocycles–potassium tetraphenylborate 1 : 1 complexes in acetonitrile.

Macrocyclic	T/K	$[K_t^+] \cdot 10^4/M$	Λ_m ($S\ cm^2\ mol^{-1}$)	Λ_c ($S\ cm^2\ mol^{-1}$)	K ($dm^3\ mol^{-1}$)
18-C-6	298	3.510	134.15 ± 2.50	114.01 ± 0.90	$(5.23 \pm 0.16) \times 10^5$
	293	3.987	129.66 ± 2.30	110.16 ± 0.75	$(7.54 \pm 0.54) \times 10^5$
	288	3.987	125.27 ± 1.50	106.40 ± 0.80	$(9.82 \pm 0.58) \times 10^5$
	283	3.987	117.87 ± 1.00	100.33 ± 0.60	$(13.52 \pm 0.52) \times 10^5$
B ₂ -18-C-6	298	6.039	134.12 ± 3.00	105.46 ± 0.70	$(5.95 \pm 0.05) \times 10^4$
	293	4.987	131.87 ± 2.50	103.56 ± 0.30	$(6.74 \pm 0.02) \times 10^4$
	288	6.160	122.33 ± 1.50	95.61 ± 0.25	$(7.50 \pm 0.43) \times 10^4$
	283	6.160	116.89 ± 2.00	91.71 ± 0.15	$(9.25 \pm 0.24) \times 10^4$
B ₂ -py-18-C-6	298	3.753	135.89 ± 2.50	105.68 ± 0.80	$(1.15 \pm 0.03) \times 10^4$
	293	4.025	126.20 ± 3.10	98.99 ± 0.63	$(1.35 \pm 0.03) \times 10^4$
	288	4.024	120.98 ± 1.90	93.41 ± 0.27	$(1.52 \pm 0.01) \times 10^4$
	283	4.024	114.53 ± 1.45	87.80 ± 0.25	$(1.72 \pm 0.05) \times 10^4$
22-DD	298	4.702	136.06 ± 2.50	97.95 ± 0.15	$(3.35 \pm 0.47) \times 10^5$
	293	4.701	129.69 ± 1.30	93.67 ± 0.36	$(6.08 \pm 0.43) \times 10^5$
	288	4.708	123.24 ± 2.00	90.41 ± 0.50	$(6.93 \pm 0.61) \times 10^5$
	283	4.708	116.23 ± 1.50	85.32 ± 0.20	$(9.07 \pm 0.50) \times 10^5$

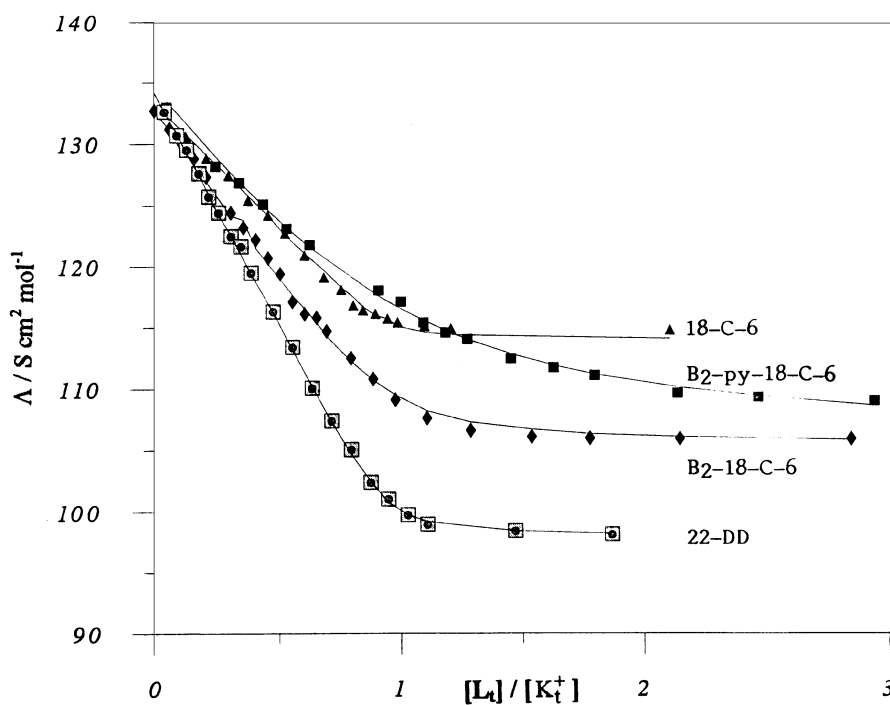

 Figure 2. Plot of the molar conductance, Λ , vs. mole ratio $[L_t]/[K_t^+]$ for the binding of K^+ by the indicated macrocycles in acetonitrile at 25 °C.

Table II. Values of the thermodynamic quantities ΔH , ΔS and ΔG of K^+ complexes with the macrocycles given in Figure 1 in acetonitrile.

Macrocyclic	$-\Delta H^a$	ΔS^b	$-\Delta G^{a,c}$	Ref.
18-C-6	43.6 ± 2.2	-36.6 ± 7.4	32.7 ± 0.0	This work
	9.9	75.8	32.5	[17]
B ₂ -18-C-6	20.1 ± 2.1	23.8 ± 7.1	27.2 ± 0.0	This work
	18.6	28.9	27.2	[17]
	28.6	-7.53	26.4	[19]
B ₂ -py-18-C-6	18.6 ± 1.1	15.5 ± 3.8	23.2 ± 0.0	This work
22-DD	43.6 ± 9.8	-39.5 ± 33.6	31.8 ± 0.2	This work

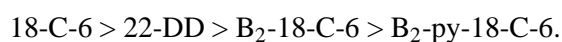
^a kJ mol⁻¹, ^b J mol⁻¹ K⁻¹, ^c Calculated at 25 °C from ΔH and ΔS values.

in Table I by applying a linear least-squares analysis according to the following thermodynamic equation

$$2.303R \log K = -\Delta H(1/T) + \Delta S \quad (4)$$

Table II shows the values of ΔH , ΔS and ΔG derived in the present study together with the relevant literature data. By comparing our results for ΔH and ΔS for the K^+ /18-crown-6 complex with the compilation of the corresponding values [1–5] in water, aqueous methanol, methanol and propylene carbonate, we find that the sign of ΔS and the magnitude of ΔH in acetonitrile are in general agreement with expectations based on solvent properties. The smallest magnitude of ΔH and the only positive ΔS are the quantities reported by Buschmann [17]. In the case of the K^+ /1,10-dibenzo-18-crown-6-complex, the values of ΔH and ΔS derived in the present work are in good agreement with those determined by Buschmann [17] in acetonitrile. The corresponding values determined by Sabirov *et al.* [19] are quite different, especially the magnitude of ΔH and the sign of ΔS .

Based on the values of ΔG given in Table II, the stability of the K^+ complexes with the macrocycles studied in the present work follows the order



It is obvious that the total number of atoms constituting the macrocycle ring, as well as the number of donor atoms is the same for all four macrocycles. However, the macrocycles differ in: (i) the basicity of the donor atom; (ii) the type of substituents in the macrocycle ring; and (iii) the flexibility of the macrocycle ring. Factors (i) and (iii) explain the stability order $18\text{-C-6} > \text{B}_2\text{-18-C-6}$ since the replacement of two $\text{CH}_2\text{—CH}_2$ units by two benzo units reduces the flexibility (unfavourable orientation of donor atoms) and weakens the electronegativity of the oxygen atoms of the macrocycle. Consideration of all three factors explains the stability order $\text{B}_2\text{-18-C-6} > \text{B}_2\text{-py-18-C-6}$, where the incorporation of the pyridino unit has the

effect of both reducing macrocycle flexibility and donor atom basicity. In the case of the $K^+/22-DD$ complex, the replacement of two oxygen donor atoms in 18-C-6 by two nitrogen atoms reduces the overall affinity of the crown ether towards K^+ . On the other hand, the two alkyl groups of 22-DD have no dramatic effect on the complex formation when compared with the substituent effects in $B_2-18-C-6$ and $B_2-py-18-C-6$. As a matter of fact the values of $\log K$ in methanol for the complexes of K^+ with 22-DD and its analogues (C_3H_7- , C_4H_9- , $C_6H_{13}-$, $C_9H_{19}-$) are nearly independent of the size of the alkyl groups attached to the two nitrogen atoms of the macrocycle [18, 20–22]. The values of the equilibrium constants of the general reaction defined by Equation 1 were found to be essentially the same when $KClO_4$ was used instead of $KBPh_4$ in the complexation reaction. This result implies that the counter-anion is not involved in the K^+ -macrocycle reaction.

By considering the Debye–Hückel–Onsager equation and substituting the corresponding parameters of acetonitrile [23] at 25 °C and the value of the molar conductance of $KBPh_4$ at infinite dilution [10], the values of Λ_m given in Table I at 25 °C were found to be 3% lower than expected. This difference is most likely due to errors encountered when working with dilute electrolyte solutions prepared by volume measurements and inadequate temperature control, as indicated by the uncertainties given in Table I. Since the electrolytes $KBPh_4$ and $KLPh_4$ are assumed to dissociate completely in dilute solutions, the difference $\Lambda_m - \Lambda_c = \lambda_{K^+} - \lambda_{KL^+}$ can be used to deduce the relative order of the mobilities of the KL^+ ions at a particular temperature. By using the data of Table I, the relative order of the mobilities of the KL^+ ions was found to be $K(22-DD)^+ < K(B_2-py-18-C-6)^+ < K(B_2-18-C-6)^+ < K(18-C-6)^+$. This trend is in accord with the expected bulkiness of the KL^+ cation where 18-C-6 has the smallest molecular size and 22-DD has the largest molecular size among the four macrocycles.

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References

1. R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen, and D. Sen: *Chem. Rev.* **85**, 271 (1985).
2. R.M. Izatt, K. Pawlak, J.S. Bradshaw, and R.L. Bruening: *Chem. Rev.* **91**, 1721 (1991).
3. R.M. Izatt, K. Pawlak, J.S. Bradshaw, and R.L. Bruening: *Chem. Rev.* **95**, 2529 (1995).
4. G. De Jong and D.N. Reinhoudt: *Adv. Phys. Org. Chem.* **17**, 279 (1980).
5. J.J. Christensen, D.J. Eatough, and R.M. Izatt: *Chem. Rev.* **74**, 351 (1974).
6. E. Mei, A.I. Popov, and J.L. Dye: *J. Am. Chem. Soc.* **99**, 6532 (1977).
7. I.M. Kolthoff and M.K. Chantooni, Jr.: *Anal. Chem.* **52**, 1039 (1980).
8. E. Mei, A.I. Popov, and J.L. Dye: *J. Phys. Chem.* **81**, 1677 (1977).
9. Y. Takeda: *Bull. Chem. Soc. Jpn.* **56**, 866 (1983).
10. J. Barthel, L. Iberl, J. Rossmair, H.J. Gores, and B. Kaukal: *J. Solution Chem.* **19**, 321 (1990).

11. K.M. Tawarah and A.A. Wazwaz: *J. Chem. Soc. Faraday Trans.* **89**, 1729 (1993).
12. K.M. Tawarah and S.A. Mized: *J. Solution Chem.* **18**, 387 (1989).
13. Y. Takeda and H. Yano: *Bull. Chem. Soc. Jpn.* **53**, 1720 (1980).
14. G.S. Kell and A.R. Gordon: *J. Am. Chem. Soc.* **81**, 3207 (1959).
15. J.A. Nedler and R. Mead: *Comput. J.* **7**, 308 (1965).
16. F.A. Ababneh: M.Sc. Thesis, Yarmouk University (1994).
17. H.J. Buschmann: *J. Solution Chem.* **17**, 277 (1988).
18. H.J. Buschmann: *Inorg. Chim. Acta* **125**, 31 (1986).
19. R.Z. Sabirov, M.G. Levkovich, and A.G. Muftakhov: *Uzb. Khim. Zh.* **5** (1982).
20. V.J. Gatto, K.A. Arnold, A.M. Viscariello, S.R. Miller and G.W. Gokel: *Tetrahedron Lett.* **27**, 327 (1986).
21. V.J. Gatto, K.A. Arnold, A.M. Viscariello, S.R. Miller, C.R. Morgan and G.W. Gokel: *J. Org. Chem.* **51**, 5373 (1986).
22. K.A. Arnold, L. Echegoyen, F.R. Fronczek, R.D. Gandour, V.J. Gatto, N.D. White, and G.W. Gokel: *J. Am. Chem. Soc.* **109**, 3716 (1987).
23. P.W. Atkins: *Physical Chemistry*, 5th edn., p. 846, Oxford University Press, Oxford (1994).