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Conductance Study of Ion-Pairing of Alkali Picrate and Tetraphenylborate Complexes with Some Macrocyclic Polyethers in Methanol

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The conductance of dibenzo-18-crown-6 (DB18C6), bis (3,5-di-tert-butylbenzo)-18-crown-6 (dtbDB18C6) and dibenzo-24-crown-8 (DB24C8) complexes with sodium and potassium picrates and tetraphenylborates was investigated in methanol at 25 °C. Shedlovsky plots gave straight lines from which the limiting conductances, λ_o, and ion-pair dissociation constants, K_D, were calculated. Generally, tetraphenylborate complexes are slightly more dissociated than the corresponding picrate complexes, as are also the potassium complexes compared to those of the sodium salts. The results obtained are compared with those obtained for the conductance of sodium and potassium picrates and tetraphenylborates in methanol, and are discussed in terms of the polyether interactions with alkali cation which are controlled by their size, solvent interactions with the polyether-cation complexes, size and charge density of the counterion, and the steric factors caused by the presence of the bulky tert-butyl substituents in the polyether molecule.

INTRODUCTION

Much interest recently has been directed to obtaining information on the complexation of macrocyclic polyethers with alkali metals, especially sodium and potassium.[1–11] These ions are important in biological systems and the macrocyclic polyethers resemble the more complex naturally occuring macrocyclic antibiotics, which are known to make cell membranes selectively permeable to cations.[12,13]

The interaction of a macrocyclic polyether with an alkali salt produces a mixture of polyether-complexed contact ion-pairs and polyether-separated ion-pairs. The proportion of the latter species is higher in more polar solvents and in diluted solutions where cation-anion interactions are known to be small. The stability of the ion-pair complexes is strongly dependent on the physicochemical properties of the solvent, size of the cation, size and charge density of the counterion, temperature, and the structure of the macrocyclic polyether, especially the size of the polyether ring relative to the cation diameter.[4,6]

An earlier report by us dealt with the association equilibria of alkali metal cations with two tert-butyl substituted derivatives of DB18C6 (mtbDB18C6 and dtbDB18C6).[11] As an extension of these studies, the results of this paper concern the ion-pair formation between the polyether-cation complex and the anion.

The well characterized complexes of macrocyclic polyethers DB18C6, dtbDB18C6 and DB24C8 with sodium and potassium picrates and tetraphenylborates were examined by electrical conductance measurements in methanol. From such measurements we obtain values of the limiting equivalent conductance and of the amount of association between complex cation and anion by explicit consideration of interionic effects on ion mobility, such as given by the Shedlovsky equation.[14–16] These results are compared with previously reported conductance data for sodium and potassium picrates[17] and tetraphenylborates[18] to demonstrate ion-pairing trends with increasing cation size.

EXPERIMENTAL

Reagents

Macrocyclic polyethers, prepared as previously described,[1,19] were purified by repeated recrystallizations from the appropriate solvents. Their crystalline complexes of sodium and potassium picrates[20] and tetraphenylborates[21] were synthesized according to the literature cited.

New tetraphenylborate complexes of the macrocyclic polyether dtbDB18C6 were prepared by the same method dissolving an equimolar amount of ligand and alkali salt in methanol. The solution was boiled under reflux for 1—2 hr with vigorous stirring, filtered, and allowed to stand at room temperature. A crystalline precipitate was gradually formed by removal of solvent, filtered off, and washed with cold methanol. The isolated complexes were dried by heating them to about 50°C under high vacuum for several hours, giving stable anhydrous compounds as confirmed by elemental and thermogravimetric analyses, and spetral data.

$Na(dtbDB18C6)BPh_4$
Yield 72%, m.p., 200—201°C.
Anal. $C_{60}H_{76}O_6BNa$ (926.43) calc'd: C 77.72; H 8.27; Na 2.48%
found: C 77.93; H 8.11; Na 2.55%
UV spectrum: λ_{max} 267 nm (ε, 5500); λ_{max} 274 nm (ε, 5800).
^1H NMR spectrum: 6.50—7.55 δ(m, 24H, aromatic); 3.33—4.22 δ(m, 16H, CH_2O); 1.26, 1.31 δ(s, 36H, tert-C_4H_9).
Significant IR absorptions: 1242 sh, 1230 s, υ_{as}(Ar-O-CH_2); 1122 vs, υ_{as}(CH_2-O-CH_2); 997 m, 982 m, ω, τ(CH_2).

$K(dtbDB18C6)BPh_4$
Yield 31%, m.p., 260°C with decomposition.
Anal. $C_{60}H_{76}O_6BK$ (942.53) calc'd: C 76.39; H 8.13; K 4.15%
found: C 76.44; H 8.37; K 4.08%
UV spectrum: λ_{max} 267 nm (ε, 5500); λ_{max} 274 nm (ε, 5800).
Significant IR absorptions: 1245 s, 1234 s, υ_{as}(Ar-O-CH_2); 1122 vs, υ_{as}(CH_2-O-CH_2); 994 m, 983 m, ω, τ(CH_2).

Elemental analyses were carried out by the Microanalytical Laboratory of the Rugjer Bošković Institute.

UV spectra were obtained in methanolic solutions with a Perkin-Elmer M-124 spectrophotometer.

^1H NMR spectrum was determined in $CDCl_3$ solution and recorded on Varian A-60A spectrometer using tetramethylsilane as an internal reference.

IR spectra were recorded on KBr pellets using a Perkin-Elmer spectrophotometer M-580B, in the region 4000—200 cm^{-1}.

Thermogravimetric measurements were made using the Chan RG electro-micro balance with a heating rate of 2°C/min, in an atmosphere of static air.

The purification of methanol was carried out by published method[22] in order to obtain a solvent whose specific conductance varied from 1 to 5×10^{-8} ohm^{-1} cm^{-1}. The physical properties of purified solvent at 25°C were 0.78658 g ml^{-1} density, 0.00547 P viscosity, and 32.63 dielectric constant. A single capillary pycnometer was used for the density measurements, while the viscosity was obtained with a Ubbelohde-type viscosimeter. The values obtained are in good agreement with the generally accepted values.[22]

Conductivity measurements

Measurements of electrolytic conductivity were performed in methanol at 25.00 ∓ 0.01°C using a CD 7A conductivity bridge (Tacussel Electronique, France). The cell constant (0.9745 cm^{-1}) was established by several calibrations with aqueous potassium chloride.[23] The cell content was thermostated with a double water bath and stirred by means of a magnetic stirrer.

The dependence of equivalent conductance on the concentration of macrocyclic polyether complex was approached experimentally by both the concentration of an initially dilute solution and the dilution of an initially concentrated complex solution. The concentration range studied was below the critical concentration limit,[24] defined as 3.2×10^{-7} D^3, above which triple ions may exist. In

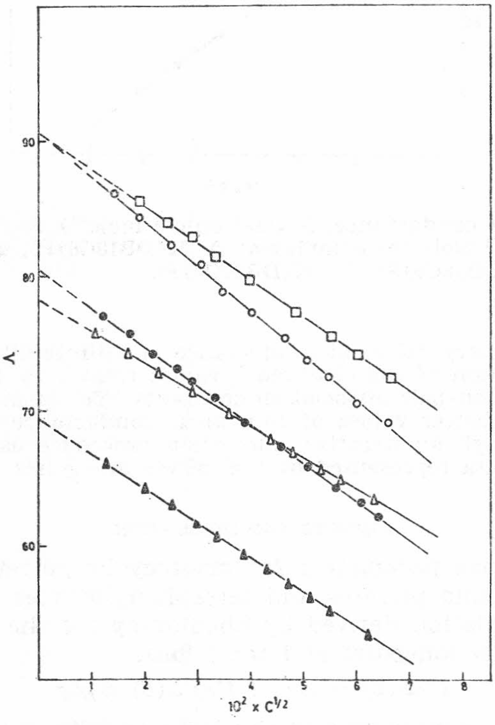

Figure 1. Equivalent conductance, Λ (cm^2 ohm^{-1} $mole^{-1}$) vs concentration$^{1/2}$, $C^{1/2}$ $(mole/1)^{1/2}$ plots for complexes: △, Na(DB18C6Pi: ▲, Na(DB18C6)BPh_4; ○, Na(dtbDB18C6)Pi; ●, Na(dtbDB18C6)BPh_4; □, Na(DB24C8)Pi.

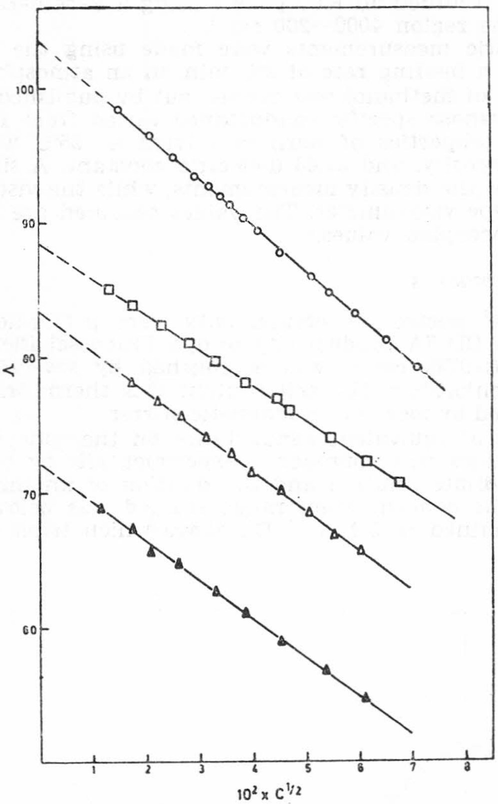

Figure 2. Equivalent conductance, Λ (cm^2 ohm^{-1} $mole^{-1}$) *vs* concentration$^{1/2}$, $C^{1/2}$ (mole/l)$^{1/2}$ plots for complexes: △, K(DB18C6)Pi; ▲, K(DB18C6)BPh_4; ○, K(dtbDB18C6)Pi; □, K(DB24C8)Pi.

order to get preliminary values of conductance at infinite dilution, λ_o was determined by extrapolation of the observed λ values from λ vs. $C^{1/2}$ curves reported in Figures 1 and 2. Ion-pair dissociation constants (K_D) of macrocyclic polyether complexes and the better values of equivalent conductance at infinite dilution were obtained through an iterative calculation procedure using the Shedlovsky equation and the data represented by the curves in Figures 1 and 2.

RESULTS AND DISCUSSION

The conductance parameters for macrocyclic polyether complexes of sodium and potassium picrates and tetraphenylborates in methanol were obtained by the relation derived by Shedlovsky for the conductivity of a system composed of ion-pairs and their ions.

$$1/\lambda S(z) = 1/\lambda_o + C\lambda f^2 S(z)/K_D \lambda_o^2$$

The functional dependence of the ionic activity coefficient *f* and the Shedlovsky extrapolation function *S*(*z*) on the equivalent conductance, on the concentration of the complex, on the dielectric constant and viscosity of the solvent, and the temperature is given in ref. [14].

The results obtained are illustrated in Figures 3 and 4, which plot $1/\lambda S(z)$ as a function of $C\lambda f^2S(z)$. The straight lines indicate that larger associates than ion-pairs can be neglected. According to this treatment the y-intercept of the straight line is $1/\lambda_o$ and the slope is $1/K_D\lambda_o^2$. The values of λ_o and K_D for all the complexes studied are summarized in Table I.

TABLE I

Limiting Equivalent Conductances and Dissociation Constants of Sodium and Potassium Picrate and Tetraphenylborate Complexes with Some Macrocyclic Polyethers in Methanol at 25°C[a]

Complex (MLX)[b]	$10^2 \times K_D$	$\lambda_o(MLX)$	$\lambda_o^+(ML^+)$	$\lambda_o^-(X^-)$[c]	$\lambda_o^+(M^+)$[c]$/\lambda_o^+(ML^+)$
Na(DB18C6)Pi	1.23	78.20	31.33	46.87	1.44
Na(DB18C6)BPh$_4$	2.07	69.37	32.87	36.50	1.38
Na(dtbDB18C6)Pi	1.56	90.42	43.55	46.87	1.04
Na(dtbDB18C6)BPh$_4$	2.08	80.00	43.50	36.50	1.04
Na(DB24C8)Pi	3.33	90.50	43.63	46.87	1.04
K(DB18C6)Pi	1.49	83.56	36.69	46.87	1.43
K(DB18C6)BPh$_4$	2.86	72.13	35.63	36.50	1.47
K(dtbDB18C6)Pi	2.12	103.09	56.22	46.87	0.93
K(DB24C8)Pi	3.56	88.34	41.47	46.87	1.26

[a] λ values in cm^2 ohm^{-1} mole^{-1}; K_D in mole/l.
[b] M=Na$^+$, K$^+$; L=macrocyclic polyether; X=Pi$^-$, BPh$_4^-$.
[c] Literature values; see text.

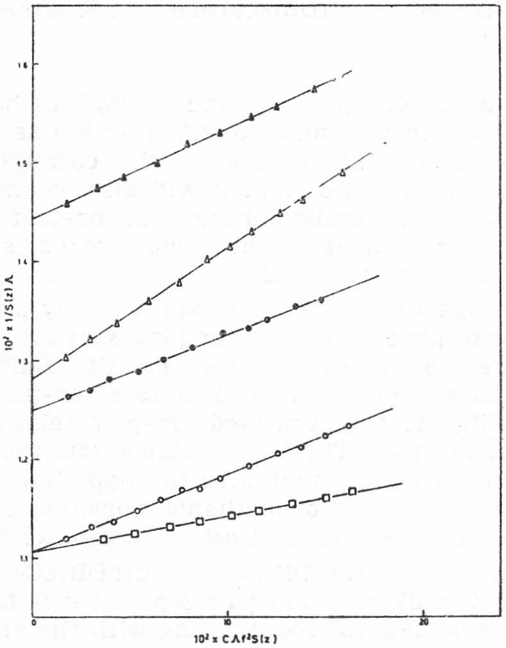

Figure 3. Shedlovsky plots $1/\Lambda S(z)$ vs $C\Lambda f^2S(z)$ for complexes: △, Na(DB18C6)Pi; ▲, Na(DB18C6)BPh$_4$; ○, Na(dtbDB18C6)Pi; ●, Na(dtbDB18C6)BPh$_4$; □, Na(DB24C8)Pi.

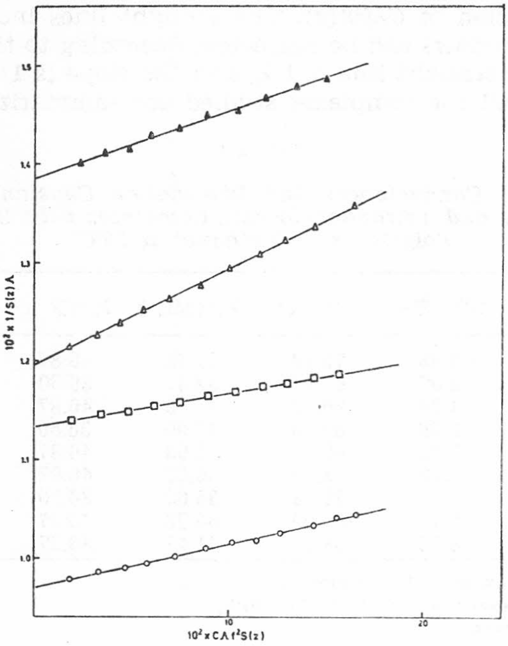

Figure 4. Shedlovsky plots $1/\Lambda S(z)$ *vs* $C\Lambda f^2S(z)$ for complexes: △, K(DB18C6)Pi) ▲, K(DB18C6)BPh$_4$; ○, K(dtbDB18C6)Pi; □, K(DB24C8)Pi.

Sodium and potassium picrates and tetraphenylborates are nearly completely dissociated in methanol solutions.[17,18] We assume on this basis that similar ion-pair formation between the corresponding polyether-cation complexes and the cited anions will also be small. This assumption corroborates with the results obtained for ion-pair dissociation constants of the polyether complexes. The values are not significantly different and are in the range from 1.2 to 3.5×10^{-2} M.

Generally, tetraphenylborate complexes are only slightly more dissociated than the corresponding picrate complexes, as are also the potassium complexes compared to those of the sodium salts. Bulky substituents on the anion and charge delocalization facilitate ion-pair separation, and enhance the stability of the separated ion-pair relative to that of the complexed contact ion-pair. The inappreciable variations of K_D with the nature of the cation are consistent with the hypothesis that in a solvent of high polarity, such as water or methanol, polyether complexes of different alkali cations can behave as isosteric complexes.[8,25]

The gradation in K_D of the DB18C6 and dtbDB18C6 complexes reflects the increase in their bulkiness. Ion-pair separation is favored when more oxygen atoms are available for coordinating with the alkali ion and when the polyether ring is large enough to accomodate the cation. Consequently, the picrate complexes of DB24C8 are more dissociated than the corresponding complexes of DB18C6 and dtbDB18C6.

From the calculations we also obtained values of $\lambda_o(MLX)$, which represent the mobilities at infinite dilution of the complexed ion-pairs. Alkali metal cations are known to be extensively solvated in methanol.[26] A larger solvation effect is expected for the smaller sodium ion than for the potassium ion, and consequently, a lower mobility is obtained for the sodium complexes.

To evaluate the change in cation mobility of the macrocyclic polyether complexes, it is more realistic to compare the conductance at infinite dilution of individual complexed cations, $\lambda_o^+(ML^+)$. These values were calculated according to Kohlrausch's law, $\lambda_o = \lambda_o^+ + \lambda_o^-$, using the following literature values: $\lambda_o^-(BPh_4^-) = 36.50$; $\lambda_o^-(Pi^-) = 46.87$.[17] It is interesting to compare these data with those for the conductance at infinite dilution of methanol solvated sodium and potassium cations: $\lambda_o^+(Na^+) = 45.18$; $\lambda_o^+(K^+) = 52.42$.[17,18] The ratios $\lambda_o^+(M^+)/\lambda_o^+(ML^+)$ roughly parallel the bulkiness of the solvated and complexed cations, and are a measure of the decreased mobilities of the complexes. The calculated $\lambda_o^+(ML^+)$ values as well as the ratios $\lambda_o^+(M^+)/\lambda_o^+(ML^+)$ are given in Table I.

With all complexes of DB18C6 the difference $\lambda_o^+(M^+) — \lambda_o^+(ML^+)$ is substantial, implying that polyether complexation considerably increases the size of the cation, and that the structure of the complex is such that solvent molecules can remain associated with the cation. Undoubtedly, the complexed ion-pairs may still carry a few solvent molecules, especially the polyether separated ion-pairs, where the alkali cation is more exposed to the solvent.[4] This assumption is consistent with the results obtained for the complexes od dtbDB18C6. Methonal solvated alkali metal cations and complexed cations of dtbDB18C6 in spite of their size, would appear to be very similar with respect to cation mobility and formation of ion--pairing. Apparently, the polyether coplexes are not solvated, and therefore, slightly lower values were obtained for the equivalent conductance of sodium complexes (about 2%), and slightly larger values for potassium complexes (about 3%) in comparation with the conductance data for sodium and potassium picrates and tetraphenylborates, respectively. The lack of solvation can be attributed to the steric hindrance produced by the bulky tert-butyl substituents.

While the λ_o value of the $K(dtbDB18C6)BPh_4$ complex could not be measured, the effect of polyether complexation on cation mobility was studied by mesauring the equivalent conductance of the complex at 10^{-3} M. Its $\lambda^+(ML^+)$ value was found from the relationship $\lambda^+(ML^+) = \lambda(MLX)$ —

TABLE II

Equivalent Conductances of dtbDB18C6 Complexes at 10^{-3} M in Methanol

Complex (MLX)[b]	$\lambda(MLX)$	$\lambda(MX)$[c]	$\lambda^+(ML^+)$	$\lambda^-(X^-)$[c]	$\lambda^+(M^+)$[c]$/\lambda^+(ML^+)$
Na(dtbDB18C6)Pi	80.01	84.30	38.40	41.60	1.11
K(dtbDB18C6)Pi	93.32	90.57	51.70	41.60	0.95
Na(dtbDB18C6)BPh$_4$	72.01	75.32	39.33	32.67	1.08
K(dtbDB18C6)BPh$_4$	85.80	81.70	53.10	32.67	0.92

[a] λ values in cm^2 ohm^{-1} mole^{-1}.

[b] $M=Na^+, K^+$; L=dtbDB18C6; $X=Pi^-, BPH_4^-$.

[c] Literature values from refs. 17 and 18; see text.

— $\lambda^-(BPh_4^-)$, where $\lambda^-(BPh_4^-)$ at 10^{-3} M was obtained by interpolation of λ values reported for triisoamylbutyl tetraphenylborate in methanol,[17] assuming that the relationship $\lambda_o^+ = \lambda_o^-$ found for this salt also holds for the equivalent conductance at 10^{-3} M. The calculated $\lambda^+(ML^+)$ values for picrate and tetraphenylborate complexes of dtbDN18C6, as well as the ratios $\lambda^+(M^+)/\lambda^+(ML^+)$ are given in Table II.

The fact, that the total drop in the equivalent conductance for the potassium picrate complex of DB24C8 is considerably larger than for the corresponding sodium picrate complex can be explained by the weaker solvation of the sodium complex. The ability of polyether DB24C8 to form stable complexes with salts of small cations such as sodium can be attributed to the high flexibility of the 24-membered polyether ring. This flexible ligand may complex the metal cation by wrapping around it with a change in conformation, which prohibits cation solvation.

The importance of solvation effects must also be considered in many other fields of macrocyclic polyether chemistry, such as template synthesis, liquid-liquid extraction, membrane equilibria etc.

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SAŽETAK

Ispitivanje vodljivosti ionskih parova kompleksa nekih makrocikličkih polietera s pikratima i tetrafenilboratima alkalnih metala u metanolu

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Ispitivana je vodljivost kompleksa polietera dibenzo-18-kruna-6 (DB18C6), bis(3,5-di-t-butilbenzo)-18-kruna-6 (dtbDB18C6) i dibenzo-24-kruna-8 (DB24C8) s natrijevim i kalijevim pikratom i tetrafenilboratom u metanolu kod 25°C. Vrijednosti za graničnu vodljivost λ_o i konstante disocijacije K_D, određene su po metodi Shedlovsky-og. Tetrafenilboratni kompleksi su neznatno jače disocirani od odgovarajućih pikratnih kompleksa, kao što su i kalijevi u odnosu na natrijeve komplekse. Dobiveni rezultati uspoređeni su s rezultatima dobivenim za vodljivost natrijevog i kalijevog pikrata odnosno tetrafenilborata u metanolu. Isti su razmatrani u svrhu ispitivanja interakcija između polietera i alkalnog kationa koje su kontrolirane odnosom njihove veličine, interakcija otapala i polieter-kation kompleksa, veličine i gustoće naboja aniona, te steričkih faktora uslijed prisutnosti prostranih t-butil supstituenata u poliesterskoj molekuli.