



Formation Constants of Complexes of Monovalent Cations with Benzocrown Ethers in Nitromethane

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Abstract. The complexation reactions between the macrocyclic polyethers dibenzo-18-crown-6, benzo-18-crown-6, benzo-15-crown-5 and polyethers bearing a stilbene unit with alkali metal and silver cations have been studied conductometrically in nitromethane. The formation constants of 1 : 1 and 1 : 2 (metal : ligand) complexes were determined and found to decrease with increasing cation diameter. The stability of the stilbene crown – metal cation complexes is lower than for complexes of other investigated crown ethers with analogous cations. There seem to be some effects of double bond-silver ion interactions.

Key words: formation constants, stilbene crown ethers, conductometric titration, alkali metal cations, silver cation, nitromethane.

1. Introduction

Since the first report given by Pedersen about the unique complexation properties of macrocyclic crown ethers there have been extensive studies in this research area [1]. The stability of the complex formed depends on many factors: the relative sizes of the metal ion and the crown ether cavity, the number of donor atoms in the crown ether, the flexibility of the ligand molecules and the solvation ability of a solvent. In the conductometric investigation of complex formation between alkali metal cations and crown ethers of 18-crown or 15-crown cavity size, the stoichiometry of the complexes was assumed to be 1 : 1 (cation : ligand) [2–5]. The formation of complexes with other stoichiometries is also taken into consideration but quantitative data concerning these types of complexes are very limited [6]. Two ligand molecules may be involved in complex formation if the crown ether is too small compared to the cation size, giving sandwich-type compounds [6–9]. Large crown ethers are able to complex two cations [10].

We have investigated the stilbene crown ethers in continuation of our previous work where we suggested that stilbene crown ethers were easy to synthesize and promised facile derivatization at the stilbene unit by epoxidation and dihydroxylation.

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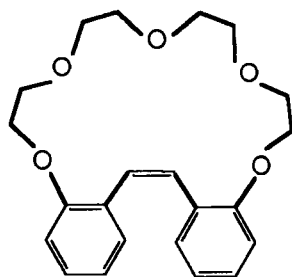
tion, including non-racemic chiral structures [11]. The crystal structures of the alkali metal cation complexes, displaying almost identical geometry of the stilbene ligand, from Li to Rb have been determined [12]. This finding provoked the determination of the complex formation constants of the stilbene crown ethers with alkali metal cations. Formation constants for complexes of related crown ethers ligands with alkali metal cations have been measured and included for comparison. All measurements have been done in nitromethane, which is weakly coordinating and a particularly suitable solvent for studying labile complexes. The usefulness of this solvent has been demonstrated in NMR studies of these complexes [12].

Many different methods can be used to investigate the trend in complexing power of crown ethers for metal ions [13]. In this work, we report conductometric studies of formation constants of crown ether – monovalent cation complexes. The conductometric method could be applied to the systems investigated due to the different mobility of the free cation and its complexes with crown ether.

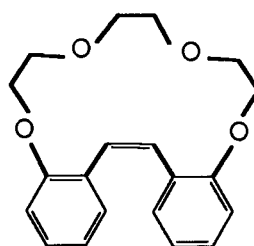
2. Experimental

2.1. MATERIAL AND INSTRUMENTATION

The crown ethers bearing stilbene units, *o, o'*- (tetraethyleneglycoldiyl)-(Z)-stilbene (Z- stilbene-5), and its analogue (Z-stilbene-4) were synthesized according to the methods described earlier [11]. The stilbene residues in both crown ethers were of *cis* conformation.



Z-stilbene-5



Z-stilbene-4

Dibenzo-18-crown-6 (DB18C6), benzo-18-crown-6 (B18C6) and benzo-15-crown-5 (B15C5) (all from Fluka) were used as received.

Lithium perchlorate was prepared from lithium hydroxide and perchloric acid, recrystallized four times from water and vacuum dried at 150 °C. Sodium perchlorate and potassium perchlorate (Merck) were of the highest commercial purity available and were used without further purification except for vacuum drying over P₂O₅. Rubidium iodide (Merck) and cesium iodide (Fluka) were used because of the low solubility of RbClO₄ and CsClO₄ in nitromethane. They were vacuum

dried before use. Nitromethane (Fluka, puriss >99%) was dried over molecular sieves and then further purified by fractional distillation. The solvent conductance was $0.15 \times 10^{-6} \text{ S cm}^{-1}$, water content <0.3%

A Philips PW-9527 conductivity meter was used together with a Philips PW-9550/60 measuring cell, (cell constant 0.84 cm^{-1}). An autoburette 665 Dosimat Metrohm was used for the addition of titrant solution. The titration vessel with the conductivity cell was kept at $298.15 \pm 0.05 \text{ K}$.

2.2. PROCEDURE

Salt solution ($1-5 \times 10^{-4} \text{ M}$) was placed in the thermostated titration vessel, and its conductance was measured. A known amount of the macrocycle solution was added stepwise using the autoburette. Titrant solutions ($1-5 \times 10^{-3} \text{ M}$) were prepared by dissolution of the crown ether in the salt solution of the same concentration as that present in the titration vessel at the start of the experiment in order to keep the ionic strength constant during the experiment. Addition of the ligand was continued until the desired ligand-to-cation mole ratio had been reached [14, 15]. The formation of 1 : 1 (M : L, cation : ligand) complexes is usually assumed in conductometric determination of formation constants. Under such conditions, when 1 : 1 and 1 : 2 complexes are formed simultaneously, the reactions describing complex formation are:



The stability constants are given by

$$K_1 = [\text{ML}^+]/[\text{M}^+][\text{L}] \quad (3)$$

$$K_2 = [\text{ML}_2^+]/[\text{ML}^+][\text{L}]. \quad (4)$$

The explicit equation expressing the total conductance as a function of the stability constants, molar conductivities, initial concentrations and degree of titration would be very complex. Therefore, for the evaluation of the formation constants from the conductometric data, a non-linear least squares curve-fitting program was developed. The original program, written in Turbo Pascal 6.0 by Chojnacki [16], is based on the Marquardt minimization method. Minimized sum \mathbf{U} was defined as a sum of squares of the differences in measured and calculated conductivities at the point of titration i :

$$\mathbf{U} = \sum_{i=1}^N (f_i^{\text{obs}} - f_i^{\text{calc}})^2, \quad (5)$$

where N is the number of experimental points in one titration

$$f_i^{\text{calc}} = 1000 \sum_{j=1}^M \Lambda_j c_{i,j}, \quad (6)$$

where f_i^{obs} is the measured conductivity, corrected for conductivity of the solvent; M is the number of conducting species in solution; and $c_{i,j}$ is the concentration of a conducting species j at point i of titration.

The sum \mathbf{U} depends on the set of stability constants assumed in the stoichiometry model (i.e. formation constants and ion-pairing constants) and on the values of equivalent conductivities Λ_j which were all regarded as adjustable parameters. The refinement of the parameters ($\log K$ and Λ_j) was continued until the sum of squares of the residuals \mathbf{U} was at a minimum.

Equilibrium concentrations $c_{i,j}$, of M^+ , ML^+ and ML_2^+ etc., were calculated at each point of the titration, based on temporary values of equilibrium constants and known balance concentrations. We utilized a multi-dimensional algorithm developed by Kostrowicki and Liwo [17] for multi-reaction systems that solves a set of non-linear equations

$$\mathbf{A} \ln \mathbf{C} = \ln \mathbf{K} \quad (7)$$

$$\mathbf{Q}\mathbf{C} = \mathbf{T} \quad (8)$$

where \mathbf{A} = the stoichiometric matrix; \mathbf{C} = the concentrations vector; \mathbf{K} = the equilibrium constants vector; \mathbf{Q} = the balance matrix; \mathbf{T} = the balance constants vector; and \ln = the natural logarithm.

The interested reader is referred to ref. [17] for details. This algorithm, modified by Chojnacki [18], has also been successfully used in extraction systems.

Some ion pair formation might occur during the experiment despite the high dielectric constant and low concentration of the salt [19, 20]. In this case the additional equilibrium equation ($M^+ + A^- = MA^0$) was introduced in the model used for calculation of formation constants. Addition of this equilibrium to the chemical model influences the equilibrium concentrations of the conducting species and in this way modifies the sum \mathbf{U} . The ion-pairing constant was not set to any arbitrary value but was freely adjusted by the program to fulfil the minimization condition.

3. Results and Discussion

The plots of molar conductance vs. crown ether/metal ion molar ratio for *Z*-stilbene-5 are shown in Figure 1. The curves for other systems investigated are similar (not shown). For all the investigated metal cations the plots show a decrease in the molar conductance with an increase in the crown ether concentration due to the lower mobility of the crown ether-cation complex in comparison to

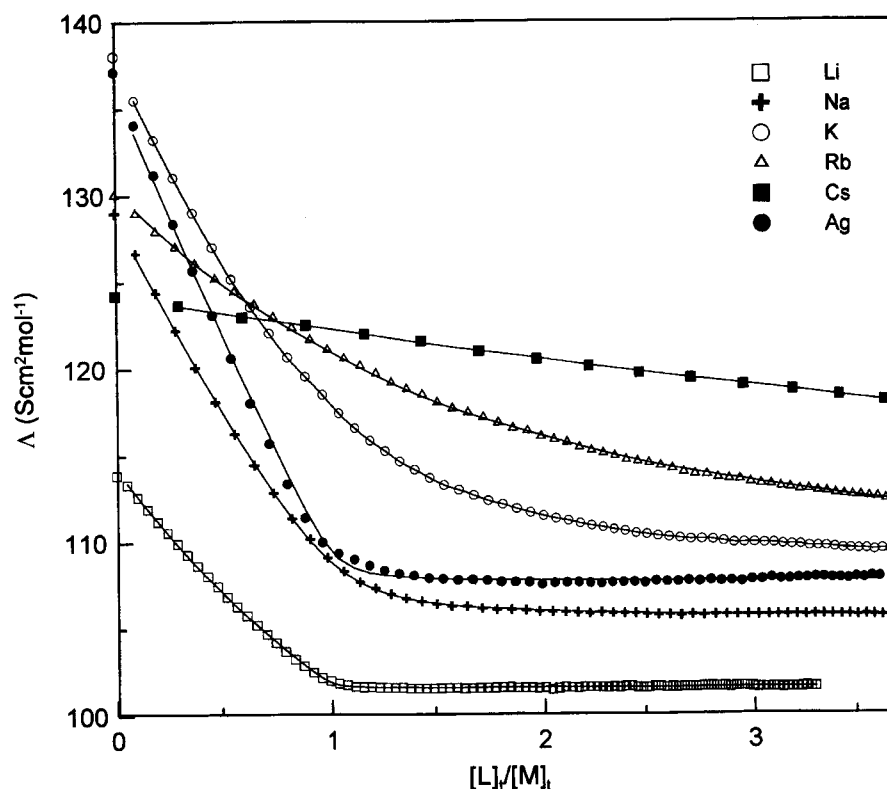


Figure 1. Molar conductance vs. $[L]_t/[M]_t$ curves for Z-stilbene-5 alkali metal salt systems in nitromethane at 298 K. Concentration of salts; LiClO_4 , 1.05×10^{-4} M; NaClO_4 , 5.08×10^{-4} M; KClO_4 , 3.16×10^{-4} M; RbI 3.15×10^{-4} M; CsI 1.03×10^{-4} M; AgClO_4 2.08×10^{-4} M. Solid lines represent the calculated curve.

the free cation. In the case of Li^+ , Na^+ and Ag^+ the slope of the titration curve changes sharply at a crown/cation mole ratio equal to one. The distinct breaking point indicates that the crown compounds form a stable 1 : 1 (M : L) complex with the cation. Some plots show a gradual decrease in molar conductance and no significant change is observed at a crown/cation mole ratio about one. This implies that weak 1 : 1 complexes are formed or both 1 : 1 and 1 : 2 (M : L) complexes are present in the solution. The selection of the best set of equilibria system was based on the residual sum of squares. The calculated values of the stability constants of the metal ion complexes with the investigated crown ethers are given in Table I.

Solvent properties are considered as the major factors influencing the formation constants of crown ether-cation complexes. The reason is that solvent and crown ether molecules compete in binding to metal cations. When the donor properties of the solvent are low, cations are poorly solvated and can easily be complexed by the crown ether. The solvation of crown ethers may also influence the formation constants of crown-cation complexes. Nitromethane is a peculiar solvent with a re-

Table I. Formation constants for polyether-cation complexes in nitromethane at 298.15 K

Cation	Z-stilbene-5		DB18C6		B18C6		Z-stilbene-4		B15C5	
	log K_1	log K_2	log K_1	log K_2	log K_1	log K_2	log K_1	log K_2	log K_1	log K_2
Li ⁺	6.0 ± 0.5		4.79 ± 0.1		4.24 ± 0.2 ^a		5.47 ± 0.02 ^a		5.60 ± 0.15 ^a	
Na ⁺	4.92 ± 0.02		6.7 ± 0.1		>6		3.83 ± 0.1		5.29 ± 0.05	
K ⁺	4.25 ± 0.02		5.39 ± 0.03		>6		(4.5) ^b	(3.2) ^b	4.46 ± 0.08	4.2 ± 0.1
Rb ⁺	3.49 ± 0.02		4.5 ± 0.04		5.25 ± 0.1		–	–	3.43 ± 0.05	(1.1) ^b
Cs ⁺	2.70 ± 0.02	2.1 ± 0.1	3.2 ± 0.1	3.2 ± 0.1	3.91 ± 0.01		–	–	3.00 ± 0.2	3.29 ± 0.2
Ag ⁺	6.04 ± 0.08		6.22 ± 0.1		4.89 ± 0.1	3.69 ± 0.1	4.5 ± 0.06	3.69 ± 0.05	4.67 ± 0.04	4.20 ± 0.04

^aAssumed stoichiometry taken into the calculations did not give a good fit.

^bValues in brackets are less certain, should be confirmed by other methods.

Each titration was repeated at least three times for all systems. Errors refer to the mean value.

lative permittivity, $\epsilon = 35.9$ (at 25 °C) and a very low Gutmann donor number (DN = 2.7) [21]. The important consequence of the properties of nitromethane is that the solvent competes poorly for position in the first coordination sphere of a metal cation due to its weak coordinating properties. This gives fairly high formation constants of the investigated complexes in the solvent. This effect should be taken into consideration in comparison of the formation constants of the investigated crown ethers with alkali metal cations in solvents of higher donor number (such as methanol or acetonitrile). The formation constants of B15C5 or DB18C6 crown ethers with alkali metal cations in methanol or acetonitrile are substantially lower [4, 22].

The cavity size–cation diameter ratio can influence the stability of the resulting alkali and silver complexes of a crown ether. The crown ether (*Z*-stilbene-5), possessing five oxygen atoms in a macrocyclic ring, appears like an ‘amputated’ 18C6, with —CH=CH— replacing a —(CH₂)₂—O—(CH₂)₂— residue, its cavity size is similar to 18C6 ether. The —CH=CH— double bond is directed towards the center of the crown but is well outside the mean plane of the oxygen atoms. The complexes of *Z*-stilbene-5 with alkali metal and silver cations formed in nitromethane solution have 1 : 1 stoichiometry except for cesium, which gives 1 : 2 sandwich-type complexes. The same complex stoichiometry for those complexes was found in the solid state by X-ray studies [12]. As can be seen in Table I, the formation constants of *Z*-stilbene-5 complexes are lower than the formation constants of DB18C6 or B18C6 complexes with alkali metal cations. The number of oxygen donor atoms in *Z*-stilbene-5 is lower and the ethylene residue double bond probably does not take part in cation bonding. This might be due to unfavorable interactions between the ‘hard’ alkali cations and the ‘soft’ π electron pair of the double bond. The stability constants decrease with increasing cation size: Li, Ag > Na > K > Rb > Cs. Unexpectedly the stability constant for the lithium *Z*-stilbene-5 complex is very high although the lithium cation is too small to fit the cavity of the ligand. Crystallographic data show that only three oxygen atoms coordinate Li⁺ – those opposite the double bond of the ethylene residue [12]. This arrangement differs from the one present in complexes with Na⁺ and larger cations which involve all five oxygen atoms for coordination. K⁺ and Rb⁺ occupy almost the center of the hole in their complexes. The situation is different in the case of the silver(I) *Z*-stilbene-5 complex where Ag⁺ can interact with the π bond of the stilbene unit. Such interactions were found in the solid state [23]. This could be an important additional factor responsible for the high formation constant of the silver complex.

The *Z*-stilbene-5 crown ether bearing two benzo groups is similar to DB18C6 but the formation constants for the DB18C6 alkali cation complexes are higher due to the presence of six donor sites in the macrocycle ring. Another 18-membered ligand, B18C6, with only one benzo group in the macrocycle, has also been investigated. The stabilities of the complexes of these two crown ethers with the same alkali metal ions decrease with an increasing number of benzo groups in the

macroring. The presence of the benzo group reduces the flexibility of the macrocyclic molecule and reduces the possibility of wrapping the crown ether around the cation in the complex. The greater flexibility of the ligand ring in B18C6 may also influence the stability of the complexes. The substituents, which decrease the basicity of the crown's donating oxygen atoms, are expected to reduce the complexing ability of the macrocyclic ring. This prediction is based on the electron withdrawing effect of the benzo groups that weakens the electron-donor properties of the oxygen atoms.

The relatively high charge density of Na^+ and the good ionic diameter – macrocyclic cavity size relationship can explain the high values of stability constants for complexes of all the above ligand with this cation.

The formation constants of smaller ligands complexes, B15C5 and *Z*-stilbene-4, with alkali cations and silver are lower than for complexes formed with the 18C6 cavity size ligands. The reason could be the lower number of donating oxygen atoms. It is known [9] that potassium ion has a tendency to form sandwich-type complexes. Complexes of such a type have been reported in the literature for different alkali metal cations with crown ethers of 15C5 or 18C6 cavity size [1, 7, 24]. Formation constants of 1 : 1- and 1 : 2-type complexes have been considered in our calculation. The differences between the calculated and measured values of molar conductance depended on the model of stoichiometry assumed. The value of residual variance was the criterion for selecting among various assumed equilibrium models.

A limited set of data on formation constants for crown ether–cation complexes in nitromethane is available in the literature. Shamsipur has measured $\log K$ for complexes of larger crown ethers with metal ions [25, 26]. The formation constants of Li^+ complexes with B15C5 and DB18C6 in nitromethane have been determined by ^7Li NMR yielding $\log K > 5$ and 4.1 ± 0.3 , respectively [27]. It seems to be in a good agreement with our data.

The complexation of the lithium ion requires that one takes ion pair association into consideration. Ion pairing of lithium salts is usually neglected in conductometric measurements of formation constants since a very low (10^{-4} M) concentration of salt is used [25, 26]. To obtain better fitting, in the cases of Li^+ complexation, an additional equilibrium describing ion pair association has been included in our calculations. This improved the fit to the points obtained in the titration of lithium cation with *Z*-stilbene-5 or DB18C6 ligands. For both systems the slopes of the corresponding molar conductance/mole ratio plots change sharply at the point where the ligand/cation mole ratio equals one, indicating formation of a 1 : 1 complex of the ligand and the lithium ion. Two equilibria were taken into consideration in the calculation: formation of a 1 : 1 complex (ML^+) and association of the lithium cation with the anion (MA^0). This gave satisfactory fitting to the measured conductivity (using two equilibria gave a statistically relevant decrease of the residues in comparison with the model using only complexation). The addition of

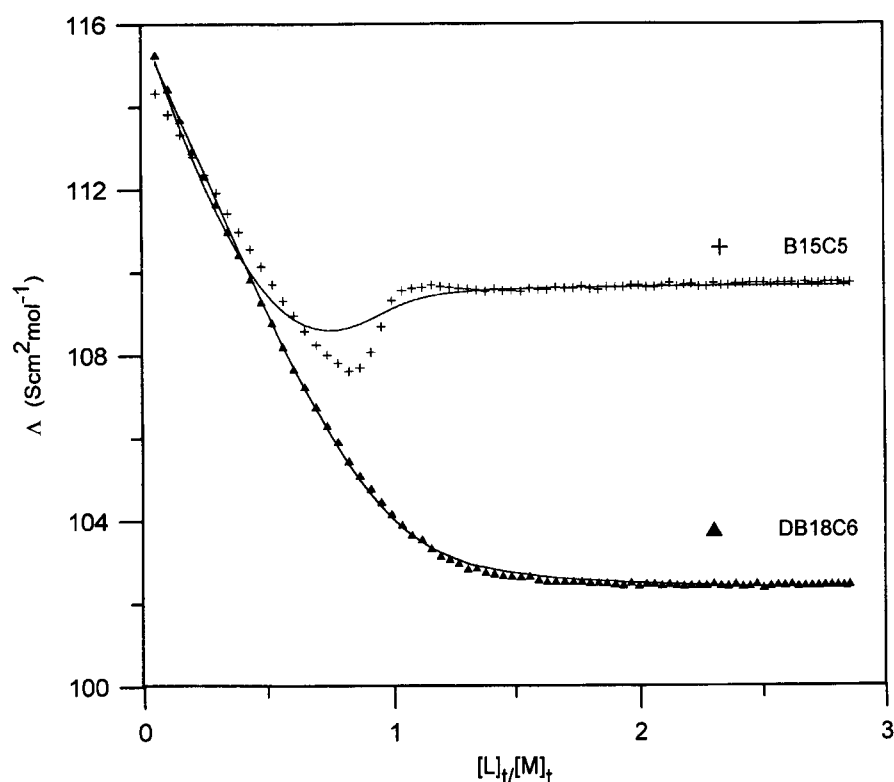


Figure 2. Molar conductance vs. $[L]_t/[M]_t$ curves for crown ether – lithium perchlorate systems in nitromethane at 298 K. Concentration of LiClO_4 : 5.05×10^{-4} M titrated with DB18C6 and 5.07×10^{-4} M titrated with B15C5. Solid lines represent the calculated curves.

the ion-pairing equilibrium did not give a statistically relevant decrease in residuals in the cases of the other metal salts.

The conductometric titration curves obtained for the complexation of B15C5, B18C6 and Z-stilbene-4 ligands with LiClO_4 in nitromethane have a non-typical shape. The titration curve for B15C5 and the 'typical' titration curve for DB18C6, for comparison, are shown in Figure 2. The titrations in these systems have been repeated several times at different concentrations to exclude any random errors, consistently giving similar results. The molar conductance decreases with increasing ligand/metal ratio and reaches a minimum before the ligand/metal ratio equals one. The conductance then increases rapidly and reaches the value, which remains constant at a ligand/metal ratio about one. In order to obtain a better theoretical curve of the molar conductivity, other possible equilibria have been considered. The formation of a 2:1 complex (metal:ligand) has been reported for small cations [10]. Unfortunately, consideration of this species in our calculation has not improved the description of the system. The best fit was obtained upon assumption of 1:1 stoichiometry of the formed complex and association of Li^+ with ClO_4^- .

Amini and Shamsipur [26] have also noticed a different shape of the conductometric titration curve for LiCl titrated with DB30C10. They considered formation of 1 : 2 complexes (ligand : metal) or ion-pair formation in nitromethane solution but did not take it into the calculation.

At present, we have no explanation of the strange behavior of the lithium ion within models including formation of ML, ML₂, M₂L and MA. More extensive studies are needed to clarify this point.

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