

A thermodynamic study of interaction of Na⁺ cation with benzo-15-crown-5 in binary mixed non-aqueous solvents

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Abstract The complexation reaction between benzo-15-crown-5 (B15C5) with Na⁺ cation was studied in acetonitrile–methanol (AN–MeOH), tetrahydrofuran–methanol (THF–MeOH), acetonitrile–tetrahydrofuran (AN–THF) and nitromethane–dimethylformamide (NM–DMF) binary mixtures at different temperatures using conductometry method. The conductometric data show that in most cases, the stoichiometry of the complex formed between B15C5 and Na⁺ cation is 1:1 (ML), but in the cases of AN–THF (mol%THF = 65.7) binary mixture and in pure THF, a 1:2 (ML₂) complex is formed in solutions, which shows that the stoichiometry of the complexes may change by the nature of the medium. The stability constant of the resulting 1:1 complex in pure non-aqueous solvents decreases in the order: AN > MeOH > DMF. The thermodynamic parameters (ΔH°_c and ΔS°_c) for formation of (B15C5.Na)⁺ complex were obtained from temperature dependence of the stability constant using the van't Hoff plots. The results show that in most cases, the complex is both enthalpy and entropy stabilized. A non-linear behavior was observed for changes of log K_f of (B15C5.Na)⁺ complex versus the composition of the binary mixed solvents, which was explained on the basis of changes occurring in the structure of the mixed solvents and also the preferential solvation of the cation, ligand and the resulting complex in solutions.

Keywords Benzo-15-crown-5 · Na⁺ · Acetonitrile–methanol · Tetrahydrofuran–methanol · Acetonitrile–tetrahydrofuran · Nitromethane–dimethylformamide · Conductometry

Introduction

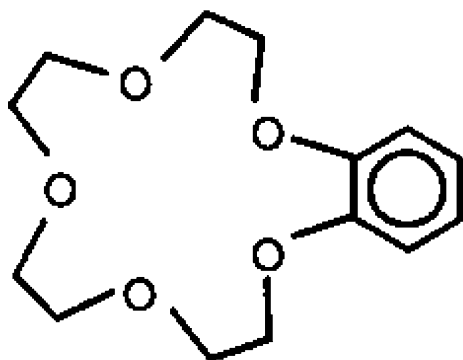
With the discovery of crown ethers [1], the focus on complexation through covalent interactions shifted to that of non-covalent interactions. These macrocyclic compounds are capable of forming complexes with alkali and alkaline earth metal ions via electrostatic attraction and encapsulation into the macrocyclic cavity [2, 3]. The macrocyclic compounds, by accepting the metal ions in a more or less 'lock and key' fashion, mimic in a relatively uncomplicated way the very complicated functions of biological materials such as enzymes. It is this mimicry that excites the scientists, therefore, these compounds can be used as models for ion transport through membranes in biological systems [4].

The study of various macrocyclic compounds in different solvents or solvent mixtures may indicate new approaches for developing pharmaceutical systems or a way to cross the blood organ barrier. Various physico-chemical techniques such as spectrophotometry [5], polarography [6], NMR spectrometry [7], calorimetry [8], potentiometry [9], and conductometry [10–16] have been used to study the complex formation between macrocyclic polyethers (crown ethers) and various metal ions in solutions. Among these various methods, the conductometric technique is a sensitive and inexpensive method with a simple experimental arrangement for such investigations.

The widespread use of non-aqueous solvents began in 1950s in various field of pure and applied chemistry and

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Scheme 1 Benzo-15-crown-5

has contributed greatly to later advances in chemical sciences and technologies [17]. Numerous data have been published on equilibrium constants and thermodynamic functions of complex formation of crown ethers with metal cations and small organic molecules in pure organic solvents [18, 19]. The very small number of such data concerning the complex formation in mixed non-aqueous solvents [20, 21] was the reason for undertaking this kind of studies in our laboratory. The nature and composition of the solvent system has been found to strongly influence the stoichiometry, selectivity, thermodynamic stability and exchange kinetics of metal ion–crown ether complexes [22]. Although the complexation process between large macrocyclic crown ethers and metal cations has been extensively studied in solutions, but the complexation of metal cations by small crown ethers such as benzo-15-crown-5 has been studied to a very limited extent especially in non-aqueous solvents and their binary solutions.

With the aim of studying the influence solvent properties on the interaction of metal ions with crown ethers, in this article we report the results of thermodynamic study for complexation reaction between B15C5 (Scheme 1) with Na^+ cation in acetonitrile–methanol (AN–MeOH), tetrahydrofuran–methanol (THF–MeOH), acetonitrile–tetrahydrofuran (AN–THF) and nitromethane–dimethylformamide (NM–DMF) binary mixtures at different temperatures using conductometric method.

Experimental

B15C5 (Fluka) and sodium perchlorate (Merck) were used without further purification. The solvents: acetonitrile, methanol, tetrahydrofuran, nitromethane and dimethylformamide all from Merck were used with the highest purity. The experimental procedure to obtain the formation constant of $(\text{B15C5.Na})^+$ complex was as follows: a solution of metal salt (5.0×10^{-4} M) was placed in a titration cell and the conductance of the solution was

measured, then the crown ether concentration was increased by adding crown ether solution in the same solvent (2.5×10^{-2} M) to the titration cell, using a microburette and the conductance of the resulted solution was measured after each step at the desired temperature. The conductance measurements were performed on a digital Metrohm conductivity apparatus (model 712) in a thermostated water-bath with a constant temperature maintained within ± 0.01 °C. The electrolytic conductance was measured using a cell consisting of two platinum electrodes to which an alternating potential was applied. A conductometric cell with a cell constant of 0.75 cm^{-1} was used throughout the studies.

Results

The changes of molar conductance (Λ_m) versus the ligand to metal cation mole ratio $[\text{L}]_t/[\text{M}]_t$, for the complexation of B15C5 with Na^+ cation in AN–MeOH, THF–MeOH, AN–THF, and NM–DMF binary systems were studied at different temperatures. $[\text{L}]_t$ is the total concentration of the ligand and $[\text{M}]_t$ is the total concentration of the metal cation. Three typical series of molar conductance values as

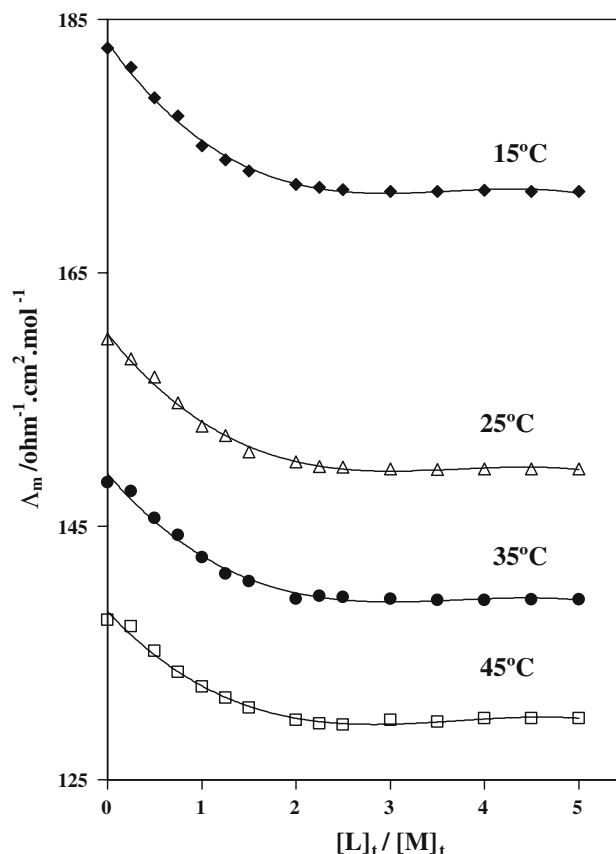


Fig. 1 Molar conductance–mole ratio plots for $(\text{B15C5.Na})^+$ complex in pure AN at different temperatures

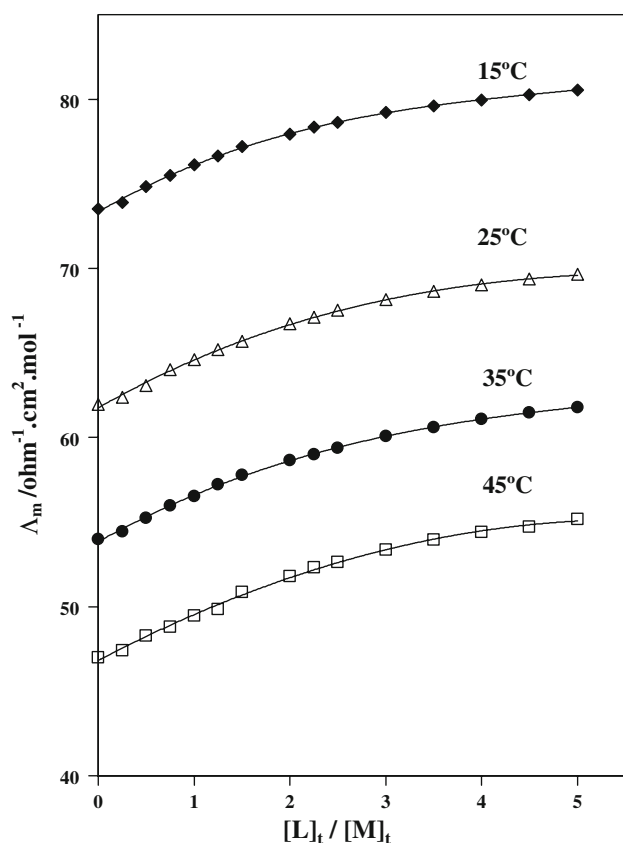


Fig. 2 Molar conductance–mole ratio plots for $(\text{B15C5.Na})^+$ complex in THF–MeOH (mol%THF = 59.9) binary system at different temperatures

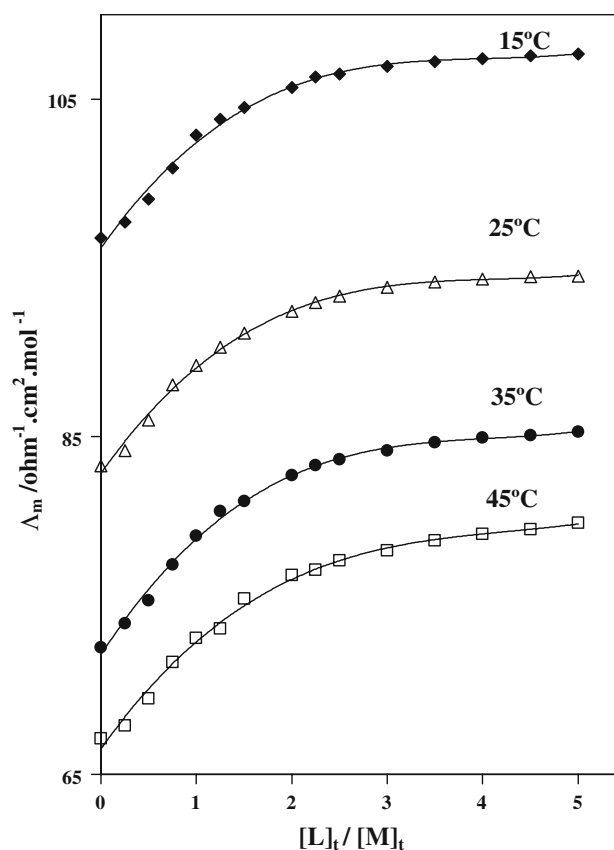


Fig. 3 Molar conductance–mole ratio plots for $(\text{B15C5.Na})^+$ complex in AN–THF (mol%THF = 65.7) at different temperatures

a function of $[\text{L}]_t/[\text{M}]_t$ in pure AN, THF–MeOH (mol%THF = 59.9), and in AN–THF (mol%THF = 65.7) binary solution are shown in Figs. 1, 2 and 3, respectively. The stability constant of the complex at each temperature was obtained from variation of molar conductance as a function of $[\text{L}]_t/[\text{M}]_t$ molar ratio plots using a GENPLOT computer program [23]. The details of calculation of the stability constants of complexes by conductometric method have been described in reference [24]. The values of the stability constant ($\log K_f$) for the $(\text{B15C5.Na})^+$ complex in various solvent systems are listed in Table 1. Plots of $\ln K_f$ versus $1/T$ in all cases were linear and a typical example of these plots is shown in Fig. 4. The changes in the standard enthalpy (ΔH°_c) for complexation reaction were determined in the usual manner from the slope of the van't Hoff plots assuming that ΔC_p is equal to zero over the entire temperature range investigated. The changes in standard entropy (ΔS°_c) were calculated from the relationship $\Delta G^\circ_{c,298.15} = \Delta H^\circ_c - 298.15\Delta S^\circ_c$. The results are summarized in Table 2. The changes of $\log K_f$ of $(\text{B15C5.Na})^+$ complex versus the mole fraction of acetonitrile in AN–MeOH binary system at different temperatures are shown in Fig. 5.

Discussion

As is seen from Fig. 1, addition of B15C5 to Na^+ cation in pure AN at different temperatures shows a decrease in molar conductivity with an increase in the ligand concentration, which indicates that the $(\text{B15C5.Na})^+$ complex in this solution is less mobile than free solvated Na^+ cation. Similar behavior was observed in most solvent systems, but in the cases of THF–MeOH (mol%THF = 59.9), AN–THF (mol%THF = 65.7) binary mixture and in pure THF, addition of B15C5 to Na^+ cation in these solutions at different temperatures results in an increase in molar conductivity with an increase in the ligand concentration which shows that the complex formed between B15C5 and sodium cation is more mobile than free solvated Na^+ cation in these solutions (see Figs. 2 and 3).

The slope of corresponding molar conductivity versus $[\text{L}]_t/[\text{M}]_t$ plots changes sharply at the point where the ligand to cation mole ratio is about 1, which is an evidence for formation of a relatively stable 1:1 complex between Na^+ cation and B15C5 in most solutions, but as evident from Fig. 3, in AN–THF (mol%THF = 65.7) binary system, the slope of molar conductance mole ratio plots

Table 1 Log K_f values of (B15C5.Na)⁺ complex in AN–MeOH, THF–MeOH, AN–THF and NM–DMF binary mixtures at different temperatures

Medium	Log $k_f \pm SD^a$			
	15 °C	25 °C	35 °C	45 °C
AN–MeOH				
Pure AN	4.01 ± 0.10	3.97 ± 0.10	3.98 ± 0.12	4.11 ± 0.16
70.0% AN–30.0% MeOH ^b	3.23 ± 0.06	3.14 ± 0.05	3.11 ± 0.04	2.95 ± 0.06
43.8% AN–56.2% MeOH	2.93 ± 0.06	2.90 ± 0.03	2.90 ± 0.03	3.04 ± 0.06
20.6% AN–79.4% MeOH	2.84 ± 0.06	2.84 ± 0.06	2.78 ± 0.04	2.80 ± 0.09
Pure MeOH	3.13 ± 0.07	2.86 ± 0.04	2.94 ± 0.03	2.82 ± 0.03
THF–MeOH				
Pure THF	e	e	e	e
59.9% THF–40.1% MeOH ^b	2.99 ± 0.04	2.91 ± 0.05	2.84 ± 0.03	2.78 ± 0.07
33.2% THF–66.8% MeOH	2.83 ± 0.08	2.61 ± 0.07	2.79 ± 0.05	2.40 ± 0.11
14.2% THF–85.8% MeOH	2.08 ± 0.17	2.78 ± 0.09	2.79 ± 0.06	d
Pure MeOH	3.13 ± 0.07	2.86 ± 0.04	2.94 ± 0.03	2.82 ± 0.03
AN–THF				
Pure AN	4.01 ± 0.10	3.97 ± 0.10	3.98 ± 0.12	4.11 ± 0.16
82.4% AN–17.6% THF ^b	4.35 ± 0.06	4.08 ± 0.08	4.09 ± 0.12	3.80 ± 0.06
61.0% AN–39.0% THF	3.18 ± 0.32	3.28 ± 0.20	3.80 ± 0.26	3.47 ± 0.27
34.3% AN–65.7% THF	e	e	e	e
Pure THF	e	e	e	e
NM–DMF				
Pure NM	c	c	c	c
96.4% NM–3.6% DMF ^b	3.95 ± 0.15	3.94 ± 0.12	3.67 ± 0.16	4.10 ± 0.13
80.9% NM–19.1% DMF	3.12 ± 0.20	3.26 ± 0.23	d	d
58.5% NM–41.5% DMF	2.53 ± 0.17	2.68 ± 0.14	2.25 ± 0.16	2.68 ± 0.12
32.0% NM–68.0% DMF	d	d	d	3.10 ± 0.13
Pure DMF	2.87 ± 0.27	2.12 ± 0.20	3.80 ± 0.10	2.90 ± 0.16

^a SD = standard deviation

^b Composition of binary mixtures is expressed in mol% for each solvent system

^c The salt is not dissolved

^d With high uncertainty

^e The data can not be fitted in equation

changes at the point where $[L]_t/[M]_t$ is about 2, which indicates the formation of a 1:2 (ML_2) complex between Na^+ cation and B15C5 in this solution. Similar behavior was observed in the case of pure THF. The results obtained in this investigation show that the stoichiometry of the crown ether–metal cation complexes may be changed by the nature of the solvent systems.

As is obvious from Table 1, the stability constant of (B15C5.Na)⁺ complex in pure non-aqueous solvents decreases in the order: AN > MeOH > DMF which is consistent with the inverse order of their solvating abilities as expressed by the Gutmann donor number. Solvent properties are considered as the major factors influencing the formation constants of crown ether–cation complexes. The reason is that the solvent and crown ether molecules compete in binding to metal cation. When the donor

properties of the solvent are low, the cation is poorly solvated and can easily be complexed by the crown ether molecule. The solvation of the crown ether may also influence the formation constant of crown–cation complex in solution. In a strong solvating solvent such as dimethylformamide with a relatively high Gutmann Donor Number (DN = 26.6), the solvation of the metal cation and possibly of the ligand should be stronger than that of solvents of lower solvating abilities such as acetonitrile (DN = 14.1) and methanol (DN = 20.0), thus, the formation of the (B15C5.Na)⁺ complex is weakened in dimethylformamide compared with the other two organic solvents. Therefore, as is expected, the stability of (B15C5.Na)⁺ complex varies inversely with the Gutmann donor numbers of these pure organic solvents. Although DMF and AN have comparable dielectric constants

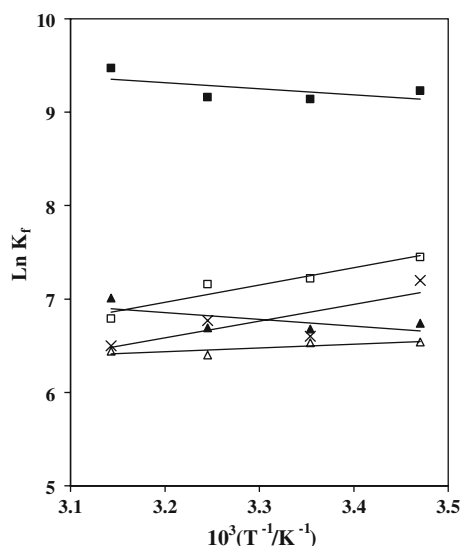


Fig. 4 van't Hoff plots for (B15C5.Na)⁺ complex in AN–MeOH binary systems: (mol%AN: is ■ 100, □ 70.0, ▲ 43.8, △ 20.6, × 0.0)

($\epsilon_{\text{DMF}} = 36.7$, $\epsilon_{\text{AN}} = 37.5$), but the formation constant of the complex in AN is much higher than in DMF. This indicates that the dielectric constant of the solvent is not a dominant factor for complexation reaction in these organic solvents.

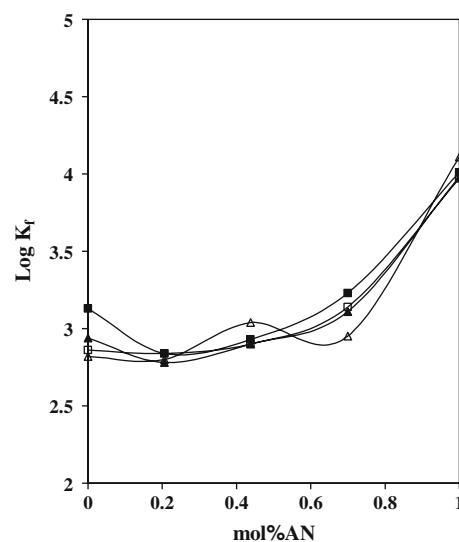


Fig. 5 Changes of the stability constant ($\log K_f$) of (B15C5.Na)⁺ complex with the composition of AN–MeOH binary systems at different temperatures: (■ 15 °C, □ 25 °C, ▲ 35 °C, △ 45 °C)

The stability constant of (B15C5.Na)⁺ complex in AN–MeOH binary mixed solvents is higher than in THF–MeOH binary solutions (Table 1). This behavior can be interpreted by considering the inherent relative solvating

Table 2 Thermodynamic parameters for (B15C5.Na)⁺ complex in AN–MeOH, THF–MeOH, AN–THF and NM–DMF binary mixtures

Medium	$-\Delta G_c^\circ \pm SD^a$ kJ/mol	$\Delta H_c^\circ \pm SD^a$ kJ/mol	$\Delta S_c^\circ \pm SD^a$ J/mol k
AN–MeOH			
Pure AN	22.7 ± 0.6	c	99.2 ± 16.7
70.0% AN–30.0% MeOH ^b	17.9 ± 0.3	-15.5 ± 3.3	c
43.8% AN–56.2% MeOH	16.6 ± 0.2	c	81.0 ± 14.9
20.6% AN–79.4% MeOH	16.2 ± 0.3	-2.7 ± 0.7	45.4 ± 2.2
Pure MeOH	16.4 ± 0.2	-17.5 ± 1.4	c
THF–MeOH			
59.9% THF–40.1% MeOH ^b	16.6 ± 0.3	-12.5 ± 0.2	13.7 ± 0.4
33.2% THF–66.8% MeOH	14.9 ± 0.4	-24.7 ± 4.4	-32.8 ± 14.7
14.2% THF–85.8% MeOH	15.9 ± 0.5	35.1 ± 7.2	c
Pure MeOH	16.4 ± 0.2	-17.5 ± 1.4	c
AN–THF			
Pure AN	22.7 ± 0.6	c	99.2 ± 16.7
82.4% AN–17.6% THF ^b	23.3 ± 0.4	-30.9 ± 4.7	-25.7 ± 15.8
61.0% AN–39.0% THF	18.7 ± 1.1	16.8 ± 0.1	119.2 ± 3.8
NM–DMF			
96.4% NM–3.6% DMF ^b	22.5 ± 0.7	c	107.5 ± 12.7
80.9% NM–19.1% DMF	18.6 ± 1.3	c	c
58.5% NM–41.5% DMF	15.3 ± 0.8	c	76.7 ± 21.7
Pure DMF	12.0 ± 1.2	c	c

^a SD = standard deviation

^b Composition of binary mixtures is expressed in mol% for each solvent system

^c With high uncertainty

ability of the pure solvents which form the mixture. Since the donor ability of acetonitrile molecules ($DN = 14.1$) is lower than tetrahydrofuran molecules ($DN = 20.0$), therefore, the $(B15C5.Na)^+$ complex is more stable in AN–MeOH binary solutions compared with THF–MeOH binary mixed solvents. It is known that the solvating ability of the solvent, as expressed by the Gutmann donor number [25], plays an important role in different complexation reactions [26]. However, as is obvious in Table 1, the stability constant ($\log K_f$) of this complex in AN–MeOH binary mixed solutions is lower than in AN–THF binary mixed solvents. This result seems to be unexpected if we only consider the donicity of the solvents. It should be noted that, while MeOH and THF have the same donor numbers ($DN = 20.0$ for MeOH and THF), they possess quite different dielectric constants ($\epsilon_{MeOH} = 32.6$, $\epsilon_{THF} = 7.3$). The high dielectric constant of MeOH with respect to THF, can exert a decrease in the electrostatic interactions between the ligand and the cation and, therefore, the complex formation between B15C5 and Na^+ cation is weakened in AN–MeOH binary solutions compared to AN–THF binary systems.

As is seen from Fig. 5, the change of the stability constant ($\log K_f$) of $(B15C5.Na)^+$ complex with the composition of AN–MeOH binary system is not linear. A non-linear behavior was also observed in all other binary solutions. This behavior may be related to changes occurring in the structure of the solvent mixtures and, therefore, changing in the solvation properties of the cyclic polyether, cation and even the resulting complex in these solvent mixtures. Some structural changes probably occur in the structure of the solvents when they mix with one another. These structural changes may result in changing the interactions of those solvents with the solutes. It has been shown that there is an interaction between acetonitrile and methanol molecules ($K_{ass} = 1.23$) via hydrogen bonding in their binary mixtures [27].

In addition, the preferential solvation of the cation, anion and ligand and the characteristics of its changes with the composition of the mixed solvents and temperature may be effective in this complexation process. Preferential solvation of ions by one of the components of a mixed solvent system depends on two factors: the relative donor–acceptor abilities of the component molecules towards the ion and the interactions between solvent molecules themselves. The solvating properties of the components in mixed solvents can even be significantly modified by solvent–solvent interactions when the energy of the latter is comparable with the energy difference of solvent–ion interactions for both components [28].

The thermodynamic data given in Table 2 reveal that, in most cases, the $(B15C5.Na)^+$ complex is both enthalpy and entropy stabilized, therefore, both of these thermodynamic

quantities are the driving force for formation this complex in these solutions.

Since during the complexation of the cation by a macrocyclic ligand, most of the coordinated solvent molecules are replaced by the donor atoms of the ligand, even when the cation–macrocycle binding is weak, the increased degree of freedom, because of the desolvation of cation, may result in some positive entropic gain. In the cases where the macrocycle has also some interaction with solvent molecules [18], the release of some solvent molecules involved in interaction with the ligand, may also contribute to the positive entropy values [29]. It should be mentioned, however, that the complexation process involves not only a change in solvation of the cation, and also that of the ligand and the change in the flexibility of the ligand upon complexation, in addition, the solvent–solvent interactions contribute to changes in entropy [30].

The changes of the enthalpy of the ligand by complexation are mainly due to the changes of solvation, intermolecular ligand–ligand repulsion, the stacking of the aromatic residues and steric deformation of the ligand induced by the bound metal ion [31].

Table 2 shows that, as expected, the thermodynamic data (ΔH_c° , ΔS_c°) vary significantly with the nature and composition of the mixed solvents [26, 29, 32, 33]. This is due to variations in the extent of the contribution of such important parameters as solvation–desolvation of the species involved in the complexation reaction (i.e., Na^+ cation, macrocycle and the resulting complex), and also the conformational changes of the macrocyclic ligand upon complexation in the binary solutions. Even though many factors contribute to changes in enthalpy and entropy of complexation reactions, it seems that solvent properties such as donor number, dielectric constant and the isosolvation point can be used to explain the unusual changes of enthalpy and entropy as a function of solvent composition [34].

The experimental values of ΔH_c° and ΔS_c° (Table 2) show that, the values of standard enthalpy (ΔH_c°) and standard entropy (ΔS_c°) for complexation reaction between B15C5 and Na^+ cation in these solutions, do not vary monotonically with the solvent composition. A non-monotonic behavior has also been observed for thermodynamic functions of several crown ether–metal ion complex formation in some binary mixed solvents [12–16, 35, 36].

This behavior may be due to strong interactions between the constituent solvent molecules which result in changing in some of the chemical and physical properties of each of the solvents, and therefore, changing their solvating ability towards the dissolved species. In addition, the heteroselective solvation of the cation and even the macrocyclic ligand and the character of its changes with the

composition of the mixed solvent and temperature may be effective in the complexation reactions [37].

The solvation of crown ethers is of great importance during the complexation process of macrocyclic ligands with the metal cations and the relative enthalpy and entropy changes can be better understood if the ligand solvation is taken into consideration. Information on the interaction of macrocyclic ligands with the solvent molecule is sparse, and additional studies on the ligand–solvent interaction are necessary to investigate of the thermodynamic behavior of macrocyclic complexes in solution.

The analysis of solvation enthalpy of some crown ethers in several mixed solvents has been studied by Jazwiak [38]. A non-linear behavior has been observed between the solvation enthalpy of some crown ethers and the composition of binary solutions. The observed behavior has been discussed in terms of preferential solvation of the crown ether molecules which in turn depends quantitatively on the structural and energetic properties of the mixed solvent system. Since there are many factors, which contribute to changes of enthalpy and entropy of complexation reactions, therefore, we should not expect a monotonic relationship between these thermodynamic quantities and the solvent composition of these mixed solvents.

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