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ORIGINAL PAPER

A combined experimental and density functional theory study on the complexation ability of 15-crown-5 with Li^+, Na^+, K^+, and NH_4^+ cations

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Abstract The complexation processes among Li^+, Na^+, K^+, and NH_4^+ cations with the macrocyclic ligand, 15-crown-5 (15C5) have been studied in acetonitrile–methanol binary mixtures at different temperatures using conductometric method. The stability constants of the resulting 1:1 complexes were calculated from the computer fitting of the molar conductance–mole ratio data at various temperatures. The values of thermodynamic parameters (ΔH_c° and ΔS_c°) for the formation of the complexes were obtained from temperature dependence of the stability constants of complexes using van't Hoff plots. In addition, a theoretical study has been carried out using density functional theory to obtain the stability of the complexes and the geometrical structure of the 15C5 and its complexes with Li^+, Na^+, K^+ and NH_4^+ cations in the gas phase. We compared the experimental data with those obtained by quantum chemistry calculations to investigate the effect of the solvent on complexation process.

Keywords Complexation process · Conductometry · DFT study · Liquid phase · Gas phase

Introduction

Since Pedersen's [1] discovery of crown ethers and their abilities to bind strongly with the metal ions in 1967, the study of these macrocyclic ligands has grown with an incredible rate. The synthesis of many different types of crown ethers (e.g., crown ether diesters, azacrown ethers, thiacrown ethers, and chiral crown ethers) has been documented in the literature and their binding properties such as binding selectivity and strength toward a wide range of metal ions, non-metal ions and also neutral molecules have been investigated [2–4]. The complexes of crown ethers with various metal cations have generally 1:1 stoichiometry, but in some cases, where the metal ions are too large to lay in the hole of the monotopic crown ether ring, 1:2 complexes with a sandwich structure are formed in solutions [5].

Although the complexation of crown ethers with metal ions has been studied in both aqueous and in some non-aqueous media, most of these investigations have been carried out in pure solvents [6, 7] and the data about the stability constants and also the thermodynamic parameters of metal ion complexes with crown ethers especially with small crown ethers such as 15-crown-5 (15C5) in mixed non-aqueous solvents are very sparse [8, 9]. Non-aqueous solvents are often mixed with water or other organic solvents to obtain desirable solvent properties. The effect of mixed solvent properties on the formation of crown ether–metal ion complexes is of interest due to the fact that the solvation capacities of crown ether molecules, metal ions and even the resulting complexes change with the changing composition of the mixed solvents. As a consequence, the thermodynamics, kinetics and even the stoichiometry of the complexation reactions and also the selectivity of the ligands for the metal cations may change with the composition of the mixed solvents.

Among the various physicochemical methods [10–15] which have been used to study the complex formation between crown ethers and metal ions in solutions, the conductometry is a very useful method for determining the stoichiometry, stability, selectivity and also the

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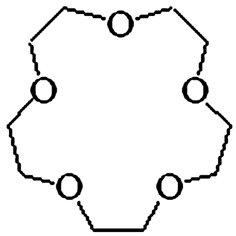

Scheme 1 Structure of 15-crown-5 (15C5)

thermodynamic parameters of the crown ether complexes with various cations in non-aqueous media [16–18].

Theoretical calculations have become a powerful tool for investigating the complexation process. To the best of our knowledge, there is not a lot of theoretical investigation on complexation process, so we perform a theoretical study of molecular structure for 15C5 and its complexes with Li^+, Na^+, K^+, and NH_4^+ cations by quantum chemistry calculation. Among quantum chemical methods for the evaluation of macrocyclic ligands, density functional theory (DFT) has some merits. It can be a useful tool in providing adequately accurate conformational analysis [19–21] and also the calculated electronic binding energies (ΔE^bs) are in excellent agreement with the experimental binding enthalpies [22].

In this work, the complexation reactions of 15C5 (Scheme 1) with Li^+, Na^+, K^+, and NH_4^+ cations were studied with both practical and theoretical methods, to underline the importance of the solvent in the complexation reactions and to investigate how the selectivity and thermodynamics of complexation reactions between these alkaline cations and the macrocyclic ligand in the liquid phase are affected by the nature and composition of binary mixed solvent solutions. Since NH_4^+ is an alkaline cation, we also included this cation with the alkaline metal cations in complexation process with 15C5 in acetonitrile–methanol binary mixtures. Yahmin et al. [23] have investigated the selectivity of 15C5 with some metal cations only from theoretical viewpoint. However, in our research work, the experimental and theoretical investigations were carried out to study the effect of solvent on the complexation ability of 15C5 with Li^+, Na^+, K^+, and NH_4^+ cations. To our knowledge, the combined experimental and theoretical investigations on complexation of 15C5 with the Li^+, Na^+, K^+, and NH_4^+ cations have not yet been reported.

Experimental setup

Reagents and solvent

15-Crown-5, lithium nitrate, sodium nitrate, potassium nitrate and ammonium nitrate all from Merck company (>99 % purity) were used without further purification. Acetonitrile and methanol (both from Merck, >99 % purity) were used as solvents. The conductivity of each solvent was $<3.0 \times 10^{-7}$ s^{-1} cm^{-1} at 298.15 K.

Apparatus

The conductance measurements were performed on a digital Genway conductivity apparatus, model 4510, in a water bath thermostated at a constant temperature which maintained within ±0.03 °C. The electrolytic conductance was measured using a cell consisting of two platinum electrodes with a cell constant of 0.98 cm^{-1}.

Procedure

The experimental procedure to obtain the formation constants of the complexes in liquid phase was as follows: a solution of metal salt (1.0×10^{-4} M) was placed in a titration cell and the conductance of the solution was measured, and then step-by-step increase of the crown ether solution (2.0×10^{-3} M) which was prepared in the same solvent was carried out by a rapid transfer to the titration cell using a microburette and the conductance of the solution in the cell was measured after each step at the desired temperature.

Computational details

All quantum calculations were carried out with the GAUSSIAN 09 software package [24], applying the modern density functional theory, DFT method. Calculations in the gas phase were performed at the B3LYP level of DFT theory using the 6-311G** basis set, for C, H, O, Li^+, Na^+, K^+, and NH_4^+.

The pair wise binding energy (ΔE) between host molecule (L) and guest (M^{n+}) is estimated as the difference between the energy of the complex $[ML]^{n+}$ and the energies of isolated partners:

$$\Delta E = E_{[\mathrm{ML}]^{\mathrm{n}+}} - \left(E_{[\mathrm{ML}]^{\mathrm{n}+}} + E_{\mathrm{L}}\right).$$

Results and discussion

Conductance studies

In order to evaluate the influence of adding 15C5 on the molar conductance of Li^+, Na^+, K^+, and NH_4^+ cations in different AN–MeOH mixtures, the molar conductance at a constant salt concentration (1.0×10^{-4} M) was monitored while increasing the crown ether concentration at various temperatures. Figures 1 and 2 illustrate the molar conductance–mole ratio plots for $(15C5{\cdot}Li)^+$ complex in pure

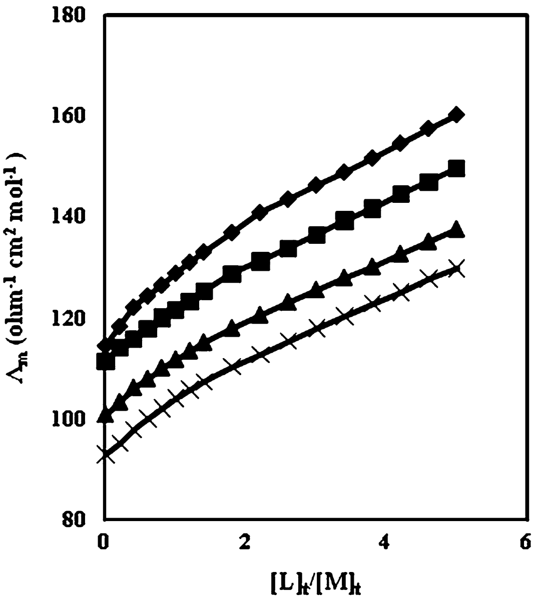

Fig. 1 Molar conductance–mole ratio plots for (15C5·Li)$^+$ complex in pure AN at different temperatures: 15 °C (*filled diamonds*), 25 °C (*filled squares*), 35 °C (*filled triangles*), 45 °C (*multiplication symbols*)

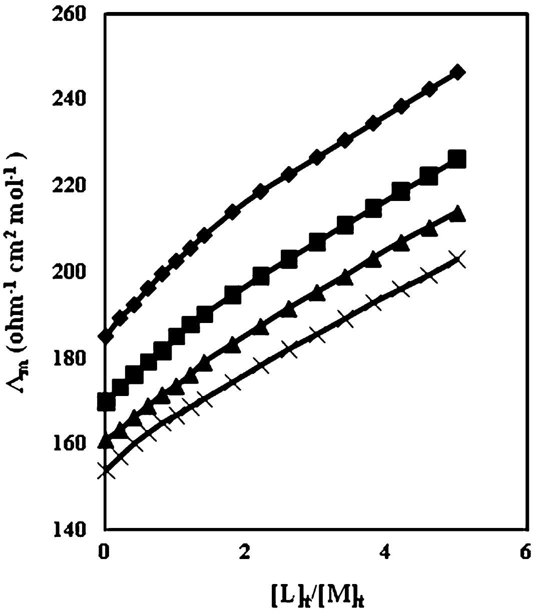

Fig. 2 Molar conductance–mole ratio plots for (15C5·NH$_4$)$^+$ complex in AN–MeOH binary system (mol % AN = 75) at different temperatures: 15 °C (*filled diamonds*), 25 °C (*filled squares*), 35 °C (*filled triangles*), 45 °C (*multiplication symbols*)

AN and for (15C5·NH$_4$)$^+$ complex in AN–MeOH binary system (mol% AN = 75), respectively.

As is evident from Figs. 1 and 2, there is a gradual increase in the molar conductance with the increasing crown ether concentration. This behavior indicates the higher mobility of the complexed cations compared to the solvated ones. Since the (15C5·Li)$^+$ and (15C5·NH$_4$)$^+$ complexes are more bulky than Li$^+$ and NH$_4$$^+$ cations, they are much less solvated by the solvent molecules, and hence the complexes are more mobile than the free solvated cations. Similar behaviors were observed in all other studied systems. A careful inspection of Figs. 1 and 2 reveals that the slope of the corresponding molar conductivity versus ligand/cation mole ratio plots changes at the point where the ligand to cation mole ratio is about 1, which is an evidence for formation of a 1:1 [M:L] complex in solutions. In order to make more clear the 1:1 [M:L] complexation model, the fitting and experimental curves for (15C5·Li)$^+$ complex in pure AN and for (15C5·NH$_4$)$^+$ complex in AN–MeOH binary system (mol% AN = 75) are shown in Figs. 3 and 4, respectively. As evident from these figures, there is a very good agreement between the fitting and the experimental data.

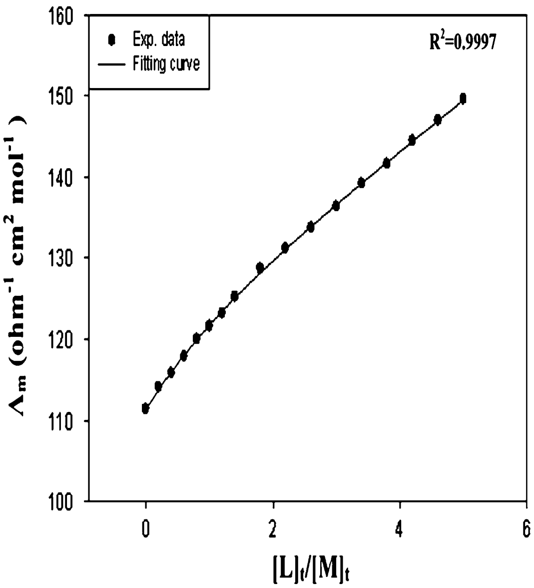

Fig. 3 The fitting and experimental curves for (15C5·Li)$^+$ complex in pure AN at 25 °C

Effect of solvent composition

The stability constants of the 15C5 complexes at each temperature were obtained from the variation of molar conductance as a function of [L]$_t$/[M]$_t$ molar ratio plots using a GENPLOT computer program [25]. The details of calculation of the stability constants of complexes by conductometric method have been described in Ref. [26]. The values of the stability constants (log K_f) for (15C5·M)$^+$ (M$^+$ = Li$^+$, Na$^+$, K$^+$, and NH$_4$$^+$) complexes in various solvent systems are given in Table 1. From this table, it can be seen that as the concentration of methanol increases in AN–MeOH binary mixtures, the stability of (15C5·Li)$^+$

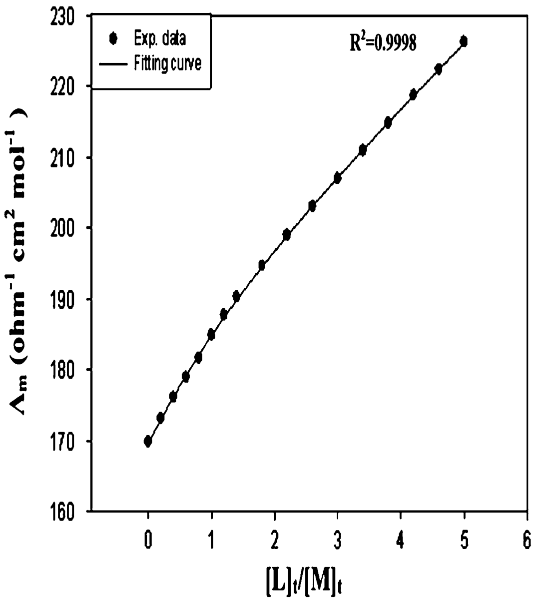

Fig. 4 The experimental data and fitting curve for $(15C5{\cdot}NH_4)^+$ complex in AN–MeOH binary system (mol% AN = 75) at 25 °C

complex decreases. Since methanol has a relatively high Gutmann Donor number (DN = 20), the solvation of the metal cation and possibly the ligand is stronger than that of acetonitrile (DN = 14.1). In addition, since the acceptor number of methanol (AN = 41.3) is much higher than that of acetonitrile (AN = 19.3), the ligand is much more solvated in MeOH than AN. Consequently, the stability of $(15C5{\cdot}Li)^+$ complex is weakened as the concentration of methanol increases in AN–MeOH binary solvent solutions.

Inspection of the data in Table 1 shows that the changes in stability constants of $(15C5{\cdot}Li)^+$, $(15C5{\cdot}Na)^+$, $(15C5{\cdot}K)^+$, and $(15C5{\cdot}NH_4)^+$ complexes in AN–MeOH binary systems are not monotonic. A typical non-monotonic behavior between the log K_f of $(15C5{\cdot}Na)^+$ complex and the composition of AN–MeOH binary system is shown in Fig. 5.

The non-linear relationship which is observed between log K_f and the composition of AN–MeOH binary solvent is probably due to the interaction between the AN and MeOH molecules via hydrogen bonding [27], which results in the structural changes of the solvent systems when they are mixed with each other. These structural changes may result in changing the interactions of those solvents with the solutes, thereby changing the solvation of the alkaline cations, the ligand and even the resulting complexes in the binary mixed solvent solutions.

Effect of ionic radii

The changes of log K_f of the complexes formed between 15C5 and Li^+, Na^+, K^+, and NH_4^+ cations versus the ionic radii in various solvent systems are shown in Fig. 6.

Table 1 Log K_f values of $(15C5{\cdot}M)^+$ ($M^+ = Li^+$, Na^+, K^+, and NH_4^+) complexes in AN–MeOH binary systems at different temperatures

mol% AN	log K_f ± SD			
	15 °C	25 °C	35 °C	45 °C
$(15C5{\cdot}Li)^{+a}$				
100	3.24 ± 0.06	2.98 ± 0.06	3.09 ± 0.07	3.11 ± 0.06
75	2.67 ± 0.20	2.69 ± 0.10	2.80 ± 0.08	2.78 ± 0.09
50	3.02 ± 0.08	2.73 ± 0.12	2.71 ± 0.12	2.69 ± 0.10
25	3.05 ± 0.10	2.69 ± 0.10	2.72 ± 0.10	2.58 ± 0.06
0	2.83 ± 0.08	2.78 ± 0.09	2.76 ± 0.10	2.74 ± 0.10
$(15C5{\cdot}Na)^{+a}$				
90	2.58 ± 0.31	2.72 ± 0.12	2.67 ± 0.15	2.70 ± 0.13
75	2.69 ± 0.13	2.85 ± 0.08	2.79 ± 0.08	2.74 ± 0.11
50	2.99 ± 0.08	2.90 ± 0.07	2.84 ± 0.07	2.88 ± 0.05
25	2.58 ± 0.17	2.72 ± 0.07	2.60 ± 0.06	2.92 ± 0.12
0	3.07 ± 0.18	3.72 ± 0.10	3.05 ± 0.12	3.06 ± 0.09
$(15C5{\cdot}K)^{+a}$				
90	2.56 ± 0.34	2.66 ± 0.17	2.61 ± 0.22	2.62 ± 0.20
75	2.67 ± 0.13	2.69 ± 0.14	2.72 ± 0.14	2.66 ± 0.18
50	2.76 ± 0.16	2.78 ± 0.10	2.62 ± 0.16	2.75 ± 0.08
25	2.80 ± 0.08	2.68 ± 0.02	2.76 ± 0.01	2.92 ± 0.03
0	2.99 ± 0.08	2.61 ± 0.10	2.73 ± 0.07	2.89 ± 0.06
$(15C5{\cdot}NH_4)^{+a}$				
100	2.99 ± 0.03	2.88 ± 0.03	2.76 ± 0.04	2.71 ± 0.13
75	3.11 ± 0.04	2.94 ± 0.04	2.79 ± 0.03	2.73 ± 0.07
50	2.83 ± 0.05	2.80 ± 0.03	2.71 ± 0.05	2.75 ± 0.09
25	2.76 ± 0.10	2.78 ± 0.09	2.79 ± 0.08	2.77 ± 0.05
0	2.84 ± 0.06	2.83 ± 0.07	2.80 ± 0.08	2.76 ± 0.09

SD Standard deviation

[a] The composition of binary mixed solvents is expressed in mol% for each solvent system

From Fig. 6, it can be seen that the sequence of stabilities of these complexes in AN–MeOH binary system (mol% AN = 50) at 25 °C is: $(15C5{\cdot}Na)^+ > (15C5{\cdot}NH_4)^+ \approx (15C5{\cdot}K)^+ > (15C5{\cdot}Li)^+$. In the case of complexation of macrocyclic ligands, there are at least three factors which can make significant contributions to the stability of their metal ion complexes: (1) the cation size and cavity size of the ligand, (2) the ionic solvation of the charged species involved, and (3) the conformations of the free and complexed crown ethers [28]. Since the ionic size of Na^+ (1.94 Å) is very close to the cavity size of 15C5 (1.7–2.2 Å), it can attain a more convenient fit condition than the other three cations, and therefore, it forms the most stable complex. On the other hand, the selectivity order of 15C5 for Li^+, Na^+, K^+, and NH_4^+ cations in the other AN–MeOH binary systems (such as mol% AN = 75 and 25) at 25 °C changes to

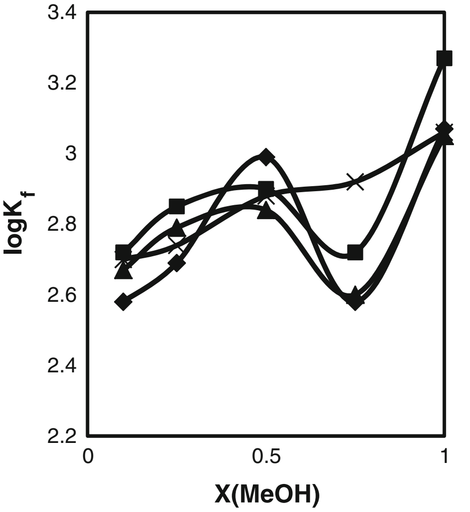

Fig. 5 Changes in stability constant of $(15C5{\cdot}Na)^+$ complex with the composition of the AN–MeOH binary mixture at different temperatures: 15 °C (*filled diamonds*), 25 °C (*filled squares*), 35 °C (*filled triangles*), 45 °C (*multiplication symbols*)

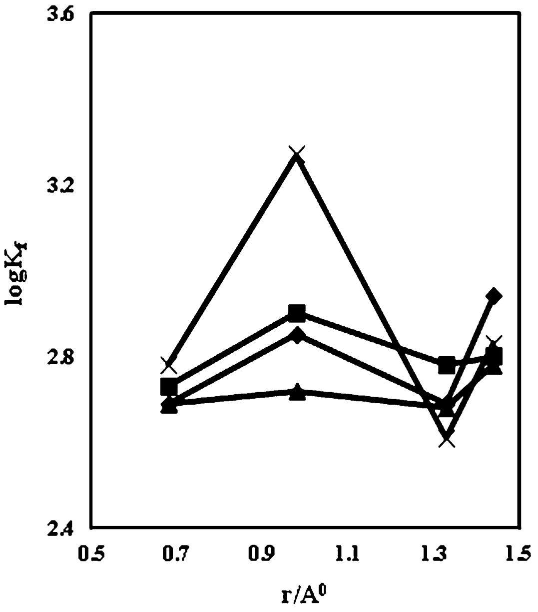

Fig. 6 Changes of $\log K_f$ for $(15C5{\cdot}Li)^+$, $(15C5{\cdot}Na)^+$, $(15C5{\cdot}K)^+$ and $(15C5{\cdot}NH_4)^+$ complexes versus cationic radii in various solvent systems at 25 °C: mol% AN: 75.0 (*filled diamonds*), 50.0 (*filled squares*), 25.0 (*filled triangles*), 0.0 (*multiplication symbols*)

$(15C5{\cdot}NH_4)^+ > (15C5{\cdot}Na)^+ > (15C5{\cdot}Li)^+ \approx (15C5{\cdot}K)^+$. These results reveal that in these two binary solvent systems, the stability of $(15C5{\cdot}NH_4)^+$ complex is more than that of $(15C5{\cdot}Na)^+$ complex. This may be related to the stronger solvation of Na^+ cation than NH_4^+ cation in these mixed non-aqueous solvent solutions. Therefore, the cavity-size effect is not the only dominant factor in complexation reactions between 15C5 and the studied alkaline cations.

Substituent effect on stability of complexes

The complexation reactions between benzo–15-crown-5 and 4′-nitrobenzo 15-crown-5 with Na^+ cation in pure MeOH at 25 °C have been studied [29, 30]. Comparison of the obtained data with our results indicates that the stability constant of $(15C5{\cdot}Na)^+$ complex ($\log K_f$ 3.27) is higher than those of the $(\text{benzo–}15C5{\cdot}Na)^+$ ($\log K_f$ 2.89) and $(4'\text{-nitrobenzo}15C5{\cdot}Na)^+$ ($\log K_f$ 2.73). The placement of a benzo group in 15C5 residue decreases the binding strength of B15C5 to the cations. This result is expected because B15C5 has two aromatic ether oxygen atoms whose basicity is lower than those of the aliphatic ether oxygen atoms [31]. Furthermore, introduction of an electron withdrawing $–NO_2$ group on the B15C5 ring reduces the donicity of the two aromatic oxygens and hence reduces the cation–crown ether interactions. Consequently, the stability constant of $(15C5{\cdot}Na)^+$ complex is higher than those of the $(\text{benzo–}15C5{\cdot}Na)^+$ and $(4'\text{-nitrobenzo}15C5{\cdot}Na)^+$. It seems that introduction of the chosen substitutions leads to a big change in the binding energy of the crown ether complexes and it may be an effective method for controlling the selectivity of the crown ethers for metal cations.

Thermodynamic calculations

In order to have a clear picture of the thermodynamics of the complexation of the studied alkaline cations with 15C5, it is useful to investigate the enthalpic and entropic contributions to the complexation reactions. The thermodynamic parameters for $(15C5{\cdot}M)^+$ ($M^+ = Li^+, Na^+, K^+$, and NH_4^+) complexes in AN–MeOH binary mixtures are summarized in Table 2. As is evident in this table, the values of enthalpy and entropy which are obtained for complexation reactions between 15C5 and Li^+, Na^+, K^+, and NH_4^+ cations change significantly with the nature and composition of the mixed solvent. This is due to the variations in the extent of contribution of important parameters such as solvation–desolvation of the species involved in the complexation reactions, and also the conformational changes of the crown ether in the binary mixed solvent solutions. As can be seen from this table, in most cases, the complexation reactions between Li^+, Na^+, K^+, and NH_4^+ cations and 15C5 are entropy stabilized, but in some cases, enthalpy destabilized. Similar thermodynamic behaviors have been previously reported for complexation of benzo–15C5 with Na^+ cation in some of the binary mixed non-aqueous solvents [32].

The thermodynamic results show an enthalpy–entropy compensation effect in AN–MeOH binary system; it means that as the complexation process becomes more enthalpically favorable, there is a greater loss of entropy. Figure 7 shows the plot of the enthalpy versus entropy for

Table 2 Thermodynamic parameters for $(15C5\cdot M)^+$ ($M^+ = Li^+$, Na^+, K^+ and NH_4^+) complexes in AN–MeOH binary mixtures

mol% AN	$\Delta G^\circ_c \pm$ SD 25 °C (kJ mol^{-1})	$\Delta H^\circ_c \pm$ SD (kJ mol^{-1})	$\Delta S^\circ_c \pm$ SD (J mol^{-1} K^{-1})
$(15C5\cdot Li)^{+}$[a]			
100	−15.36 ± 0.50	−8.42 ± 4.48	32.60 ± 14.76
75	−15.83 ± 1.55	6.46 ± 1.05	72.56 ± 3.52
50	−15.57 ± 0.56	−17.80 ± 7.95	–[b]
25	−16.66 ± 0.03	−27.86 ± 7.47	−38.18 ± 2.46
0	−15.36 ± 0.50	−5.08 ± 0.83	36.39 ± 3.51
$(15C5\cdot Na)^{+}$[a]			
90	−15.50 ± 0.59	–[b]	74.58 ± 16.47
75	−16.24 ± 0.29	–[b]	55.45 ± 17.89
50	−16.54 ± 0.22	−6.94 ± 3.76	32.71 ± 12.41
25	−15.52 ± 0.35	–[b]	102.48 ± 34.09
0	−18.66 ± 0.13	–[b]	–[b]
$(15C5\cdot K)^{+}$[a]			
90	−15.19 ± 0.93	–[b]	57.79 ± 12.21
75	−15.36 ± 0.68	–[b]	52.90 ± 13.00
50	−18.90 ± 0.39	–[b]	–[b]
25	−15.29 ± 0.09	21.60 ± 4.86	123.37 ± 15.80
0	−14.89 ± 0.59	25.54 ± 2.88	135.33 ± 9.03
$(15C5\cdot NH_4)^{+}$[a]			
100	−16.43 ± 0.10	−17.04 ± 2.10	–[b]
75	−16.79 ± 0.11	−22.71 ± 3.13	–[b]
50	−15.98 ± 0.12	−5.82 ± 3.22	33.88 ± 10.65
25	−15.85 ± 0.37	–[b]	55.77 ± 2.88
0	−16.15 ± 0.26	−4.82 ± 1.07	37.78 ± 3.54

SD standard deviation

[a] The composition of binary mixed solvents is expressed in mol% for each solvent system

[b] With high uncertainty

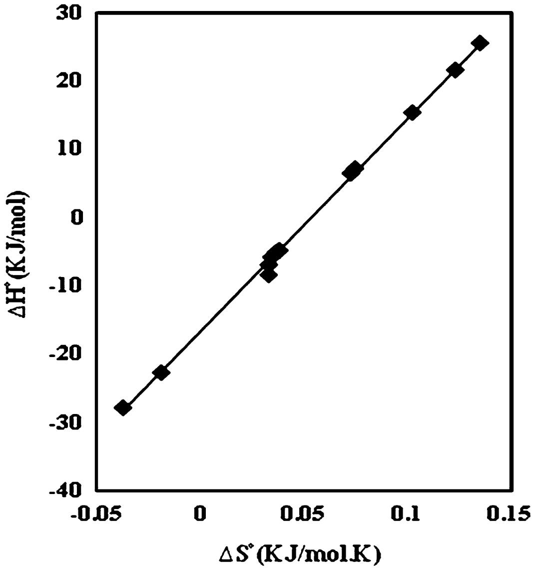

Fig. 7 Plot of the enthalpy versus entropy values for $(15C5\cdot Li)^+$, $(15C5\cdot Na)^+$, $(15C5\cdot K)^+$ and $(15C5\cdot NH_4)^+$ complexes in AN–MeOH binary systems

$(15C5\cdot Li)^+$, $(15C5\cdot Na)^+$, $(15C5\cdot K)^+$, and $(15C5\cdot NH_4)^+$ complexes in AN–MeOH binary systems.

It can be seen from Fig. 7 that there is a good fit ($R^2 = 0.998$) to a straight line with a slope of 311.1 and an intercept of 16.63. In all cases, the observed increase (or decrease, depending on the nature of the metal ion) in ΔH_c° value upon addition of methanol to the solvent mixture will be compensated by an increase (or decrease) in the corresponding ΔS°_c value. The existence of such a compensating effect between ΔH°_c and ΔS°_c values, which has been frequently reported for a variety of metal–ligand systems [33, 34], would cause the overall change in the ΔG° value of the complex to be smaller than might be expected from the change in either ΔH° or ΔS° independently.

Comparison between theoretical and experimental data

The optimized structures of the uncomplexed and complexed ligand with Li^+, Na^+, K^+, and NH_4^+ are presented in Fig. 8.

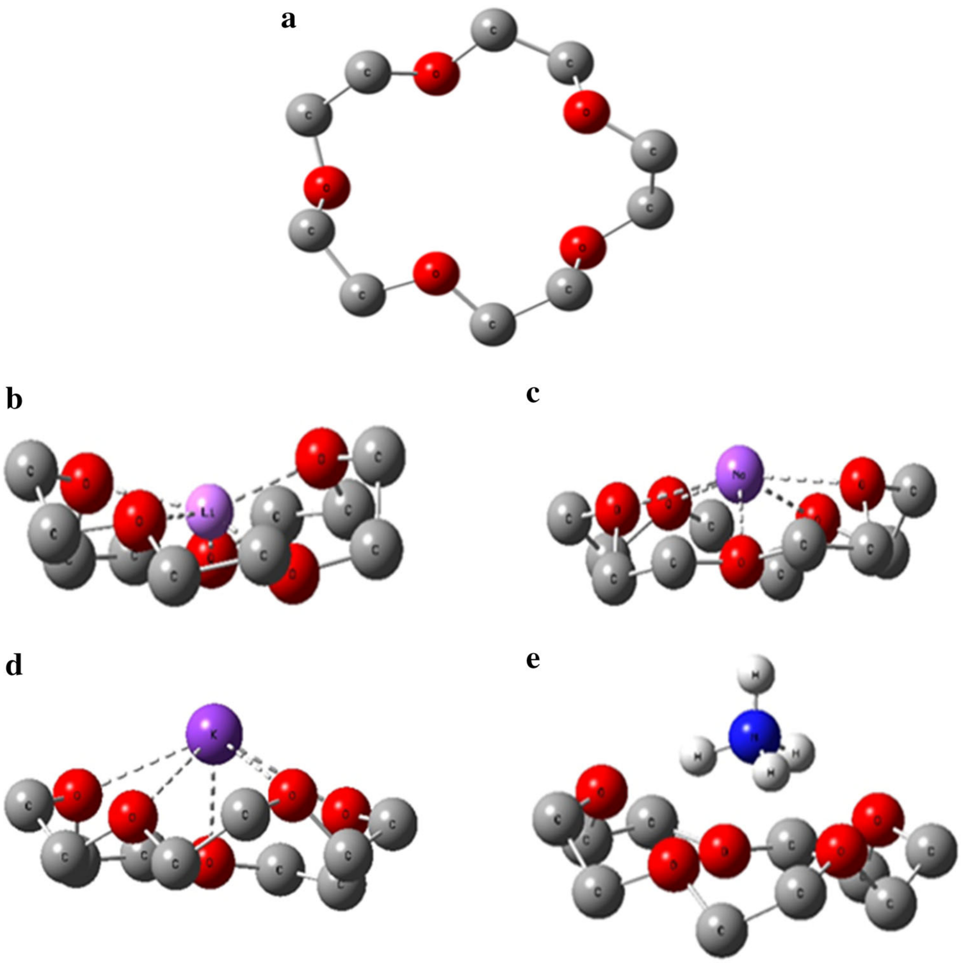

Fig. 8 Optimized structures of the: **a** uncomplexed ligand and complexed ligand with **b** Li^+, **c** Na^+, **d** K^+, and **e** NH_4^+ calculated with the B3LYP/6-311G** model chemistry

Table 3 The calculated binding energies (ΔE) in gas phase for $(15C5{\cdot}M)^+$ ($M^+ = Li^+$, Na^+, K^+, and NH_4^+) complexes at 25 °C

Cations	Energy of complex (Hartree)[a]	Energy of cations (Hartree)[b]	Energy of ligand (Hartree)[c]	Binding energy (Hartree)[d]	Binding energy (kJ mol^{-1})[d]
Li^+	−776.8197086	−7.28490582	−769.3525287	−0.18227417	−478.554
Na^+	−931.5834115	−162.0874615	–	−0.14342139	−376.547
K^+	−1369.220706	−599.7610167	–	−0.1071606	−281.346
NH_4^+	−826.3791507	−56.92009125	–	−0.10653079	−279.692

[a] $E_{[ML]^{n+}}$

[b] $E_{M^{n+}}$

[c] E_L

[d] $\Delta E = E_{[ML]^{n+}} - (E_{M^{n+}} + E_L)$

The calculated binding energies ΔE (kJ/mol) in gas phase for $(15C5{\cdot}M)^+$ ($M^+ = Li^+$, Na^+, K^+, and NH_4^+) complexes at 25 °C are summarized in Table 3. In order to study the effect of the solvent upon complexation, we compared the sequence of stability of the complexes formed between 15C5 and these cations in the gas phase (which was obtained based on binding energies) with the order of stability of the complexes formed between 15C5 and these alkaline cations in liquid phase (which was obtained by experiments). According to the data in Table 3, the order of the stability of complexes based on binding energy formed between 15C5 and the cations in gas phase is: $(15C5{\cdot}Li)^+ > (15C5{\cdot}Na)^+ > (15C5{\cdot}K)^+ > (15C5{\cdot}NH_4)^+$, but as can be seen in Table 1, the order of stability of the complexes formed between 15C5 and these alkaline cations in pure methanol at 25 °C was found to be: $(15C5\cdot Na)^+ > (15C5\cdot NH_4)^+ > (15C5\cdot Li)^+ > (15C5\cdot K)^+$. As a matter of fact, in the host–guest recognition processes, the solvent plays a critical role in local structure optimization and complex stabilization; thus, the complex stability is known to vary drastically according to the chemical and physical properties of the solvent in which the reactions occur [29]. The calculated values of the gas phase binding energies indicate that, in the gas phase, 15C5 binds the Li^+ cation most strongly than Na^+, K^+, $NH_4{}^+$ cations for simple electrostatic reasons. But in solution phase, the binding preference of the crown ethers is shifted away from lithium ion toward one of the larger cations because lithium ion is more strongly solvated than the other larger cations.

Conclusion

The complexation processes between Li^+, Na^+, K^+, and $NH_4{}^+$ cations with the 15-crown-5 have been studied in liquid and gas phases. The results show that the enthalpy, entropy and the stability constants of the complexes formed between Li^+, Na^+, K^+, and $NH_4{}^+$ cations and 15-crown-5 in liquid phase are affected by the nature and composition of the binary mixed solvents as well as by the substituents in the ligand and ionic radii.

The values of formation constants of the complexes show that the order of stability of complexes formed between 15C5 and the studied cations in pure methanol at 25 °C is: $(15C5\cdot Na)^+ > (15C5\cdot NH_4)^+ > (15C5\cdot Li)^+ > (15C5\cdot K)^+$. But the order of stability of the complexes in the gas phase, which was obtained by theoretical quantum calculations, was found to be: $(15C5\cdot Li)^+ > (15C5\cdot Na)^+ > (15C5\cdot K)^+ > (15C5\cdot NH_4)^+$. Comparison of the experimental and theoretical results shows that the solvent plays a critical role in local structure optimization and complex stabilization in solutions.

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