ORIGINAL ARTICLE

Solvent influence upon complex formation between benzo-15-crown-5 and Mg^{2+}, Ca^{2+} and Sr^{2+} cations in some pure and binary mixed solvents using conductometric method

G. H. Rounaghi · M. Mohajeri · M. Doaei · A. Ghaemi

Abstract The complexation reactions between Mg^{2+}, Ca^{2+} and Sr^{2+} cations with the macrocyclic ligand, benzo-15-crown-5 (B15C5), in pure acetonitrile, water, methanol and tetrahydrofuran and also in acetonitrile–water (AN–H_2O) and in methanol–tetrahydrofuran (MeOH–THF) binary mixtures have been studied at different temperatures using conductometric method. The conductance data show that the stoichiometry of the complexes in most cases is 1:1 [ML]. But in the case of Ca^{2+} cation a 1:2 [ML_2] complex is formed in pure THF, which shows that the stoichiometry of the complexes may be changed by the nature of the medium. The values of stability constants of complexes, which were obtained from conductometric data, show that the stability of complexes is affected by the nature and composition of the binary mixed solvents and a non-linear behavior was observed for variation of $logK_f$ of the complexes versus the composition of the solvent systems. The results show that the selectivity order of B15C5 for the metal cations in two AN–H_2O binary solutions (mol% AN = 25.71 and 50.94) at 25 °C is: $Mg^{2+} > Sr^{2+} > Ca^{2+}$. The values of thermodynamic parameters (ΔH_c^0, ΔS_c^0) for formation of complexes were obtained from temperature dependence of stability constants of complexes using the van't Hoff plots. The results show that the values and also the sign of these parameters are influenced by the nature and also the composition of the binary mixed solvents.

G. H. Rounaghi (✉) · A. Ghaemi
Department of Chemistry, Faculty of Sciences, Ferdowsi
University of Mashhad, Mashhad, Iran
e-mail: ghrounaghi@yahoo.com

A. Ghaemi
e-mail: arezooghaemi@yahoo.com

M. Mohajeri · M. Doaei
Department of Chemistry, Faculty of Sciences, Islamic Azad
University, Mashhad Branch, Mashhad, Iran

Introduction

It is well-known that the coordination chemistry of the heavier alkali and alkaline-earth metal ions is almost entirely restricted to their complexes with chelating ligands having ''hard'' oxygen or oxygen and saturated nitrogen donor atoms. The best known and most important ligands for complexation with such metal cations, are polyethers, crown ethers [1, 2] and cryptands [3, 4].

Crown ether is a macrocyclic polyether whose structure contains hydrogen, carbon and oxygen atoms. Each oxygen atoms are confined between two carbon atoms and exhibits a conformation with a hole (accordingly called "crown"). As an ether, crown ethers are soluble in non-polar solvents. They are capable of strong solvency binding cations in their central cavity. The exterior of the ring is hydrophobic. The size of the interior central cavity, fused ring systems, and side chains and functional groups determine the solvency capacity of the cation and the power of hydrophobic.

The main characteristic of a crown ether is the complexation of the ether oxygens with various ionic species. If metallic elements pass through the center of the hole, they stick to oxygen atoms. The crown compound is then termed "host–guest" chemistry; crown ether acts as the "host" taking ionic species as its "guest". Crown compounds locks guest atoms in a solution and wrap around it. Crown ethers are used in PTC (phase-transfer catalysts) system [5] and in encouraging the solubility of inorganic compounds in organic solvents to promote the chemical reactions.

''Host–guest'' chemistry of crown ethers can be a key to identify the move of essential elements in the body and can play the part of very complicated biological reactions [6] such as enzyme's functions, which can be applied to develop new pharmaceuticals.
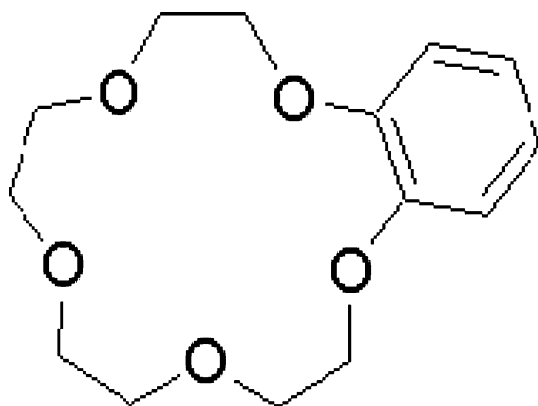
Studies of complexation reactions of crown ethers with metal ions in different solvents show that the thermodynamic and kinetic parameters are affected by the nature and composition of the solvent systems [7–9]. Non-aqueous solvents are often mixed with water or some other organic solvents in order to obtain desirable solvent properties. Although the complexation of crown ethers with metal cations has been studied in both aqueous and non-aqueous media, but most of these investigations have been carried out in neat solvents [10, 11] 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 benzo-15-crown-5 in mixed solvents are very sparse [12, 13].

Among the various physicochemical methods [14–17] which have been used for investigation of cation–macrocyclic crown ether interactions in solutions, the conductometry is a very useful method for determining the stability, selectivity and also the thermodynamic parameters of the crown ether complexes with various cations in non-aqueous media.

In this paper, the results of thermodynamic study for complexation reactions between benzo-15-crown-5 (Scheme 1) with Mg^{2+}, Ca^{2+} and Sr^{2+} cations in AN, H_2O, MeOH and THF and AN–H_2O and MeOH–THF binary mixtures at different temperatures using conductometric method are reported and the dependence of stability, selectivity and also the thermodynamic quantities for these complexation processes on the nature and composition of the binary solutions is discussed.

Experimental

B15C5, magnesium nitrate, calcium nitrate and strontium nitrate all from Merck were used without further purification. Acetonitrile (Merck), methanol (Merck) and

tetrahydrofuran (Merck) with the highest purity and triplet distilled water were used as solvents.

The experimental procedure to obtain the stability constants of complexes was as follows: a solution of metal salt $(5.0 \times 10^{-4}$ M$)$ was placed in a titration cell and the conductance of the solution was measured, then a step-by-

Fig. 1 Molar conductance–mole ratio plots for $(B15C5 \cdot Mg)^{2+}$ complex in pure acetonitrile at different temperatures: (*times*, 15 °C; *filled square*, 25 °C; *triangle*, 35 °C; *filled diamond*, 45 °C)
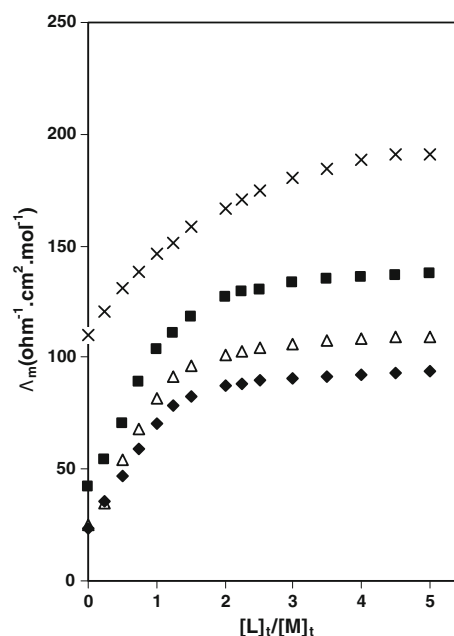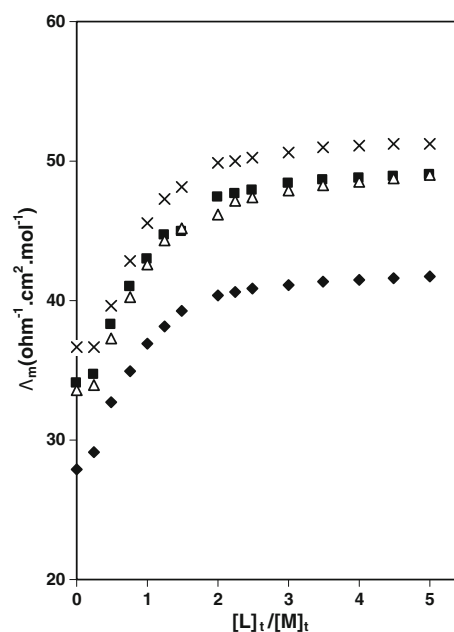

Fig. 2 Molar conductance–mole ratio plots for $(B15C5 \cdot Ca)^{2+}$ complex in pure acetonitrile at different temperatures: (*times*, 15 °C; *filled square*, 25 °C; *triangle*, 35 °C; *filled diamond*, 45 °C)
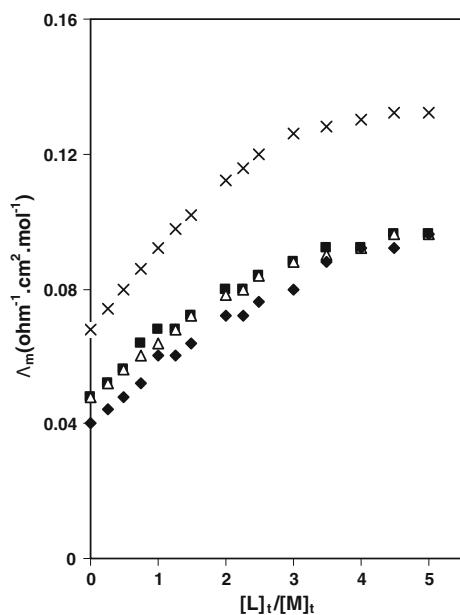

Scheme 1 Structure of benzo-15-crown-5 (B15C5)

Fig. 3 Molar conductance–mole ratio plots for $(B15C5 \cdot Ca)^{2+}$ complex in pure tetrahydrofuran at different temperatures: (*times*, 15 °C; *filled square*, 25 °C; *triangle*, 35 °C; *filled diamond*, 45 °C)

step increase of the crown ether solution prepared in the same solvent (2.5×10^{-2} M) 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 transfer at the desired temperature.

The conductance measurements were performed using a digital Metrohm conductivity apparatus, model 712, in a water bath thermostated at a constant temperature which

maintained within ±0.1 °C. The electrolytic conductance was measured using a cell consisting of two platinum electrodes to which an alternating potential was applied. The cell constant was 0.75 cm^{-1}.

Results

The changes of molar conductance, Λ_m, versus the ligand to cation molar ratio ($[L]_t/[M]_t$) for $(B15C5 \cdot Mg)^{2+}$, $(B15C5 \cdot Ca)^{2+}$ and $(B15C5 \cdot Sr)^{2+}$ complexes in AN, H_2O, MeOH and THF and their binary mixtures were studied at different temperatures. Three typical series of molar conductance values as a function of $[L]_t/[M]_t$ for $(B15C5 \cdot Mg)^{2+}$ complex in pure AN and for $(B15C5 \cdot Ca)^{2+}$ complex in pure AN and pure THF are shown in Figs. 1, 2 and 3, respectively.

The stability constants ($\log K_f$) of the B15C5 crown ether complexes at each temperature were calculated from the changes of the molar conductance as a function of $[L]_t/[M]_t$ mole ratios using a GENPLOT computer program [18]. The details of the calculation of the stability constants of complexes by conductometric method has been described elsewhere [19]. The values of $\log K_f$ for $(B15C5 \cdot M)^{2+}$ ($M^{2+}= Mg^{2+}$, Ca^{2+} and Sr^{2+}) complexes in various solvent systems are listed in Tables 1, 2.

The van't Hoff plots of $\ln K_f$ versus 1/T for all of the investigated systems were constructed. A typical example of these plots is shown in Fig. 4. The changes in the standard enthalpy (ΔH_c^0) for the complexation reactions were obtained from the slope of the van't Hoff plots, and the changes in the standard entropy (ΔS_c^0) were calculated from the relationship $\Delta G_{c,298.15}^0 = \Delta H_c^0 - 298.15 \Delta S_c^0$. The thermodynamic data

Table 1 $\log K_f$ values of $(B15C5 \cdot Mg)^{2+}$, $(B15C5 \cdot Ca)^{2+}$ and $(B15C5 \cdot Sr)^{2+}$ complexes in AN–H_2O binary mixtures at different temperatures

Medium	$\log K_f \pm$ SD			
	15 °C	25 °C	35 °C	45 °C
$(B15C5 \cdot Mg)^{2+,a}$				
Pure AN	3.58 ± 0.08	3.75 ± 0.14	3.24 ± 0.18	2.70 ± 0.17
50.94%AN–49.06%H_2O^b	3.64 ± 0.10	3.13 ± 0.07	3.00 ± 0.05	2.70 ± 0.16
25.71%AN–74.29%H_2O	3.11 ± 0.17	3.08 ± 0.07	4.19 ± 0.06	2.55 ± 0.15
10.34%AN–89.66%H_2O	3.63 ± 0.06	3.51 ± 0.04	4.07 ± 0.05	3.60 ± 0.13
Pure H_2O	3.17 ± 0.03	3.88 ± 0.04	4.09 ± 0.03	4.02 ± 0.06
$(B15C5 \cdot Ca)^{2+,a}$				
Pure AN	3.84 ± 0.13	3.84 ± 0.09	3.77 ± 0.10	3.97 ± 0.07
50.94%AN–49.06%H_2O^b	2.98 ± 0.06	2.88 ± 0.06	2.24 ± 0.06	2.24 ± 0.10
25.71%AN–74.29%H_2O	2.68 ± 0.10	2.51 ± 0.12	2.86 ± 0.14	2.52 ± 0.04
$(B15C5 \cdot Sr)^{2+,a}$				
86.80%AN–13.20%H_2O^b	2.68 ± 0.15	2.79 ± 0.14	2.72 ± 0.15	3.21 ± 0.17
50.94%AN–49.06%H_2O	3.88 ± 0.08	3.03 ± 0.06	2.46 ± 0.03	2.46 ± 0.10
25.71%AN–74.29%H_2O	2.91 ± 0.06	2.91 ± 0.04	2.46 ± 0.07	2.69 ± 0.03
10.34%AN–89.66%H_2O	4.10 ± 0.10	2.59 ± 0.07	2.37 ± 0.07	2.75 ± 0.09
Pure H_2O	3.17 ± 0.05	2.12 ± 0.06	2.60 ± 0.08	2.29 ± 0.06

SD standard deviation

[a] The concentration of each metal cation was 5.0×10^{-4} M

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

are summarized in Table 3. The variations of $\log K_f$ versus the solvent composition for (B15C5·Ca)$^{2+}$ complex in AN–H$_2$O and for (B15C5·Mg)$^{2+}$ complex in MeOH–THF binary systems at different temperatures are shown in Figs. 5 and 6, respectively. The variations of the stability constants of (B15C5·Mg)$^{2+}$, (B15C5·Ca)$^{2+}$ and (B15C5·Sr)$^{2+}$ complexes as a function of cationic radii in two AN–H$_2$O binary systems at 25 °C is shown in Fig. 7.

Discussion

As is seen from Figs. 1, 2 and 3, addition of B15C5 to Mg^{2+} and Ca^{2+} cations in pure acetonitrile and tetrahydrofuran at different temperatures results in an increase in the molar conductivity which indicates that (B15C5·Mg)$^{2+}$ and (B15C5·Ca)$^{2+}$ complexes are more mobile than free solvated Mg^{2+} and Ca^{2+} cations. Similar behavior was also observed for Mg^{2+}, Ca^{2+} and Sr^{2+} cations in the binary mixed systems. As is evident from Figs. 1 and 2, the slope of the corresponding molar conductivity versus [L]$_t$/[M]$_t$ plots changes at the point where the ligand to cation mole ratio is about 1, which is an evidence for the formation of a relatively stable 1:1 [ML] complex between Mg^{2+} and Ca^{2+} cations and benzo-15-crown-5. Similar behavior was observed for most of the complexes in AN–H$_2$O and MeOH–THF binary mixtures. In order to make more clear the 1:1 [M:L] complexation model, the fitting and experimental curves for (B15C5·Mg)$^{2+}$ complex in pure acetonitrile at 25 °C are shown in Fig. 8. As is evident in this figure, there is a good agreement between the fitting and experimental data. But in the case of Ca^{2+} cation in pure THF, the slope of molar conductance mole ratio curves changes at the point where [L]$_t$/[M]$_t$ is about 2 which indicates the formation of a 1:2 [ML$_2$] complex at different temperatures in this non-aqueous solvent (see Fig. 3). The

results obtained in this investigation show that the stoichiometry of the macrocyclic complexes may be changed by the nature of the medium. As is evident in Fig. 3, the complexation equilibria at 25, 35 and 45 °C seems to be complex. This behaviour may be due to the changes of the solvation number of the cation, ligand and even the resulting complex with temperature.

The data in Table 1 show that as the concentration of water is increased in AN–H$_2$O binary mixtures, the stability of (B15C5·Ca)$^{2+}$ complex decreases. In a strong solvating solvent such as H$_2$O with a relatively high Gutmann Donor Number (DN = 33), the solvation of the
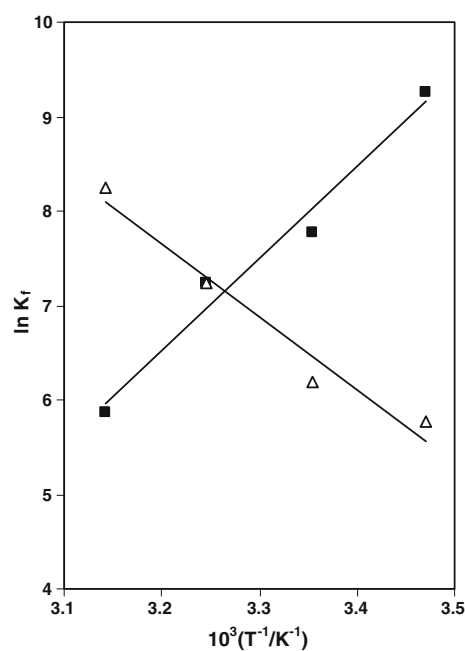

Fig. 4 van't Hoff plots for (B15C5·Mg)$^{2+}$ complex in MeOH–THF binary systems: (*filled square*, mol% THF = 0; *triangle*, mol% THF = 33.23)

Table 2 LogK$_f$ values of (B15C5·Mg)$^{2+}$ and (B15C5·Ca)$^{2+}$ complexes in MeOH–THF binary mixtures at different temperatures

Medium	LogKf ± SD			
	15 °C	25 °C	35 °C	45 °C
(B15C5·Mg)$^{2+,a}$				
Pure THF	3.46 ± 0.08	2.87 ± 0.11	3.02 ± 0.10	2.75 ± 0.09
59.91%THF–40.09%MeOH^b	2.76 ± 0.13	2.66 ± 0.17	2.62 ± 0.14	3.41 ± 0.12
33.23%THF–66.77%MeOH	2.51 ± 0.16	2.69 ± 0.13	3.14 ± 0.06	3.58 ± 0.19
14.22%THF–85.78%MeOH	3.05 ± 0.11	2.70 ± 0.07	3.14 ± 0.15	2.87 ± 0.11
Pure MeOH	4.02 ± 0.08	3.38 ± 0.18	3.14 ± 0.14	2.55 ± 0.10
(B15C5·Ca)$^{2+,a}$				
Pure THF	c	c	c	c
59.91%THF–40.09%MeOH^b	2.32 ± 0.09	2.30 ± 0.10	3.21 ± 0.15	2.30 ± 0.08
33.23%THF–66.77%MeOH	2.78 ± 0.19	2.96 ± 0.10	3.04 ± 0.16	3.85 ± 0.04
14.22%THF–85.78%MeOH	3.45 ± 0.09	3.48 ± 0.18	3.05 ± 0.11	2.72 ± 0.09
Pure MeOH	2.96 ± 0.08	2.45 ± 0.10	2.34 ± 0.18	2.41 ± 0.12

SD standard deviation

^{a} The concentration of each metal cation was 5.0 × 10^{-4} M

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

^{c} The data can not be fitted in equation

Table 3 Thermodynamic parameters for $(B15C5 \cdot Mg)^{2+}$, $(B15C5 \cdot Ca)^{2+}$ and $(B15C5 \cdot Sr)^{2+}$ complexes in $AN–H_2O$ and $THF–MeOH$ binary mixtures

Medium	$-\Delta G_c^\circ \pm SD$ (25 °C) (kJ/mol)	$\Delta H_c^\circ \pm SD$ (kJ/mol)	$\Delta S_c^\circ \pm SD$ (kJ/mol)
$(B15C5 \cdot Mg)^{2+}$			
Pure AN	22.16 ± 0.37	b	240.05 ± 69.95
$50.94\%AN–49.06\%H_2O^a$	17.85 ± 1.03	-52.65 ± 8.95	-116.72 ± 29.81
$25.71\%AN–74.29\%H_2O$	17.57 ± 0.78	b	b
$10.34\%AN–89.66\%H_2O$	20.03 ± 0.13	b	b
Pure H_2O	21.39 ± 0.82	b	b
$(B15C5 \cdot Ca)^{2+}$			
Pure AN	21.94 ± 0.54	b	91.83 ± 24.72
$50.94\%AN–49.06\%H_2O^a$	16.46 ± 0.35	-37.88 ± 10.66	c
$25.71\%AN–74.29\%H_2O$	14.33 ± 0.69	c	c
$(B15C5 \cdot Sr)^{2+}$			
$86.80\%AN–13.20\%H_2O^a$	15.94 ± 0.81	b	b
$50.94\%AN–49.06\%H_2O$	17.28 ± 0.32	-87.03 ± 22.85	-233.94 ± 75.63
$25.71\%AN–74.29\%H_2O$	16.61 ± 0.21	b	b
$10.34\%AN–89.66\%H_2O$	14.70 ± 0.42	b	b
Pure H_2O	12.17 ± 0.33	b	b
$(B15C5 \cdot Mg)^{2+}$			
Pure THF	16.41 ± 0.64	b	b
$59.91\%THF–40.09\%MeOH^a$	15.17 ± 0.95	b	b
$33.23\%THF–66.77\%MeOH$	15.37 ± 0.76	65.06 ± 8.81	269.76 ± 29.44
$14.22\%THF–85.78\%MeOH$	15.39 ± 0.38	b	b
Pure MeOH	19.26 ± 1.06	-82.95 ± 10.07	-213.62 ± 33.59
$(B15C5 \cdot Ca)^{2+}$			
$59.91\%THF–40.09\%MeOH^a$	13.14 ± 0.89	b	b
$33.23\%THF–66.77\%MeOH$	16.88 ± 0.61	b	252.09 ± 72.65
$14.22\%THF–85.78\%MeOH$	19.83 ± 1.03	-47.70 ± 12.52	b
Pure MeOH	15.29 ± 0.60	b	b

SD standard deviation

[a] Composition of binary mixtures is expressed in mol% for each solvent system

[b] With high uncertainty

metal cation and possibly of the ligand should be stronger than AN with a medium donor ability (DN = 14.1), thus, the formation of the $(B15C5 \cdot Ca)^{2+}$ complex is weakened as the concentration of water increases in $AN–H_2O$ binary solutions. As is obvious from Table 1, the changes in stability constants of $(B15C5 \cdot Mg)^{2+}$ and $(B15C5 \cdot Sr)^{2+}$ complexes in $AN–H_2O$ binary mixtures are not monotonic. This behavior may be due to interaction between the water and acetonitrile molecules via hydrogen bonding in their binary mixtures which results in changing the structure of the mixed solvents and, therefore, changing the solvation of the alkaline earth metal cations, the ligand and the resulting $(B15C5 \cdot M)^{2+}$ complexes in $AN–H_2O$ binary solutions. In addition, the preferential solvation of the studied metal cations and the macrocyclic ligand in these binary solutions may affect complexation processes [20, 21].

Although MeOH and THF have the same donor numbers (DN = 20 for MeOH and THF), but as is evident in Table 2, in some cases, the stability of $(B15C5 \cdot Mg)^{2+}$ complex increases as the concentration of MeOH is increased. This behavior may be due to the formation of hydrogen bond between NO_3^- anion and MeOH molecules because the anions are usually solvated in protic and amphiprotic solvents via hydrogen bonding. Therefore, the competition between this counter ion with the macrocyclic ligand for Mg^{2+} cation is decreased as the concentration of MeOH increases in MeOH–THF binary mixed solvents. Moreover, these two solvents possess quite different dielectric constants ($\varepsilon_{MeOH} = 32.6$ and $\varepsilon_{THF} = 7.3$). The high dielectric constant of MeOH, can exert a decrease in the electrostatic interactions between the NO_3^- anion and the Mg^{2+} cation in solution and, therefore, the stability constant of $(B15C5 \cdot Mg)^{2+}$ complex increases by increasing the concentration of MeOH in this binary solutions.

As is shown in Fig. 5, the variation of the stability constant of the $(B15C5 \cdot Ca)^{2+}$ complex versus the solvent composition in $AN–H_2O$ binary mixtures, is not linear at 35 and 45 °C and it shows a minimum at mol% AN ≈ 50, but in the case of 15 and 25 °C, a linear relationship is observed. The different behavior which is observed for $(B15C5 \cdot Ca)^{2+}$ complex in $AN–H_2O$ binary solutions, may

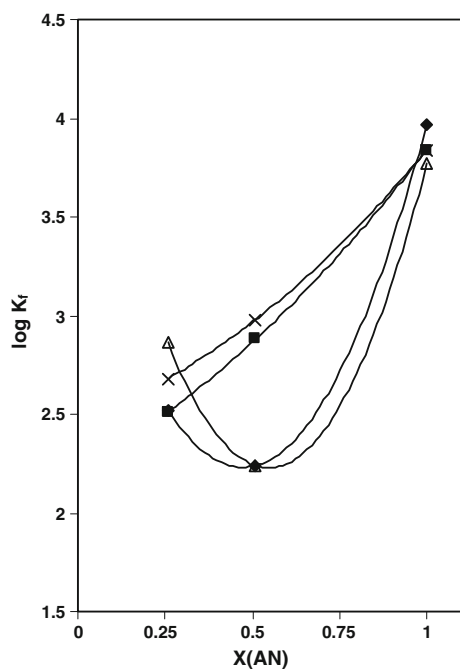**Fig. 5** Changes of the stability constant of (B15C5·Ca)$^{2+}$ complex with the composition of the AN–H$_2$O binary mixture at different temperatures: (*times*, 15 °C; *filled square*, 25 °C; *triangle*, 35 °C; *filled diamond*, 45 °C)
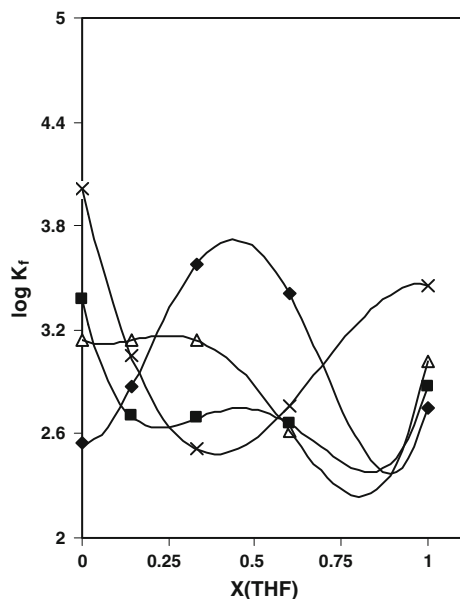

Fig. 7 Changes of logK$_f$ for (B15C5·Mg)$^{2+}$, (B15C5·Ca)$^{2+}$ and (B15C5·Sr)$^{2+}$ complexes versus cationic radii in two AN–H$_2$O binary systems at 25 °C: (*filled triangle*, mol% AN = 25.71; *filled diamond*, mol% AN = 50.94)

Fig. 6 Changes of the stability constant of (B15C5·Mg)$^{2+}$ complex with the composition of the MeOH–THF binary mixture at different temperatures: (*times*, 15 °C; *filled square*, 25 °C; *triangle*, 35 °C; *filled diamond*, 45 °C)

Fig. 8 The fitting and experimental curves for (B15C5·Mg)$^{2+}$ complex in pure acetonitrile at 25 °C (*filled square*)

be related to the changes occurring in the structure of the solvent mixtures with changing the temperature. As illustrated in Fig. 6, the change of the stability constant of the (B15C5·Mg)$^{2+}$ complex with the composition of MeOH–

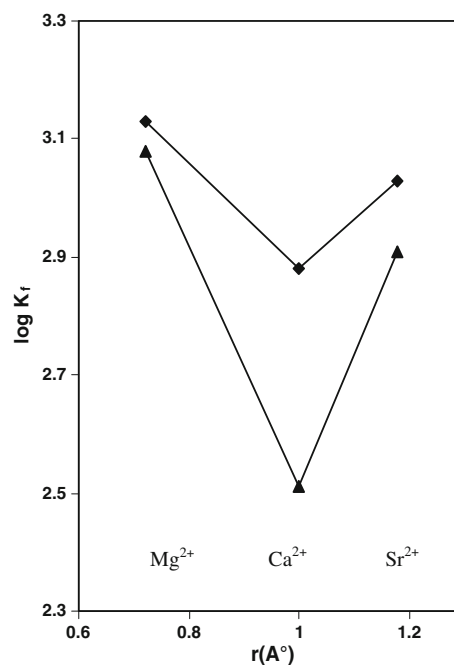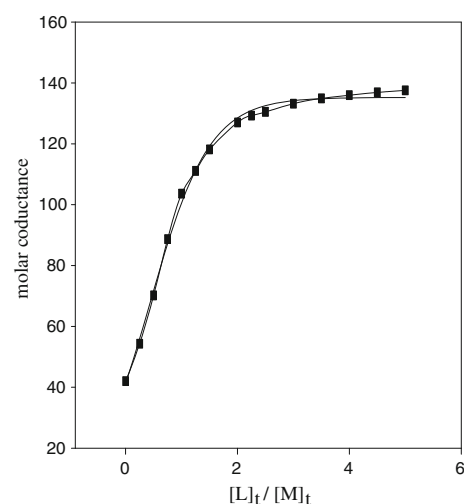THF binary system is not linear. Somewhat similar behavior was observed for other complexes in AN–H$_2$O and MeOH–THF binary mixtures. The non-linear relationship which is observed for these systems is probably related to structural changes of the solvent systems when they are mixed with one another. These structural changes may result in changing the interactions of those solvents with the solute. The effect of properties of AN–H$_2$O and

other organic-water mixtures on the solvation enthalpy of 15C5 and some of the other crown ethers has been studied by Jozwiak [22] and it has been shown that the crown ethers are preferentially solvated by organic solvents in these binary mixtures and it has been discussed that in these mixed solvents, the energetic effect of the preferential solvation depends quantitatively on the structural and energetic properties of the mixtures. In addition, the non-monotonic behaviour observed for variation of $\log K_f$ of complexes with the composition of the mixed solvents, probably reflects a balance between solvation properties, donicity, hydrogen bonding ability, etc. of the solvent systems.

The changes of $\log K_f$ for the formation of $(B15C5\cdot Mg)^{2+}$, $(B15C5\cdot Ca)^{2+}$ and $(B15C5\cdot Sr)^{2+}$ complexes versus ionic radii in two AN–H_2O binary mixtures (mol% AN = 25.71 and 50.94) is shown in Fig. 7. The selectivity order of B15C5 for Mg^{2+}, Ca^{2+} and Sr^{2+} cations in these two binary systems at 25 °C is: $Mg^{2+} > Sr^{2+} > Ca^{2+}$. This result is expected since the Mg^{2+} ion with a small ionic size can attain a more convenient fit condition than the other two metal cations for the ligand's cavity. Although Ca^{2+} cation has a smaller size than Sr^{2+} cation, the stability of $(B15C5\cdot Sr)^{2+}$ complex is more than the stability of $(B15C5\cdot Ca)^{2+}$ complex. This may be related to the strong solvation of Ca^{2+} cation in compare with Sr^{2+} cation in these binary solutions. The results obtained in this study show that the selection of solvents as mixture components and their concentration may create possibilities to change the properties of the solvent system in a desired direction.

The thermodynamic quantities (ΔH_c^0, ΔS_c^0) for complexation processes between B15C5 and Mg^{2+}, Ca^{2+} and Sr^{2+} metal cations are given in Table 3. As expected, the values of thermodynamic quantities depend strongly on the nature and composition of the mixed solvents [23, 24]. 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., cations, macrocycle and the resulting complexes), and also the conformational changes of the macrocyclic ligand in the binary solutions. The experimental results in this Table, indicate that in some of the binary solutions, the changes in standard enthalpy for the complexation reactions is negligible, therefore, it seems that the complexation processes in these solvent systems are probably athermic. But in some cases of other binary solutions, the complexation reactions are exothermic or endothermic.

References

1. Brown, M.D., Davis, M.F., Dyke, J.M., Ferrante, F., Levason, W., Ogden, J.S., Webster, M.: Synthesis, structures and DFT calculations on alkaline-earth metal azide-crown ether complexes. Chem. A Eur. J. **14**, 2615–2624 (2008). doi:10.1002/chem.200701502

2. Hay, B.P., Rustad, J.R.: Structural criteria for the rational design of selective ligands: extension of the MM3 force field to aliphatic ether complexes of the alkali and alkaline earth cations. J. Am. Chem. Soc. **116**, 6316–6326 (1994). doi:10.1021/ja00093a035

3. Cox, B.G., Truong, N.V., Schneider, H.: Alkaline earth cryptates: dynamics and stabilities in different solvents. J. Am. Chem. Soc. **106**, 1028–1273 (1984). doi:10.1021/ja00317a01

4. Hundal, G., Hundal, M.S., Obrai, S., Poonia, N.S., Kumar, S.: Metal complexes of tetrapodal ligands: synthesis, spectroscopic and thermal studies, and X-ray crystal structure studies of Na(I), Ca(II), Sr (II), and Ba(II) complexes of tetrapodal ligands N,N,N′,N′-tetrakis (2-hydroxypropyl) ethylenediamine and N,N,N′,N′-tetrakis (2-hydroxyethyl) ethylenediamine. Inorg. Chem. **41**, 2077–2086 (2002). doi:10.1021/ic0100727

5. Anderson, J.D., Paulsen, E.S., Dearden, D.V.: Alkali metal binding energies of dibenzo-18-crown-6: experimental and computational results. Int. J. Mass Spectrom. **227**, 63–76 (2003)

6. Stolwijk, T.B., Sudholter, E.J.R., Reinhoudt, D.N.: Crown ether mediated transport: a kinetic study of potassium perchlorate transport through a supported liquid membrane containing dibenzo-18-crown-6. J. Am. Chem. Soc. **109**, 7042–7047 (1987). doi:10.1021/ja00257a023

7. Rounaghi, G.H., Sanavi, R.: Discussion on the complexing ability of macrocyclic ligand, 12-crown-4 with Li^+ cation in some binary mixed non-aqueous solvents. Polish J. Chem. **80**, 719–727 (2006)

8. Taghdiri, M., Rofouei, M.K., Shamsipur, M.: Conductance study of the thermodynamics of complexation of K^+, Rb^+, Cs^+ and Tl^+ ions with dibenzo-24-crown-8 in binary acetonitrile-nitromethane mixtures. J. Incl. Phenom. Macrocycl. Chem. **58**, 181–186 (2007). doi:10.1007/s10847-006-9142-x

9. Rounaghi, G.H., Tarahomi, S., Mohajeri, M.: A conductometric study of complexation reaction between dibenzo-24-crown-8 with yttrium cation in some binary mixed non-aqueous solvents. J. Incl. Phenom. Macrocycl. Chem. **63**, 319–325 (2009). doi:10.1007/s10847-008-9525-2

10. Takeda, Y.: A conductance study of alkali metal ion-18-crown-6 complexes in N,N-dimethylformamide. Bull. Chem. Soc. Jpn. **54**, 3133–3136 (1981). doi:10.1246/bcsj.54.3133

11. D'Aprano, A., Sesta, B.: Complexation of diaza crown compounds with some alkali metal ions in acetonitrile and in methanol at 25 °C. J. Phys. Chem. **99**, 2415–2422 (1987). doi:10.1021/j100293a042

12. Rounaghi, G.H., Mohajeri, M., Ahmadzadeh, S., Tarahomi, S.: A thermodynamic study of interaction of Na^+ cation with benzo-15-crown-5 in binary mixed non-aqueous solvents. J. Incl. Phenom. Macrocycl. Chem. **63**, 365–372 (2009). doi:10.1007/s10847-009-9530-0

13. Boosaeeidi, F., Rounaghi, G.H., Ghaemi, A.: Conductometric studies of solvent influence upon complex formation between 4′-nitrobenzo-15-crown-5 and Ni^{2+}, Co^{2+} and Cu^{2+} in acetonitrile-methanol binary mixtures. Asian J. Chem. **20**, 6369–6375 (2008)

14. Chamsaz, M., Rounaghi, G.H., Sovizi, M.R.: Polarographic study of the interaction of Tl^+, Pb^{2+} and Cd^{2+} cations with 18-crown-6 in binary nonaqueous solvents. Russ. J. Inorg. Chem. **50**, 413–417 (2005)

15. Thaler, A., Cox, B.G., Schneider, H.: Stability constants of aza-oxa-crown ether complexes with silver(I) in nonaqueous polar

solvents. Inorg. Chim. Acta **351**, 123–132 (2003). doi:10.1016/S0020-1693(03)00193-2

16. Rounagh, G.H., Popov, A.I.: Thermodynamic studies of the complexation of dibenzo-27-crown-9 and dibenzo-24-crown-8 with cesium ion in mixed nonaqueous solvents. J. Inorg. Chim. Acta **114**, 145–149 (1986). doi:10.1016/S0020-1693(00)86446-4

17. Volkova, N.L., Parfenyuk, E.V.: Selective interactions of 18-crown-6 with D-glucose and D-galactose in aqueous solutions: titration calorimetry, densimetry, viscosimetry. Thermochim. Acta **435**, 108–112 (2005). doi:10.1016/j.tca.2005.05.002

18. GENPLOT, A Data Analysis and Graphical Plotting Program for Scientist and Engineers. Computer Graphic Service, Ltd., Ithaca, NY, USA (1989)

19. Rounaghi, G.H., Eshaghi, Z., Ghiamati, E.: Thermodynamic study of complex formation between 18-crown-6 and potassium ion in some binary non-aqueous solvents using conductometric method. Talanta **44**, 275–282 (1997). doi:10.1016/S0039-9140(96)02045-0

20. Rounaghi, G.H., Rahimi Bajestani, M., Ghaemi, A.: Stabilities of alkaline earth metal ion complexes with dicyclohexano-18-crown-6 in acetonitrile-water binary solutions. Asian J. Chem. **20**, 299–307 (2008)

21. Rounaghi, G.H., Masroornia, M., Ghaemi, A., Rahchamani, H.A.: Thermodynamic behaviour of complexation process between 15-crown-5 with Li^+, Na^+ and K^+ cations in acetonitrile-water and 1-propanol-water binary media. Asian J. Chem. **19**, 1679–1686 (2007)

22. Jóźzwiak, M.: The effect of properties of water-organic solvent mixtures on the salvation enthalpy of 12-crown-4, 15-crown-5, 18-crown-6 and benzo-15-crown-5 ethers at 298.15 K. Thermochim. Acta **417**, 31–41 (2004). doi:10.1016/j.tca.2004.01.003

23. Rounaghi, G.H., Mohammad Zade Kakhki, R.: Thermodynamic study of complex formation between dibenzo-18-crown-6 and UO_2^{2+} cation in different non-aqueous binary solutions. J. Incl. Phenom. Macrocycl. Chem. **63**, 117–122 (2009). doi:10.1007/s10847-008-9494-5

24. Buschmann, H.J., Mutihac, R.C., Schollmeyer, E.: Complex formation of 18-crown-6 with metal cations and ammonium ions in dioxane-water mixtures. Thermochim. Acta **472**, 17–19 (2008). doi:10.1016/j.tca.2008.03.010