ORIGINAL ARTICLE

Thermodynamic behavior of complexation process between benzo-15-crown-5 with Li$^+$, Na$^+$, K$^+$, and NH$_4^+$ cations in acetonitrile–methanol binary media

G. H. Rounaghi · E. Razavipanah · F. Kaveh

Abstract The stability constants of 1:1 (M:L) complexes of benzo-15-crown-5 (B15C5) with Li$^+$, Na$^+$, K$^+$ and NH$_4^+$ cations, the Gibbs standard free energies (ΔG_c°), the standard enthalpy changes (ΔH_c°) and standard entropy changes (ΔS_c°) for formation of these complexes in acetonitrile–methanol (AN–MeOH) binary mixtures have been determined conductometrically. The conductance data show that the stoichiometry of the complexes formed between the macrocyclic ligand and the studied cations is 1:1 (M:L). In most cases, addition of B15C5 to solutions of these cations, causes a continuous increase in the molar conductivities which indicates that the mobility of complexed cations is more than the uncomplexed ones. The stability constants of the complexes were obtained from fitting of molar conductivity curves using a computer program, GENPLOT. The results show that the selectivity order of B15C5 for the metal cations changes with the nature and composition of the binary mixed solvent. The values of standard enthalpy changes (ΔH_c°) for complexation reactions were obtained from the slope of the van't Hoff plots and the changes in standard entropy (ΔS_c°) were calculated from the relationship $\Delta G_{c,298.15}^\circ = \Delta H_c^\circ - 298.15\Delta S_c^\circ$. A non-linear behavior was observed between the stability constants (log K$_f$) of the complexes and the composition of the acetonitrile–methanol (AN–MeOH) binary solution. The results obtained in this study, show that in most cases, the complexes formed between B15C5 and Li$^+$, Na$^+$, K$^+$ and NH$_4^+$ cations are both enthalpy and entropy stabilized and the values of these thermodynamic quantities change with the composition of the binary solution.

Introduction

Crown ethers are known for their ability to strongly solvate cations. In other words the equilibrium is strongly towards the formation of complex. The oxygen atoms in polar ring, are ideally situated to coordinate with a cation in the interior of the ring, whereas the exterior of the ring is hydrophobic. The result is that the complexed cations are soluble in nonpolar solvents. Due to their ability to bind strongly and selectivity to metal cations and substrate molecules, macrocyclic polyethers and their derivatives can find use in many diverse processes such as construction of ion-selective electrodes [1–3], phase transfer catalysts [4, 5], extraction of metal ions [6–8], chiral separation [9] and membrane separation process [10].

It has been suggested [11] that the formation of a complex between an alkali metal cation and a macrocyclic polyether is due to ion–dipole interactions and is, therefore, similar in nature to ordinary solvation, although more favorable because of the appropriate configuration and the polydentate character of the ligand. The specificity of the complexation is due to the required fit between the ionic size and the size of the macrocyclic ring, nevertheless, it may be affected by the medium [12], as the macrocyclic polyether must compete with the surrounding solvent for the cation.

Complexing of alkali cations by neutral molecules is an uncommon phenomenon, however, it has now been observed not only with the cyclic polyethers, but also with a number of antibiotics, such as valinomycin, nanoctin, monactin, etc.,

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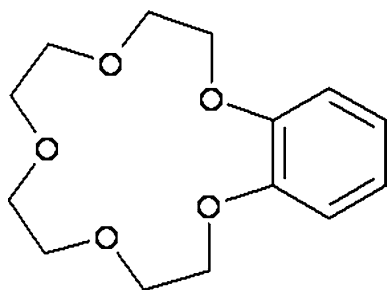e-mail: ghrounaghi@yahoo.com

which have macrocyclic structures containing ester, ether and peptide groups. Stability constants for several antibiotic-alkali cation systems have been reported [13–15].

The thermodynamics of formation of some ionic complexes of macrocyclic polyethers in various pure solvents, has recently been investigated by several researchers [16, 17], but the data in mixed non-aqueous solutions especially for complexation of small crown ethers with metal cations are scarce [18–22].

In this paper, we report the results of thermodynamic study of complexation reactions between benzo-15-crown-5 with Li^+, Na^+, K^+ and NH_4^+ cations in acetonitrile–methanol (AN–MeOH) binary mixtures at different temperatures using conductometric method. The goal of the present work is to study the influence of nature and composition of solvent systems in selectivity and thermodynamics of complexation processes between these alkali cations and macrocyclic ligand, B15C5.

Experimental

Reagents and solvents: benzo-15C5 (Scheme 1) (Merck, Darmstadt, Germany), sodium nitrate and potassium nitrate both from (Riedel de Häen, Seelze, Germany), ammonium nitrate (Merck, Darmstadt, Germany) and lithium nitrate (Merck, Darmstadt, Germany) were used without further purification. Acetonitrile (Merck, Darmstadt, Germany) and methanol (Merck, Darmstadt, Germany) with the highest purity were used as solvents. The experimental procedure to obtain the stability constants of complexes was as follows: a solution of metal salt (1×10^{-4} M) was placed in a titration cell and the conductance of the solution was measured, then a step-by-step increase of the crown ether solution prepared in the same solvent (2×10^{-3} 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.

Scheme 1 Benzo-15-crown-5

Apparatus

The conductance measurements were performed on a digital AMEL conductivity apparatus, model 60, 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 to which an alternating potential was applied. A conductometric cell with a cell constant of 0.73 cm^{-1} was used throughout the studies.

Results

The conductometric profiles, for complexation of B15C5 with Li^+, Na^+, K^+ and NH_4^+ cations in AN–MeOH binary systems were studied at different temperatures. In these profiles, the changes of molar conductivity (Λ_m) versus the ligand to cation mole ratios, $[L]_t/[M]_t$, were studied at various temperatures. The stability constants of the complexes at each temperature were calculated from variation of molar conductivity as a function of $[B15C5]_t/[M^+]_t$ molar ratio plots using a GENPLOT computer program [23]. The details of calculation of stability constants of 1:1 [M:L] complexes by conductometric method have been described in Ref. [24].

Two conductometric profiles for $(B15C5.K)^+$ and $(B15C5.Na)^+$ complexes in AN–MeOH binary solutions are shown in Figs. 1 and 2, respectively. The stability constants (log K_f) for $(B15C5.M)^+$ ($M^+ = Li^+$, Na^+, K^+ and NH_4^+) complexes in various solvent systems are listed in Table 1. Assuming that the activity coefficients of the cation and the complex have the same value, K_f is a thermodynamic equilibrium constant on the molar concentration scale, related to the Gibbs standard free energy of complexation reaction, ΔG_c°. The van't Hoff plots of ln K_f versus 1/T for complexes were constructed. The changes in the standard enthalpy (ΔH_c°) for complexation reactions were obtained 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 the standard entropy (ΔS_c°) were calculated from the relationship $\Delta G_{c,298.15}^\circ = \Delta H_c^\circ - 298.15\Delta S_c^\circ$. The thermodynamic data are summarized in Table 2. The changes of stability constants (log K_f) versus the mole fraction of methanol in AN–MeOH binary system at different temperatures are shown in Fig. 4. The changes of stability constants (log K_f) versus the ionic radii of the studied cations in various solvent systems are shown in Fig. 5.

Discussion

As is seen from Fig. 1, addition of B15C5 to K^+ cation solution in AN–MeOH binary systems at different
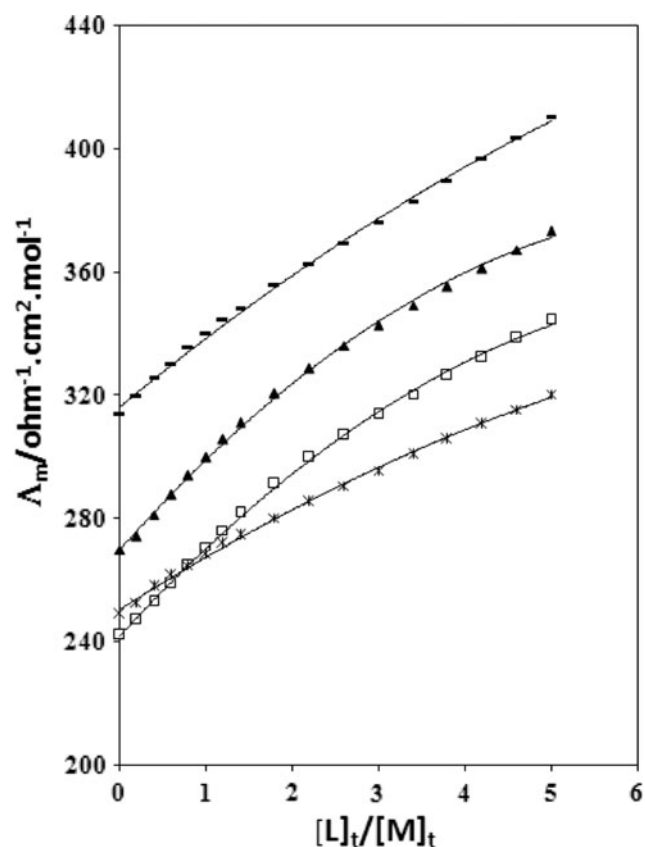
Fig. 1 Molar conductivity–mole ratio plots for (Benzo-15C5.K)$^+$ complex in AN–MeOH binary system (mol%AN = 50) at different temperatures: 45 °C (*solid line*), 35 °C (*filled triangle*), 25 °C (*open square*) 15 °C (*asterisk*)
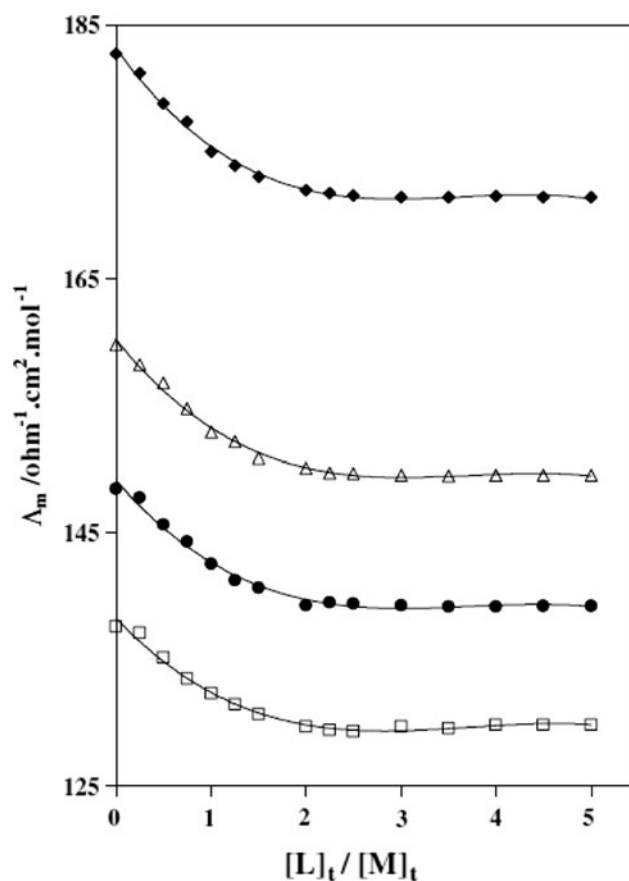

Fig. 2 Molar conductivity-mole ratio plots for (Benzo-15C5.Na)$^+$ complex in pure AN at the different temperatures: 45 °C (*open square*), 35 °C (*filled circle*), 25 °C (*open triangle*), 15 °C (*filled diamond*)

temperatures results in an increase in molar conductivity which indicates that the (B15C5.K)$^+$ complex is more mobile than free solvated K$^+$ cation. Similar behavior was observed for most of the systems, but as is seen from Fig. 2, addition of B15C5 to Na$^+$ cation in pure AN shows a decrease in molar conductivity which indicates that the (B15C5.Na)$^+$ complex in this solution is less mobile than free solvated Na$^+$ cation.

It is clear from Figs. 1 and 2 that the slope of each curve 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 order to make more clear the 1:1 [M: L] complexation model, the fitting and experimental curves for (B15C5.K)$^+$ complex in AN–MeOH binary solution (mol%AN = 50) are shown in Fig. 3. As evident from this figure, there is a very good agreement between the fitting and the experimental data.

The changes of stability constant (log K$_f$) of (B15C5. NH$_4$)$^+$ complex versus the mole fraction of methanol in AN–MeOH binary system at different temperatures are shown in Fig. 4. As is obvious in this figure, the change of the stability constant of (B15C5.NH$_4$)$^+$ complex with the

composition of acetonitrile–methanol binary solution is not linear. A non-linear behavior was also observed for (B15C5.Li)$^+$, (B15C5.Na)$^+$ and (B15C5.K)$^+$ complexes in this binary system. This behavior is probably due to heteroselective solvation of the cation and ligand and also it can be due to some kinds of solvent–solvent interactions between these two solvent molecules, which results in changing the structure of the solvents when they are mixed with one another. It has been shown that there is an interaction between acetonitrile and methanol molecules (Kass. = 1.23) via hydrogen bonding in their binary mixtures [25].

The changes of log K$_f$ of complexes formed between B15C5 and Li$^+$, Na$^+$, K$^+$ and NH$_4^+$ cations versus the ionic diameter in AN–MeOH binary mixtures, in pure AN and in pure MeOH and also in their binary solutions are shown in Fig. 4. The sequence of stabilities of these complexes in a binary solution of AN–MeOH (mol% AN 75) is: (B15C5.NH$_4$)$^+$ > (B15C5.Na)$^+$ > (B15C5.Li)$^+$ > (B15C5.K)$^+$, but in the case of another AN–MeOH binary system (mol% AN 50) it was found to be: (B15C5.K)$^+$ > (B15C5.Na)$^+$ > (B15C5.Li)$^+$ > (B15C5.NH$_4$)$^+$. The

Table 1 log K_f values of B15C5.M^+ (M^+ = Li^+, Na^+, K^+ and NH_4^+) complexes in AN–MeOH binary mixtures at different temperatures

Medium	log K_f ± SD[a]			
	15 °C	25 °C	35 °C	45 °C
(Benzo-15C5.Li)$^+$				
Pure AN[b]	2.70 ± 0.14	2.73 ± 0.10	2.73 ± 0.11	2.75 ± 0.10
75%AN–25%MeOH	2.70 ± 0.11	2.70 ± 0.12	2.55 ± 0.13	2.70 ± 0.12
50%AN–50%MeOH	2.70 ± 0.12	2.56 ± 0.13	2.55 ± 0.14	2.71 ± 0.10
25%AN–75%MeOH	2.71 ± 0.10	2.55 ± 0.12	2.54 ± 0.15	2.55 ± 0.14
Pure MeOH	2.72 ± 0.10	2.72 ± 0.11	2.70 ± 0.10	2.70 ± 0.12
(Benzo-15C5.Na)$^{+c}$				
Pure AN[b]	4.01 ± 0.10	3.97 ± 0.10	3.98 ± 0.12	4.11 ± 0.16
70.0%AN–30.0%MeOH	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
(Benzo-15C5.K)$^+$				
Pure AN[b]	2.50 ± 0.30	2.50 ± 0.30	2.50 ± 0.20	2.53 ± 0.18
75%AN–25%MeOH	2.73 ± 0.10	2.52 ± 0.20	2.70 ± 0.12	2.70 ± 0.12
50%AN–50%MeOH	2.91 ± 0.06	3.20 ± 0.03	3.27 ± 0.03	2.83 ± 0.08
25%AN–75%MeOH	2.53 ± 0.17	2.81 ± 0.07	2.60 ± 0.28	2.70 ± 0.09
Pure MeOH	3.20 ± 0.12	2.82 ± 0.06	2.70 ± 0.14	2.79 ± 0.06
(Benzo-15C5.NH$_4$)$^+$				
Pure AN[b]	3.14 ± 0.03	3.40 ± 0.02	3.22 ± 0.06	2.80 ± 0.08
75%AN–25%MeOH	3.10 ± 0.06	3.30 ± 0.09	2.60 ± 0.30	3.10 ± 0.06
50%AN–50%MeOH	2.53 ± 0.20	2.50 ± 0.20	2.51 ± 0.20	2.53 ± 0.23
25%AN–75%MeOH	2.74 ± 0.10	2.71 ± 0.12	2.71 ± 0.12	2.51 ± 0.20
Pure MeOH	2.77 ± 0.12	2.82 ± 0.09	2.65 ± 0.04	2.58 ± 0.04

[a] SD = standard deviation

[b] The composition of each solvent system is expressed in mol% of each solvent

[c] Reference [34]

order of stability of the complexes in pure MeOH and pure AN is: (B15C5.Na)$^+$ > (B15C5.K)$^+$ ≈ (B15C5.NH$_4$)$^+$ > (B15C5.Li)$^+$ and (B15C5.Na)$^+$ > (B15C5.NH$_4$)$^+$ > (B15C5.Li)$^+$ > (B15C5.K)$^+$, respectively. The results obtained in this study, reveal that the selectivity of benzo-15-crown-5 for the studied cations in pure and also in binary mixed non-aqueous solutions changes with the nature and composition of the solvent systems.

It is difficult to generalize from such limited data set about the effect of factors that influence the cation selectivity. Cavity size, through the hole-size relationship, has generally been regarded as the prime parameter for selectivity. Other parameters are the number and type of donor atoms in the polyether ring, possible variation in ring conformation and the solvation energies of the species involved in complexation processes [26]. The changes of stability constants (log K_f) of complexes versus the ionic diameter, as illustrated in Fig. 5 are not as straight forward

as is suggested by the simple hole-size consideration in all solvent systems. The hole-size concept states that when the diameter of the cation and the hole in the crown ether are the same size, the latter is selective for the former [27]. However, this generalization dose not really holds for all studied cases. The cavity size of B15C5 (0.86–1.1 Å) closely matches the ionic size of Na$^+$ cation (0.98 Å), but the results reveal that in some of the AN–MeOH binary solutions, B15C5 binds to the K$^+$ and NH$_4^+$ cations more strongly than Na$^+$ cation. Therefore, the cavity-size effect is no longer the dominant factor in complexation reactions between B15C5 and the studied cations, in these binary solutions. It seems reasonable that the hole size idea would be most valid with the most rigid systems. A flexible ligand can accommodate a wider variety of cations than can a rigid one. In the case of flexible ligands such as crown ethers, other factors such as the cation's solvation enthalpy and ligand conformations become important [27]. The

Table 2 Thermodynamic parameters for B15C5.M$^+$ (M$^+$ = Li$^+$, Na$^+$, K$^+$ and NH$_4^+$) complexes in AN–MeOH binary mixtures

Medium	log K$_f$ ± SD[a] (25 °C)	$-\Delta G_c^\circ$ ± SD[a] (KJ/mol)	ΔH_c° ± SD[a] (KJ/mol)	ΔS_c° ± SD[a] (J/mol K)
(Benzo-15C5.Li)$^+$				
Pure AN[b]	2.73 ± 0.10	15.60 ± 0.61	3 ± 1	61 ± 2
75%AN–25%MeOH	2.70 ± 0.12	15.40 ± 0.76	c	44 ± 22
50%AN–50%MeOH	2.56 ± 0.13	14.58 ± 0.77	c	c
25%AN–75%MeOH	2.55 ± 0.12	14.60 ± 0.77	−9 ± 4	19 ± 15
Pure MeOH	2.72 ± 0.11	15.52 ± 0.72	c	c
(Benzo-15C5.Na)$^{+d}$				
Pure AN[b]	3.97 ± 0.10	22.70 ± 0.60	c	99.2 ± 16.7
75%AN–25%MeOH	3.14 ± 0.05	17.90 ± 0.30	−15.5 ± 3.3	c
50%AN–50%MeOH	2.90 ± 0.03	16.60 ± 0.20	c	81.0 ± 14.9
25%AN–75%MeOH	2.84 ± 0.06	16.20 ± 0.30	−2.7 ± 0.7	45.4 ± 2.2
Pure MeOH	2.86 ± 0.04	16.40 ± 0.20	−17.5 ± 1.4	c
(Benzo-15C5.K)$^+$				
Pure AN[b]	2.50 ± 0.30	14.10 ± 1.70	3 ± 1	58 ± 4
75%AN–25%MeOH	2.52 ± 0.20	14.40 ± 1.10	c	52 ± 31
50%AN–50%MeOH	3.20 ± 0.03	18.34 ± 0.16	c	c
25%AN–75%MeOH	2.81 ± 0.07	16.12 ± 0.43	c	69 ± 41
Pure MeOH	2.82 ± 0.06	16.11 ± 0.32	c	c
(Benzo-15C5.NH$_4$)$^+$				
Pure AN[b]	3.40 ± 0.02	18.90 ± 0.14	c	c
75%AN–25%MeOH	3.30 ± 0.09	18.60 ± 0.53	c	c
50%AN–50%MeOH	2.50 ± 0.20	14.40 ± 1.20	c	c
25%AN–75%MeOH	2.71 ± 0.12	15.50 ± 0.69	−12 ± 5	c
Pure MeOH	2.82 ± 0.09	16.11 ± 0.52	−13 ± 5	c

[a] SD = standard deviation

[b] The composition of each solvent system is expressed in mol% of each solvent

[c] With high uncertainty

[d] Reference [34]

hole-size relationship is better represented by the cryptands which are relatively rigid species [27].

The results obtained from studying of complexation reactions of 15-crown-5 (15C5) and benzo-15-crown-5 (B15C5) with Li$^+$, Na$^+$, K$^+$ and NH$_4^+$ cations in methanol solution at 25 °C are given in Table 3. As is obvious from these data, the placement of a benzo group in a 15C5 residue decreases the binding strength of B15C5 to Li$^+$, Na$^+$, K$^+$ and NH$_4^+$ cations. This is attributable to the fact that B15C5 has two aromatic ether oxygen atoms whose basicity is lower than those of the aliphatic ether oxygen atoms [28]. Since the sp^2 hybridized oxygen atoms are less basic than the sp^3 hybridized oxygen atoms in the parent and sp^2-hybridized electron pairs are perpendicular to the aromatic ring [27], therefore, the two aromatic ether oxygen atoms have lower basicity than those of the aliphatic ether oxygen atoms.

The thermodynamic data for complexation processes between B15C5 and the studied cations, are summarized in Table 2. As is evident from this Table, in most cases, the Gibbs standard free energy (ΔG_c°) for the complexation reactions between Li$^+$, Na$^+$ and NH$_4^+$ cations and B15C5 becomes more negative with increasing the concentration of acetonitrile in AN–MeOH binary solutions. Therefore, the complexes become more stabilized as the mole fraction of AN increases in these binary solvents. In the complexation process, the solvent and crown ether molecules compete in binding to the metal cations. When the donor properties of the solvent are low, the cation is poorly solvated and can easily be complexed by the crown ether which results in formation of a strong complex in solution. In a strong solvating solvent such as MeOH with a relatively high Gutmann Donor Number (DN = 20), the solvation of the metal cations and possibly of the ligand should be stronger
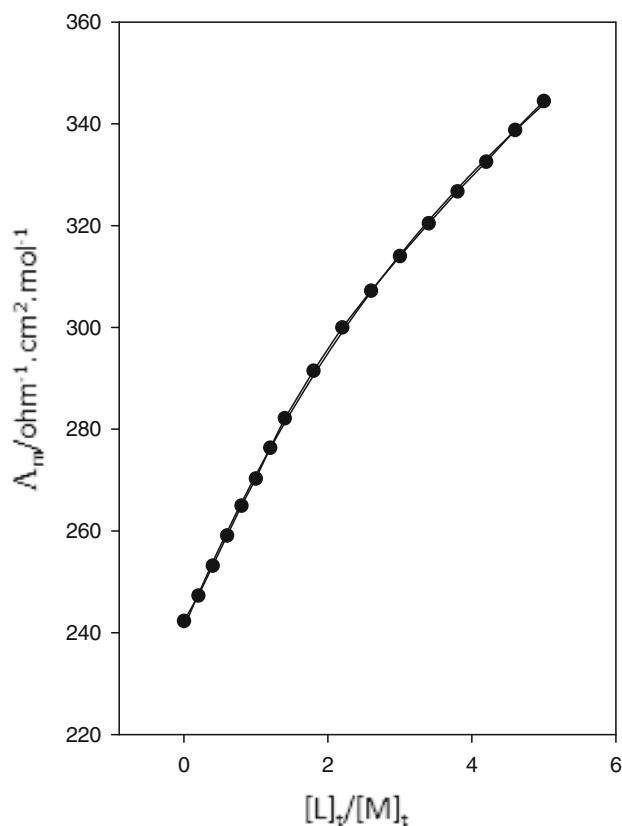
Fig. 3 The fitting and experimental curves for (B15C5.K)$^+$ complex in AN–MeOH binary system (mol%AN = 50) at 25 °C
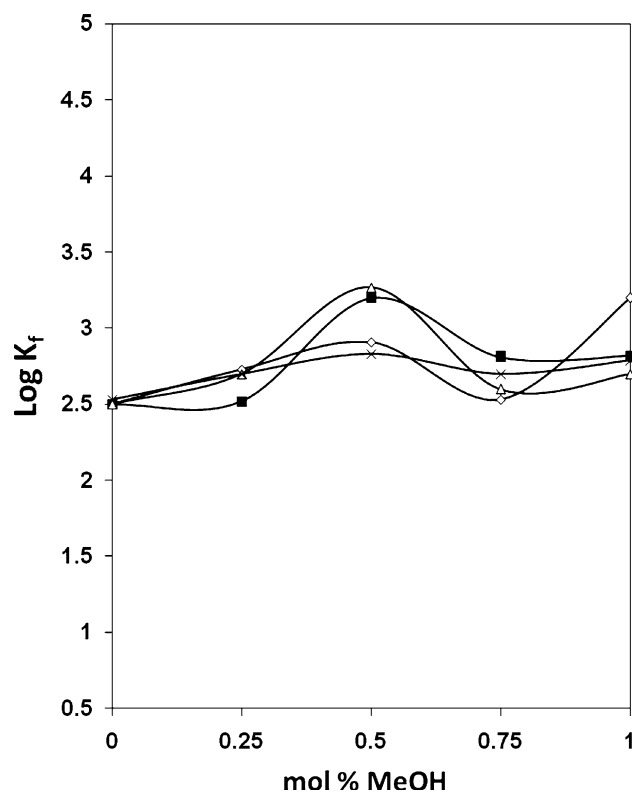

Fig. 4 Changes of the stability constant (log K_f) of (B15C5.NH4)$^+$ complex with the composition of AN–MeOH binary system at different temperatures: 45 °C (*cross*), 35 °C (*open triangle*), 25 °C (*filled square*), 15 °C (*open diamond*)

than those of solvents of lower solvating abilities such as AN (DN = 14.1), therefore, the formation of the complexes is weakened as the concentration of MeOH increases in AN–MeOH binary system. As is seen in Table 2, the values of standard enthalpy changes (ΔH_c°) for formation of all complexes (with a few exceptions) are negative, therefore, the complexation reactions between B15C5 and the studied cations are enthalpy stabilized. Furthermore, for some of the complexation processes the slope of the van't Hoff plots is very small which shows that the complex formation reactions between the studied cations and B15C5 are athermic. In addition, as is obvious from this Table, a non-linear behaviour is observed for changes of ΔH_c° values for the complexation reactions with the composition of AN–MeOH binary solutions. The data in Table 2, show that in most cases, the values of standard entropy changes (ΔS_c°) for formation of (B15C5.Li)$^+$, (B15C5.Na)$^+$ and (B15C5.K)$^+$ complexes are positive, therefore, the complexation reactions between B15C5 and Li$^+$, Na$^+$ and K$^+$ cations are stabilized from entropy view point.
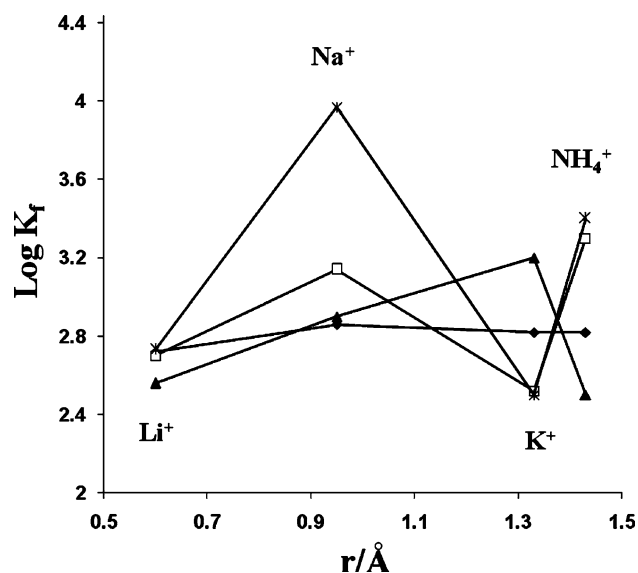

Fig. 5 Changes of log K_f for (B15C5.Li)$^+$, (B15C5.Na)$^+$, (B15C5.K)$^+$ and (B15C5.NH$_4$)$^+$ complexes versus cationic radii in various solvent systems at 25 °C: (mol%AN: *filled diamond* = 0.0, *filled triangle* = 50, *open square* = 75, *asterisk* = 100)

Table 3 log K_f values of the 15-crown-5 and benzo-15-crown-5 complexes with alkali cations in methanol solution at 25 °C

MeOH	Li$^+$	Na$^+$	K$^+$	NH$_4^+$
15C5	–	3.27[a]	3.6[b]	3.03[c]
B15C5	2.72[d] (2.31[b])	2.86[d] (2.87[c])	2.82[d] (2.80[c])	2.82[d]

[a] Reference [31–33 (Average of three published values)]

[b] Reference [30]

[c] Reference [29]

[d] This work

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