

Complexation of 4'-nitrobenzo-15-crown-5 with Li^+ , Na^+ , K^+ , and NH_4^+ cations in acetonitrile–methanol binary solutions

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Abstract The complexation processes between Li^+ , Na^+ , K^+ and NH_4^+ cations with macrocyclic ligand, 4'-nitrobenzo-15C5, were studied in acetonitrile–methanol (AN–MeOH) binary mixtures at different temperatures using conductometric method. The conductance data show that the stoichiometry of the complexes formed between the ligand and Li^+ , Na^+ , K^+ and NH_4^+ cations is 1:1(M:L). Addition of 4'-nitrobenzo-15C5 to these cations solution, causes a continuous increase in the molar conductivities which indicates that the mobility of the complexed cations is more than the uncomplexed ones. The values of stability constants of the complexes were determined from conductometric data using GENPLOT computer program. The obtained results show that the selectivity order of the ligand for Li^+ , Na^+ , K^+ and NH_4^+ cations changes with the nature and composition of the binary mixed solvent. The values of thermodynamic parameters (ΔH°_c , ΔS°_c) for formation of the complexes were obtained from temperature dependence of the stability constants using the van't Hoff plot. The results show that the complexes are both enthalpy and entropy stabilized. A non-linear behavior was observed between the stability constants ($\log K_f$) of the complexes and the composition of the AN–MeOH binary solution.

Keywords 4'-Nitrobenzo-15-crown-5 · Li^+ , Na^+ , K^+ and NH_4^+ ; Acetonitrile–methanol · Conductometry

Introduction

The first macrocyclic polyethers were reported by Luttringhaus and Ziegler in 1937. However, the importance of these compounds began from 1967 with the synthesis of dibenzo-18-crown-6 (DB18C6) by Pedersen [1] and the observation that this compound and its homologues form very strong complexes with alkali and alkaline earth metal cations. Macrocyclic compounds play an important role in chemistry such as their application in construction of ion-selective electrodes [2–6], membrane separation process [7], fiber optic chemical sensors [8], chiral separation [9], preconcentration of metal ions [10, 11] and phase transfer catalysts [12].

Studies of crown ether complexation in different solvents show that the thermodynamic and kinetic parameters are affected by the nature and composition of the solvent system [13, 14]. Although the complexation of crown ethers with metal cations has been extensively studied in both aqueous and non-aqueous media, but most of these investigations have been carried out in pure solvents [15, 16] and the data about the stability constants and also the thermodynamic parameters of metal ion complexes with crown ethers in mixed non-aqueous solvents are sparse [17–22].

In this paper, the results of thermodynamic study for complexation reactions between 4'-nitrobenzo-15-crown-5 (Scheme 1) with Li^+ , Na^+ , K^+ and NH_4^+ cations in acetonitrile–methanol (AN–MeOH) binary mixtures at different temperatures using conductometric method are reported. The purpose of this work is to see how the selectivity and thermodynamics of complexation reactions between the alkali cations and the macrocyclic ligand are affected by the nature of cations, substituent in the ligand and also by the composition of acetonitrile–methanol binary solution.

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Experimental

Reagents and solvents: 4'-nitrobenzo-15C5 (Merck, Darmstadt, Germany), sodium nitrate and potassium nitrate (Riedel de Haen, 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.

Apparatus

The conductance measurements were performed on a digital AMEL conductivity apparatus, model 60, in a water bath thermostated at a constant temperature which

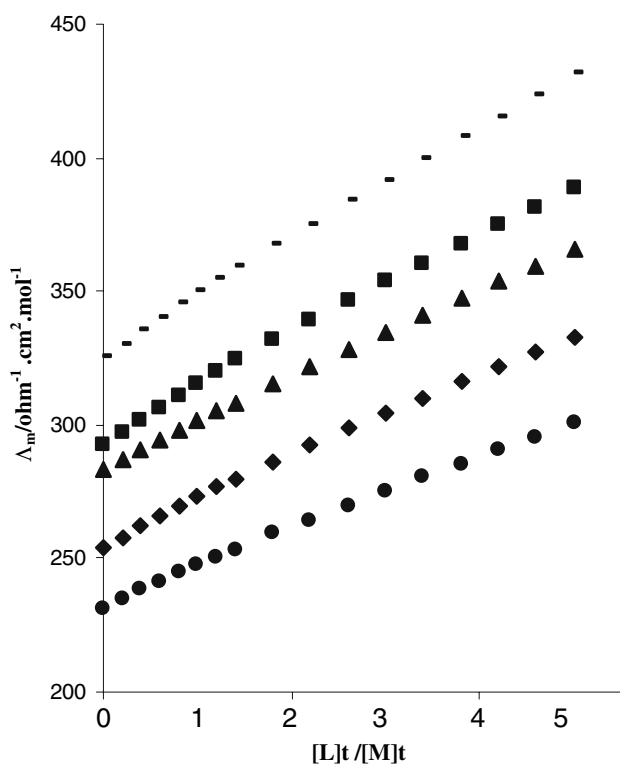


Fig. 1 Molar conductance-mole ratio plots for (4'-nitrobenzo-15C5.Li⁺) complex in AN–MeOH (mol% AN = 25) binary system at different temperatures: 55 °C (□), 45 °C (■), 35 °C (▲), 25 °C (◆), 15 °C (●)

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 changes of molar conductance (Λ_m) versus the ligand to cation mole ratios, $[L]_t/[M]_t$, for complexation of 4'-nitrobenzo-15C5 with Li⁺, Na⁺, K⁺ and NH₄⁺ cations in acetonitrile–methanol binary systems were studied at different temperatures. $[L]_t$ is the total concentration of 4'-nitrobenzo-15C5 and $[M]_t$ is the total concentration of the Li⁺, Na⁺, K⁺ and NH₄⁺ cations. Two typical series of molar conductance values as a function of $[L]_t/[M]_t$ for (4'-nitrobenzo 15C5.K⁺) and (4'-nitrobenzo 15C5.Li⁺) in AN–MeOH binary solutions are shown in Figs. 1 and 2, respectively.

The stability constants of the complexes at each temperature were obtained from variation of molar conductance as a function of $[L]_t/[M]_t$ molar ratio plots using a GENPLOT computer program. The stability constants ($\log K_f$) for 4'-nitrobenzo-15C5. M⁺ (M⁺ = Li⁺, Na⁺, K⁺ and NH₄⁺)

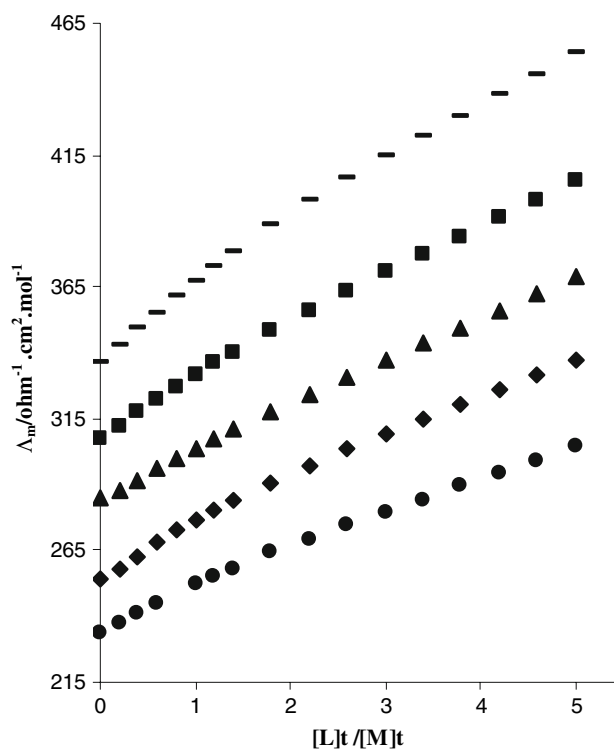


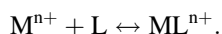
Fig. 2 Molar conductance-mole ratio plots for (4'-nitrobenzo-15C5.K⁺) complex in AN–MeOH (mol% AN = 50) binary system at different temperatures: 55 °C (□), 45 °C (■), 35 °C (▲), 25 °C (◆), 15 °C (●)

Table 1 Log K_f values of 4'-nitrobenzo-15C5.Mⁿ⁺ (Mⁿ⁺ = Li⁺, Na⁺, K⁺ and NH₄⁺) complexes in AN–MeOH binary mixtures at different temperatures

Medium	Log $K_f \pm$ SD ^a			
	15 °C	25 °C	35 °C	45 °C
(4'-nitrobenzo-15C5.Na ⁺)				
90%AN-10% MeOH ^b	2.83 ± 0.06	2.73 ± 0.12	2.72 ± 0.12	2.78 ± 0.08
75%AN-25% MeOH	2.70 ± 0.06	2.80 ± 0.07	2.70 ± 0.10	2.80 ± 0.09
50%AN-50% MeOH	2.80 ± 0.09	2.70 ± 0.10	2.80 ± 0.09	2.80 ± 0.06
25%AN-75% MeOH	2.75 ± 0.09	2.91 ± 0.07	2.67 ± 0.15	2.70 ± 0.12
Pure MeOH	2.60 ± 0.08	2.71 ± 0.15	2.60 ± 0.30	2.73 ± 0.10
(4'-nitrobenzo-15C5.K ⁺)				
90%AN-10% MeOH ^b	3.01 ± 0.02	3.01 ± 0.04	2.63 ± 0.05	2.81 ± 0.07
75%AN-25% MeOH	2.93 ± 0.04	2.85 ± 0.06	2.75 ± 0.04	2.59 ± 0.04
50%AN-50% MeOH	2.82 ± 0.05	2.98 ± 0.05	2.83 ± 0.07	2.78 ± 0.04
25%AN-75% MeOH	2.73 ± 0.05	2.60 ± 0.04	2.03 ± 0.07	2.63 ± 0.06
Pure MeOH	2.75 ± 0.04	2.73 ± 0.06	2.73 ± 0.17	2.73 ± 0.13
(4'-nitrobenzo-15C5. NH ₄ ⁺)				
90%AN-10% MeOH ^b	2.61 ± 0.05	2.81 ± 0.07	2.81 ± 0.08	2.75 ± 0.10
75%AN-25% MeOH	2.69 ± 0.05	2.83 ± 0.08	2.78 ± 0.08	2.76 ± 0.09
50%AN-50% MeOH	2.77 ± 0.09	2.59 ± 0.05	2.81 ± 0.07	2.77 ± 0.09
25%AN-75% MeOH	2.88 ± 0.04	2.92 ± 0.06	2.72 ± 0.05	2.73 ± 0.11
Pure MeOH	3.01 ± 0.05	2.82 ± 0.07	2.79 ± 0.07	2.71 ± 0.06
(4'-nitrobenzo-15C5.Li ⁺)				
90%AN-10% MeOH ^b	c	c	c	c
75%AN-25% MeOH	2.82 ± 0.07	2.81 ± 0.07	2.75 ± 0.09	2.70 ± 0.10
50%AN-50% MeOH	2.81 ± 0.06	2.81 ± 0.08	2.82 ± 0.07	2.70 ± 0.10
25%AN-75% MeOH	2.61 ± 0.04	2.73 ± 0.04	2.83 ± 0.08	2.74 ± 0.05
Pure MeOH	2.81 ± 0.04	3.05 ± 0.03	2.70 ± 0.11	2.72 ± 0.10

^a SD = Standard deviation^b The composition of each solvent system is expressed in mole% of each solvent^c Crown ether is insoluble

complexes in various solvent systems are listed in Table 1. The 1:1 complexation reaction of a metal cation, Mⁿ⁺, with a crown ether is represented by the following equilibrium:



The corresponding equilibrium constant, K_f , is given by:

$$K_f = \frac{[ML^{n+}] f_{ML}^{n+}}{[M^{n+}][L] f_M^{n+} f_L}$$

where $[ML^{n+}]$, $[M^{n+}]$ and $[L]$ denote the molar concentration of the complex, metal cation and crown ether and f indicates the activity coefficient of the species indicated. Under the highly dilute conditions which employed in these experiments, the $f_{ML}^{n+}/f_M^{n+} f_L$ is essentially unity and, therefore, the equilibrium constants obtained in this study are thermodynamic equilibrium constants.

The van't Hoff plots of $\ln K_f$ versus $1/T$ for all of the investigated systems 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 $\Delta G^\circ_c = \Delta H^\circ_c -$

$298.15\Delta S^\circ_c$. The thermodynamic data are summarized in Table 2. The changes of stability constants ($\log K_f$) versus the ionic radii in various solvent systems are shown in Fig. 4.

Discussion

As is seen from Figs. 1 and 2, addition of 4'-nitrobenzo-15C5 to Li⁺ and K⁺ cations in AN–MeOH binary solutions at different temperatures results in an increase in molar conductivity which indicates that the (4'-nitrobenzo-15C5.Li⁺) and (4'-nitrobenzo-15C5.K⁺) complexes are more mobile than free solvated Li⁺ and K⁺ cations. Similar behavior was observed for (4'-nitrobenzo-15C5.Na⁺) and (4'-nitrobenzo-15C5.NH₄⁺) complexes in AN–MeOH binary solutions. It seems that the studied cations are strongly solvated by the solvent molecules. But upon complexation of the cations with 4'-nitrobenzo-15C5 in AN–MeOH binary systems, the crown ether molecule replaces the solvation sheath around the metal ions and as a result, the entities become less bulky and more mobile than the free solvated cations, therefore, addition of 4'-nitrobenzo-15C5

Table 2 Thermodynamic parameters for 4'-nitrobenzo-15C5.M⁺ (M⁺ = Li⁺, Na⁺, K⁺ and NH₄⁺) complexes in AN–MeOH binary mixtures

Medium	Log $K_f \pm SD^a$ (25 °C)	$-\Delta G_c^\circ \pm SD^a$ (KJ/mol)	$\Delta H_c \pm SD^a$ (KJ/mol)	$\Delta S_c \pm SD^a$ (J/mol K)
(4'-nitrobenzo-15C5.Na ⁺)				
90%AN-10% MeOH ^b	2.73 ± 0.12	15.57 ± 0.67	9 ± 5	81 ± 16
75%AN-25% MeOH	2.80 ± 0.07	16.21 ± 0.38	c	66 ± 12
50%AN-50% MeOH	2.70 ± 0.10	15.67 ± 0.58	4 ± 1	65 ± 4.0
25%AN-75% MeOH	2.91 ± 0.07	16.63 ± 0.42	c	36 ± 19
Pure MeOH	2.71 ± 0.15	15.50 ± 1.00	7.3 ± 3.5	c
(4'-nitrobenzo-15C5.K ⁺)				
90%AN-10% MeOH ^b	3.01 ± 0.04	17.23 ± 0.25	−19 ± 8	c
75%AN-25% MeOH	2.85 ± 0.06	16.24 ± 0.35	−9 ± 7	c
50%AN-50% MeOH	2.98 ± 0.05	16.98 ± 0.27	c	64 ± 20
25%AN-75% MeOH	2.60 ± 0.04	14.80 ± 0.20	c	64 ± 21
Pure MeOH	2.73 ± 0.06	15.60 ± 0.30	c	71 ± 14
(4'-nitrobenzo-15C5. NH ₄ ⁺)				
90%AN-10% MeOH ^b	2.81 ± 0.07	16.09 ± 0.41	c	72 ± 17
75%AN-25% MeOH	2.83 ± 0.08	16.16 ± 0.44	c	59 ± 11
50%AN-50% MeOH	2.59 ± 0.05	14.77 ± 0.30	c	63 ± 18
25%AN-75% MeOH	2.92 ± 0.06	16.71 ± 0.33	−10.1 ± 3.8	22 ± 13
Pure MeOH	2.82 ± 0.07	16.09 ± 0.38	−17.6 ± 2.4	c
(4'-nitrobenzo-15C5. Li ⁺)				
75%AN-25% MeOH ^b	2.81 ± 0.07	15.99 ± 0.45	−3.35 ± 1.80	42 ± 6.0
50%AN-50% MeOH	2.81 ± 0.08	15.89 ± 0.47	−3.12 ± 0.90	42 ± 3.0
25%AN-75% MeOH	2.73 ± 0.04	15.32 ± 0.27	9.24 ± 3.51	82 ± 11
Pure MeOH	3.05 ± 0.03	17.40 ± 0.16	c	39 ± 25

^a SD = Standard deviation^b The composition of each solvent system is expressed in mol% of each solvent^c With high uncertainty

to these cations in AN–MeOH binary systems at different temperatures results in an increase in molar conductivity. The slope of the corresponding molar conductivity versus ligand/cations mole ratio plots changes at the point where the ligand to cation mole ratio is about one, which is an evidence for formation of a relatively stable 1:1 [M:L] complex in solutions. As is shown in Fig. 3, the change of the stability constant of (4'-nitrobenzo-15C5.K⁺) complex with the composition of acetonitrile–methanol binary solution is not linear. A non-linear behavior was also observed for (4'-nitrobenzo-15C5.Li⁺), (4'-nitrobenzo-15C5.Na⁺) and (4'-nitrobenzo-15C5.NH₄⁺) complexes in this binary system. This behavior may be due to the interactions between the methanol and acetonitrile molecules via hydrogen bonding in their binary mixtures which result in changing the solvation of the cations, the ligand and the resulting (4'-nitrobenzo-15C5.M⁺) complexes in AN–MeOH binary solutions. 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 [23].

The changes of stability constants (log K_f) of (4'-nitrobenzo-15C5.Li⁺), (4'-nitrobenzo-15C5.Na⁺), (4'-nitrobenzo-15C5.K⁺) and (4'-nitrobenzo-15C5.NH₄⁺) complexes

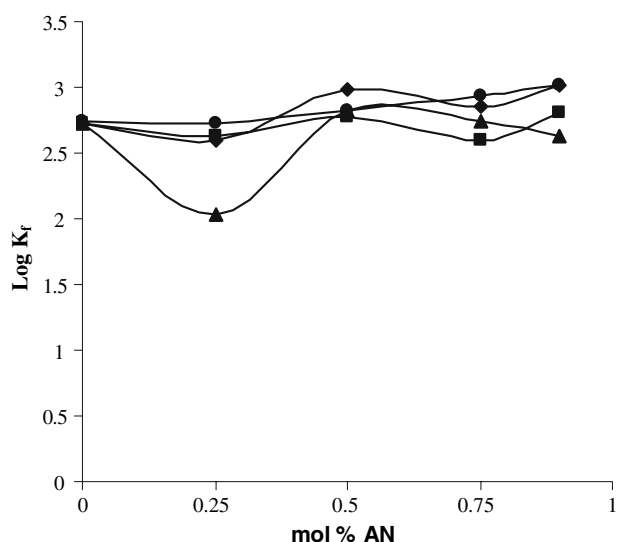


Fig. 3 Changes of the stability constant (log K_f) of (4'-nitrobenzo-15C5.K⁺) with the composition of the AN–MeOH binary system at different temperatures: 55 °C (○), 45 °C (■), 35 °C (▲), 25 °C (◆), 15 °C (●)

versus the ionic diameter in various AN–MeOH binary mixtures is shown in Fig. 4. As is evident from Fig. 4, the order of stability of complexes formed between 4'-

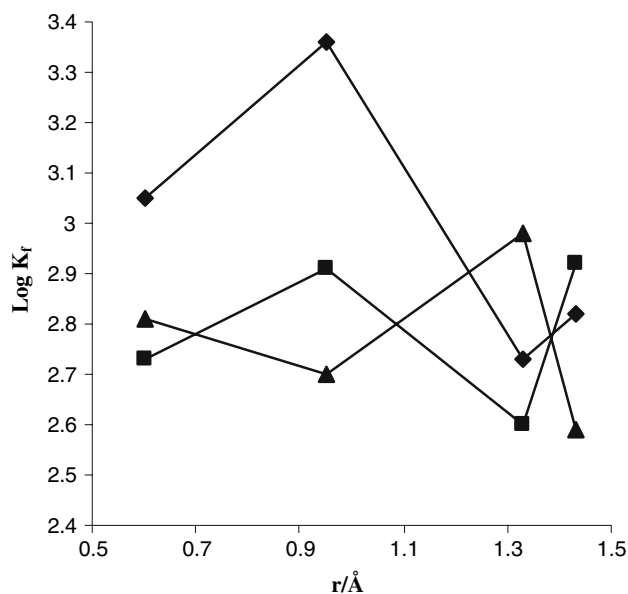


Fig. 4 Changes of $\log K_f$ for ($4'$ -nitrobenzo-15C5.Li⁺), ($4'$ -nitrobenzo-15C5.Na⁺), ($4'$ -nitrobenzo-15C5.K⁺) and ($4'$ -nitrobenzo-15C5.NH₄⁺) complexes versus cationic radii in various solvent systems at 25 °C:(mol% AN: ♦ 0.0, ■ 25, ▲ 50)

nitrobenzo-15C5 and these cations in pure methanol is: ($4'$ -nitrobenzo-15C5.Na⁺) > ($4'$ -nitrobenzo-15C5.Li⁺) > ($4'$ -nitrobenzo-15C5.NH₄⁺) > ($4'$ -nitrobenzo-15C5.K⁺) which show that the crown ether forms the more stable complex with the cation which is more suitable in size for the crown ether cavity and since the ionic size of Na⁺ cation (0.98 Å) is very close to the cavity size of $4'$ -nitrobenzo-15C5 (0.86–1.1 Å), it forms the most stable complex. But some reversals in stabilities can be observed with the composition of the mixed solvent which show that the selectivity order of the ligand for these cations is affected by the nature and composition of the solvent system. For instance, the order of stability of the complexes formed between $4'$ -nitrobenzo-15C5 and these metal cations in 50–50 mole% AN–MeOH binary mixture is: ($4'$ -nitrobenzo-15C5.K⁺) > ($4'$ -nitrobenzo-15C5.Li⁺) > ($4'$ -nitrobenzo-15C5.Na⁺) > ($4'$ -nitrobenzo-15C5.NH₄⁺), but in the case of 25–75 mole% AN–MeOH binary solution is: ($4'$ -nitrobenzo-15C5.NH₄⁺) ≈ ($4'$ -nitrobenzo-15C5.Na⁺) > ($4'$ -nitrobenzo-15C5.Li⁺) > ($4'$ -nitrobenzo-15C5.K⁺).

The results obtained from studying of complexation reactions of 15-crown-5, benzo15-crown-5 and $4'$ -nitrobenzo15-crown-5 with NH₄⁺, Na⁺, and K⁺ cations in methanol solutions at 25 °C are given in the Table 3. Comparison of these results reveals that the complex formation constants of these cations with $4'$ -nitrobenzo-15-crown-5 in methanol are lower than those for 15-crown-5 and benzo15-crown-5. The strength of alkali ion interactions with ethers is known to depend on the basicity of the ether oxygen [24]. It seems that the withdraw electron

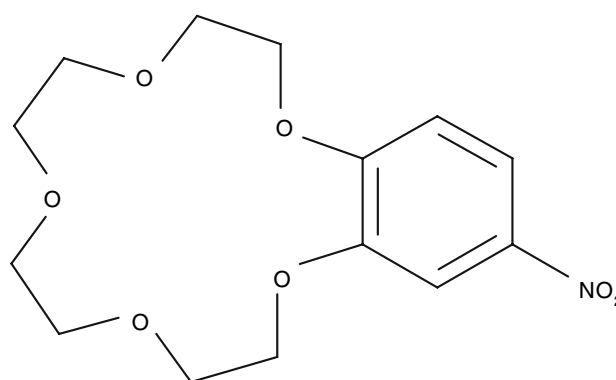
Table 3 Log K_f values of some of the 15-Crown-5 derivatives complexes with alkali cations in methanol solution at 25 °C

MeOH	NH ₄ ⁺	Na ⁺	K ⁺
15C5	3.03 ^a	3.31 ^b	3.6 ^b
B15C5	–	3.05 ^b	3.05 ^b
$4'$ -nitro-B15C5	2.82 ^d	2.71 ^d (2.73 ^c)	2.73 ^d (2.7 ^b)

^a Reference [26], ^b reference [27], ^c reference [28], ^d this work

character of the –NO₂ group decreases the basicity of the two aromatic oxygens and, therefore, the stability constants of the complexes are lowered in the presence of –NO₂ group present in the aromatic crown ether. A theoretical study has revealed that introducing the –NO₂ group, electron-accepter group, into the benzo15-crown-5 ligand results in the binding of Na⁺ to decrease by 10.5 Kcalmol^{–1} [25]. It seems that introduction of chosen substitutions results 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 ether for metal cations.

As is evident from Table 2, the thermodynamics of complexation reactions between $4'$ -nitrobenzo-15C5 with Li⁺, Na⁺, K⁺ and NH₄⁺ cations is affected by the nature and composition of the mixed solvents and in most cases, the complexes are both enthalpy and entropy stabilized, therefore, the enthalpies and entropies of complexation reactions are the driving forces for formation of $4'$ -nitrobenzo-15C5.M⁺ (M⁺ = Li⁺, Na⁺, K⁺ and NH₄⁺) complexes. The experimental values of ΔH°_c and ΔS°_c (Table 2) show that the enthalpies and entropies of complexation reactions in acetonitrile–methanol binary solutions do not vary monotonically with the solvent composition. 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



Scheme 1 $4'$ -nitrobenzo-15-Crown-5

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. In addition, since there are many factors, which contribute to enthalpies and entropies of complexation reactions, therefore, we should not expect a monotonic relationship between these thermodynamic quantities and the solvent composition of the binary mixtures of these two dipolar protic and aprotic solvents.

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