

Complexation of 4'-Nitrobenzo-15-Crown-5 with Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺ Metal Cations in Acetonitrile-Methanol Binary Solutions¹

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Abstract—The complex formation reactions between Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺ metal cations with macrocyclic ligand, 4'-nitrobenzo-15C5, were studied in acetonitrile (AN)-methanol (MeOH) binary mixtures at different temperatures using conductometric method. The results show that 4'-nitrobenzo-15C5 forms 1:1 [ML] complexes with Mg²⁺, Ca²⁺ and Sr²⁺ metal cations in solutions. But in the case of Ba²⁺ cation a 1:2 [ML₂] complex is formed in these solvent systems. The stability of the complexes is sensitive to the solvent composition and a non-linear behavior was observed for variation of logK_f of the complexes versus the composition of the binary mixed solvents. The stability constants of complexes decrease suddenly with increasing the concentration of methanol in this binary system. The values of thermodynamic parameters (ΔH_c° and ΔS_c°) for formation of (4'-nitrobenzo-15C5.Mg)²⁺, (4'-nitrobenzo-15C5.Ca)²⁺ and (4'-nitrobenzo-15C5.Sr)²⁺ complexes were obtained from temperature dependence of the stability constants and the results show that these parameters are affected by the nature and composition of the mixed solvents. A non-linear behavior is observed between the ΔS_c° and the composition of the mixed solvents.

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INTRODUCTION

In 1967 Pedersen discovered crown ethers and described their capability to form complexes with metal cations [1]. The ability of crown ethers to form stable complexes with cations, mainly with alkali and alkaline earth metal cations, has spurred interest in these compounds [2]. These compounds have aroused a great interest in recent years because of their characteristics which are of importance in preparation chemistry and in biology.

New fields of application in research and potential uses in industry have been found for these macrocyclic compounds [3, 4]. One of the unique features of crown ethers is that they can chelate metal ions. Different sized macrocyclic polyethers chelate different sized metal ions. In these particular complexes, the crown ether is referred to as the host, while the metal ion is called the guest [5]. Crown ethers function as phase transfer catalysts by complexing a cation then bringing the complexed-cation-anion pair into the non-polar phase [6, 7]. By complexing the cation in the cavity of the crown ether, these compounds act as solubilizing

agents. Macrocyclic compounds play an important role in chemistry such as their application in separation of metal cations [8, 9], in construction of ion selective electrodes [10, 11], chemical analysis [12] and chiral separation [13].

Although the complexation reactions of crown ethers with metal cations have been studied in both aqueous and non-aqueous solvents, the data about stability of crown ether complexes in mixed solvents have been carried out to a limited extent and little attention has been paid to these complexes in mixed solvent systems. Studies of crown ether complexes in various solvents, show that the thermodynamic and kinetic parameters for complexation processes and even the stoichiometry of crown ether complexes are affected by the nature and composition of the solvent system [14, 15]. The goal of the present investigation is to study the effect of the nature and composition of the mixed solvents on selectivity and thermodynamics of complexation reactions of 4'-nitrobenzo-15C5 with Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺ metal cations in AN-MeOH binary systems using the conductometric technique.

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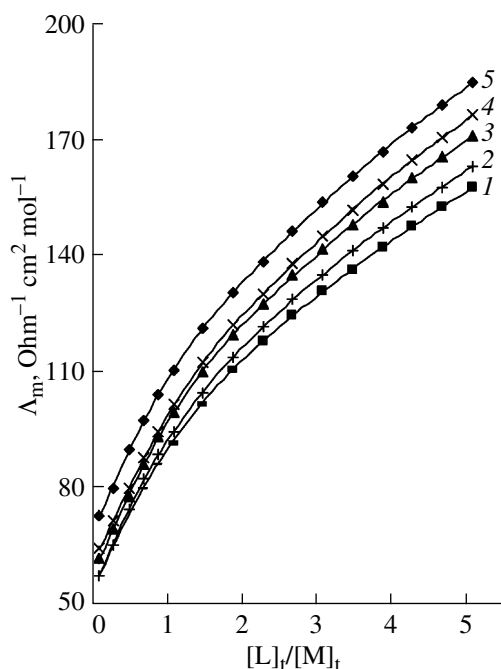


Fig. 1. Molar conductance–mole ratio plots for (4'-nitrobenzo-15C5.Mg)²⁺ complex in pure acetonitrile at different temperatures: 1 – 15, 2 – 25, 3 – 35, 4 – 45, 5 – 55°C.

EXPERIMENTAL

4'-Nitrobenzo-15C5 (Fluka), magnesium nitrate (Merck), calcium nitrate (Merck), strontium nitrate (Merck) and barium perchlorate (Merck) were used without further purification. The solvents: acetonitrile and methanol (both from Merck company) were used with highest purity.

The experimental procedure to obtain the stability constants of complexes is 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, then a step-by-step increase of the crown ether solution prepared in the same solvent (2.0×10^{-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.

The conductance measurements were performed on a digital AMEL conductivity apparatus, model 160, in a water bath thermostated at a constant temperature which maintained within $\pm 0.03^\circ\text{C}$. 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 AND DISCUSSION

The changes of molar conductance (Λ_m) versus the ligand to cation mole ratio for the complexation of 4'-nitrobenzo-15C5 with Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} cat-

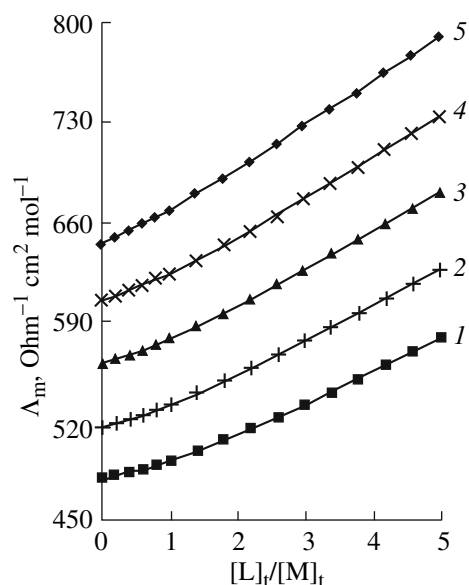


Fig. 2. Molar conductance–mole ratio plots for (4'-nitrobenzo-15C5.Ba)²⁺ complex in pure acetonitrile at different temperatures: 1 – 15, 2 – 25, 3 – 35, 4 – 45, 5 – 55°C.

ions in acetonitrile-methanol binary systems were studied at different temperatures. The changes of Λ_m versus ligand/cation mole ratio ($[L]_l/[M]_t$) for (4'-nitrobenzo-15C5.Mg)²⁺ and (4'-nitrobenzo-15C5.Ba)²⁺ complexes in pure acetonitrile and also for (4'-nitrobenzo-15C5.Ba)²⁺ complex in a binary mixture of acetonitrile-nitromethane (mol % nitromethane = 90) are shown in Figs. 1–3, respectively.

The stability constants of the crown ether complexes at each temperature were calculated from variation of molar conductance as a function of ligand/cation mole ratios using a GENPLOT computer program [16]. The details of calculation of the stability constants of complexes by conductometric method have been described elsewhere [17]. The stability constants ($\log K_f$) for (4'-nitrobenzo-15C5.M)²⁺ ($M^{2+} = \text{Mg}^{2+}$, Ca^{2+} and Sr^{2+}) complexes in various solvent systems are listed in Table 1. Assuming that the activity coefficients of cation and complex have the same value, K_f is a thermodynamic equilibrium constant on the molar concentration scale. Plots of $\ln K_f$ versus $1/T$ in all cases were linear. A typical example of these plots is shown in Fig. 4.

The changes in standard enthalpy (ΔH_c°) for the complexation reactions were determined in usual manner from the slopes of the van't Hoff plots, and the changes in standard entropy (ΔS_c°) were calculated

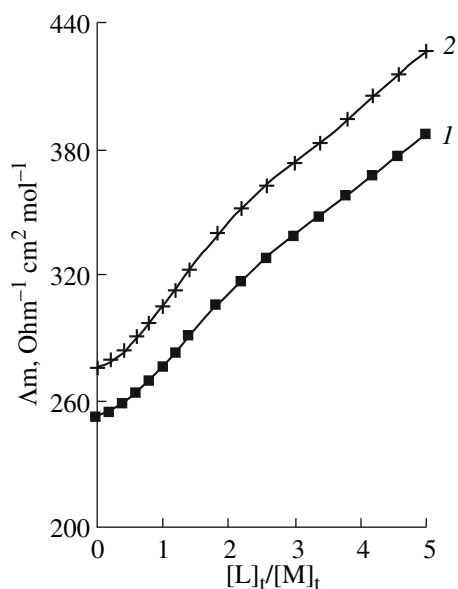


Fig. 3. Molar conductance–mole ratio plots for (4'-nitrobenzo-15C5.Ba) $^{2+}$ complex in acetonitrile–nitromethane (mol % NM = 90.0) binary system at two different temperatures: 1 – 15, 2 – 25°C.

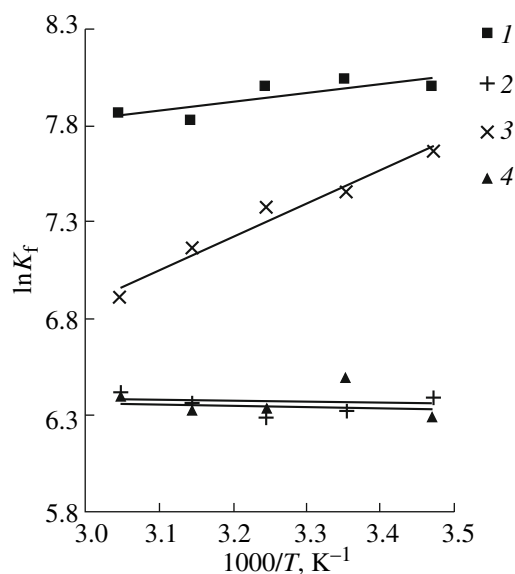


Fig. 4. van't Hoff plots for (4'-nitrobenzo-15C5.Mg) $^{2+}$ and (4'-nitrobenzo-15C5.Ca) $^{2+}$ complexes in AN-MeOH binary systems: 1 – Mg $^{2+}$ (mol % AN = 100.0), 2 – Mg $^{2+}$ (mol % AN = 75.0), 3 – Ca $^{2+}$ (mol % AN = 100.0), 4 – Ca $^{2+}$ (mol % AN = 75.0).

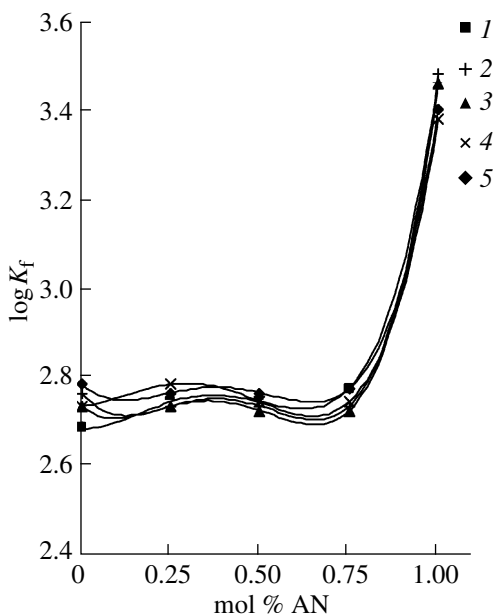


Fig. 5. Changes of stability constant of (4'-nitrobenzo-15C5.Mg) $^{2+}$ complex with the mole fraction of AN at different temperatures: 1 – 15, 2 – 25, 3 – 35, 4 – 45, 5 – 55°C.

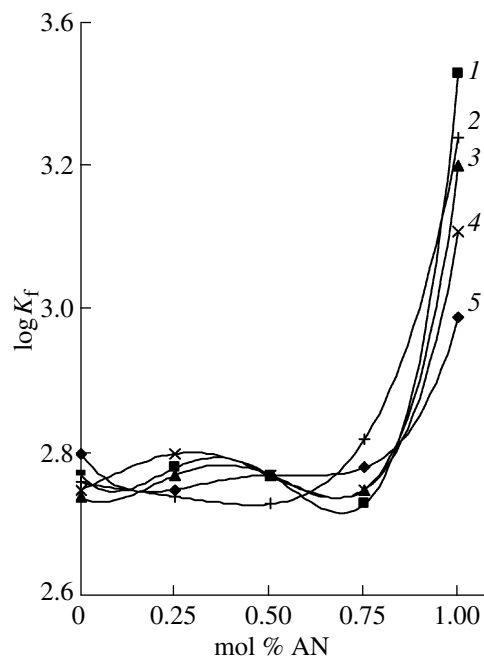


Fig. 6. Changes of stability constant of (4'-nitrobenzo-15C5.Ca) $^{2+}$ complex with the mole fraction of AN at different temperatures: 1 – 15, 2 – 25, 3 – 35, 4 – 45, 5 – 55°C.

from the relationship $\Delta G_{c, 298.15}^{\circ} = \Delta H_c^{\circ} - 298.15 \Delta S_c^{\circ}$. The results are summarized in Table 2.

The changes of $\log K_f$ versus the mole fraction of AN for (4'-nitrobenzo-15C5.Mg) $^{2+}$ and (4'-nitrobenzo-

15C5.Ca) $^{2+}$ complexes are shown in Figs. 5 and 6, respectively. The changes of the standard entropy of complexation of Mg $^{2+}$ and Ca $^{2+}$ cations by 4'-nitrobenzo-15C5 with the mole fraction of AN is shown in Fig. 7.

Table 1. Log K_f values of (4'-nitrobenzo-15C5.Mg) $^{2+}$, (4'-nitrobenzo-15C5.Ca) $^{2+}$ and (4'-nitrobenzo-15C5.Sr) $^{2+}$ complexes in AN-MeOH binary mixtures at different temperatures

Medium	log $K_f \pm SD^a$				
	15°C	25°C	35°C	45°C	55°C
(4'-Nitrobenzo-15C5.Mg) $^{2+}$ ^b					
Pure AN	3.48 ± 0.04	3.49 ± 0.03	3.47 ± 0.03	3.39 ± 0.03	3.41 ± 0.04
75.0% AN-25.0% MeOH ^c	2.78 ± 0.11	2.74 ± 0.10	2.73 ± 0.14	2.75 ± 0.12	2.78 ± 0.11
50.0% AN-50.0% MeOH	2.75 ± 0.13	2.74 ± 0.13	2.73 ± 0.14	2.75 ± 0.12	2.77 ± 0.11
25.0% AN-75.0% MeOH	2.75 ± 0.13	2.74 ± 0.14	2.74 ± 0.14	2.79 ± 0.10	2.77 ± 0.11
Pure MeOH	2.69 ± 0.14	2.77 ± 0.12	2.74 ± 0.13	2.74 ± 0.14	2.79 ± 0.10
(4'-Nitrobenzo-15C5.Ca) $^{2+}$ ^b					
Pure AN	3.33 ± 0.02	3.24 ± 0.03	3.20 ± 0.03	3.11 ± 0.02	2.99 ± 0.03
75.0% AN-25.0% MeOH ^c	2.73 ± 0.14	2.82 ± 0.09	2.75 ± 0.13	2.75 ± 0.12	2.78 ± 0.11
50.0% AN-50.0% MeOH	2.77 ± 0.12	2.73 ± 0.15	2.77 ± 0.12	2.77 ± 0.11	2.77 ± 0.11
25.0% AN-75.0% MeOH	2.78 ± 0.11	2.74 ± 0.14	2.77 ± 0.12	2.80 ± 0.10	2.75 ± 0.13
Pure MeOH	2.77 ± 0.11	2.76 ± 0.12	2.74 ± 0.13	2.75 ± 0.13	2.80 ± 0.10
(4'-Nitrobenzo-15C5.Sr) $^{2+}$ ^b					
Pure AN	d	d	d	d	d
75.0% AN-25.0% MeOH ^c	d	d	d	d	d
50.0% AN-50.0% MeOH	2.77 ± 0.12	2.77 ± 0.12	2.75 ± 0.13	2.76 ± 0.11	2.80 ± 0.10
25.0% AN-75.0% MeOH	2.77 ± 0.12	2.72 ± 0.12	2.76 ± 0.12	2.75 ± 0.13	2.83 ± 0.08
Pure MeOH	2.70 ± 0.06	2.81 ± 0.09	2.73 ± 0.14	2.76 ± 0.12	2.77 ± 0.11

^a SD = standard deviation.

^b The concentration of each metal cation was 1.0×10^{-4} M.

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

^d The salt is not dissolved in these solvent systems.

As is evident in Fig. 1, addition of 4'-nitrobenzo-15C5 to Mg $^{2+}$ cation solutions causes an increase in the molar conductivity which indicates that (4'-nitrobenzo-15C5.Mg) $^{2+}$ complex is more mobile than free solvated Mg $^{2+}$ ion. Similar behavior was observed for complexation of Ca $^{2+}$ and Sr $^{2+}$ cations with the ligand. It is clear from Fig. 1 that the slope of each curve changes at the point where $[L]_t/[M]_t$ is about 1 which is an evidence for formation of a relatively stable 1:1 complex between 4'-nitrobenzo-15C5 and Mg $^{2+}$ cation in solution. However, in the case of Mg $^{2+}$ cation in the mixed solvents, a gradual increase in molar conductance is observed upon addition of the ligand to this metal ion solution which does not show a considerable change in curvature at mole ratio of 1, indicating that a weaker 1:1 complex is formed in solution. Somewhat similar behavior was observed for Ca $^{2+}$ and Sr $^{2+}$ cations in the binary mixed solvents. But in the case of Ba $^{2+}$ cation, 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 in solution (Fig. 2). Since the slope of the molar conductivity plots which are shown in Fig. 2 is not sharp and, therefore, it does

not show clearly a 1:2 stoichiometry, so we also studied the complexation of Ba $^{2+}$ ion with 4'-nitrobenzo-15C5 in a binary mixture of nitromethane (NM) and acetonitrile (AN) (mole % NM = 90) at two different temperatures. The graphical results are shown in Fig. 3. The changes of the slope of the molar conductivity plots in this figure, clearly show the formation of (4'-nitrobenzo-15C5) $_2$ Ba $^{2+}$ complex in this binary solution. Similar results have been obtained for complexation of Ba $^{2+}$ cation with 15C5 in nitrobenzene and methanol solutions [18].

As shown in Figs. 5 and 6, the changes of the stability constants (log K_f) of the (4'-nitrobenzo-15C5.Mg) $^{2+}$ and (4'-nitrobenzo-15C5.Ca) $^{2+}$ complexes with the mixed solvent composition of AN-MeOH are not linear. A non-linear behavior was also observed for the stability constant (log K_f) of (4'-nitrobenzo-15C5.Sr) $^{2+}$ complex with the composition of AN-MeOH binary systems. This behavior is probably due to interactions between the constituent solvents of the binary solvents which result in some of the chemical and physical properties of each solvent such as acidity, basicity and polarity change when acetonitrile and methanol mix with

Table 2. Thermodynamic parameters for (4'-nitrobenzo-15C5.Mg)²⁺, (4'-nitrobenzo-15C5.Ca)²⁺ and (4'-nitrobenzo-15C5.Sr)²⁺ complexes in AN-MeOH binary mixtures

Medium	$-\Delta G_c^\circ \pm SD^a$ (25°C) (kJ/mol)	$\Delta H_c^\circ \pm SD^a$ (kJ/mol)	$\Delta S_c^\circ \pm SD^a$ (kJ/mol)
(4'-Nitrobenzo-15C5.Mg) ²⁺			
Pure AN	19.93 ± 0.20	-1.27 ± 0.77	62.58 ± 0.80
75.0 %AN-25.0% MeOH ^b	15.67 ± 0.59	c	51.15 ± 1.20
50.0 %AN-50.0% MeOH	15.62 ± 0.78	c	52.62 ± 2.48
25.0 %AN-75.0% MeOH	15.62 ± 0.80	c	54.33 ± 1.92
Pure MeOH	15.79 ± 0.68	c	54.94 ± 1.35
(4'-Nitrobenzo-15C5.Ca) ²⁺			
Pure AN	18.49 ± 0.17	-3.65 ± 0.33	49.77 ± 0.95
75.0% AN-25.0% MeOH ^b	16.09 ± 0.54	c	53.76 ± 3.71
50.0% AN-50.0% MeOH	15.57 ± 0.85	c	53.19 ± 2.11
25.0% AN-75.0% MeOH	15.64 ± 0.80	c	53.63 ± 1.52
Pure MeOH	15.74 ± 0.70	c	54.33 ± 2.10
(4'-Nitrobenzo-15C5.Sr) ²⁺			
50.0% AN-50.0% MeOH ^b	15.79 ± 0.68	c	53.39 ± 2.12
25.0% AN-75.0% MeOH	15.52 ± 0.69	c	52.46 ± 0.86
Pure MeOH	16.01 ± 0.55	c	55.61 ± 3.61

^a SD = standard deviation.

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

^c With high uncertainty.

each other [19] and, therefore, changing the solvation properties towards the metal cations and the ligand and even the resulting complexes formed in solutions.

Prasad and co-workers have studied the interactions between AN and MeOH molecules by excess adiabatic compressibility (β^E) and excess intermolecular free length (L_f^E) measurements at 303.15 K and they showed that these parameters become increasingly negative with increasing strength of interaction between the component molecules [20]. In addition, it has been shown that there is an interaction between AN and MeOH molecules ($K_{ass} = 1.23$) via hydrogen bonding in their binary mixtures [21].

As is obvious in Figs. 5 and 6, the values of $\log K_f$ for formation of (4'-nitrobenzo-15C5.Mg)²⁺ and (4'-nitrobenzo-15C5.Ca)²⁺ complexes in pure acetonitrile at all temperatures are bigger than the other solvent systems. In a strong solvating solvent such as methanol with a relatively high Guttmann donicity (Donor Number = 20.0), the solvation of the metal ions and possibly of the ligand should be stronger than that of the solvents of lower solvating abilities such as acetonitrile (Donor Number = 14.1). Therefore, addition of methanol to acetonitrile results in formation of weaker complexes in solutions.

As illustrated in Table 1 and in Figs. 5 and 6, the stability constants for formation of (4'-nitrobenzo-

15C5.Mg)²⁺ and (4'-nitrobenzo-15C5.Ca)²⁺ complexes are maximum in pure acetonitrile at various temperatures and then decrease suddenly until the mole fraction of acetonitrile reaches to about 0.75 and then there is no significant changes in stability constants with increasing the concentration of methanol in AN-MeOH binary system.

The values of thermodynamic quantities for complex formation between 4'-nitrobenzo-15C5 and Mg²⁺, Ca²⁺ and Sr²⁺ metal ions are given in Table 2. The values of ΔH_c° and ΔS_c° depend on the nature and composition of the mixed solvents. The values and the sign of the standard entropy changes are expected to vary with different parameters such as changes in flexibility of the macrocyclic ligands during the complexation processes and the extent of cation-solvent and also ligand-solvent interactions [22] and even the complex-solvent interaction. In most cases, the changes in enthalpy for formation of the complexes are small along with high uncertainties, therefore, it seems that the complexation process between these metal ions with the ligand is athermic in the studied solvent systems. The data in Table 2 show that, positive values of ΔS_c° characterize the formation of these complexes. Therefore, the complex formation reactions between Mg²⁺, Ca²⁺ and Sr²⁺ metal cations with 4'-nitrobenzo-15C5 are entropy stabilized.

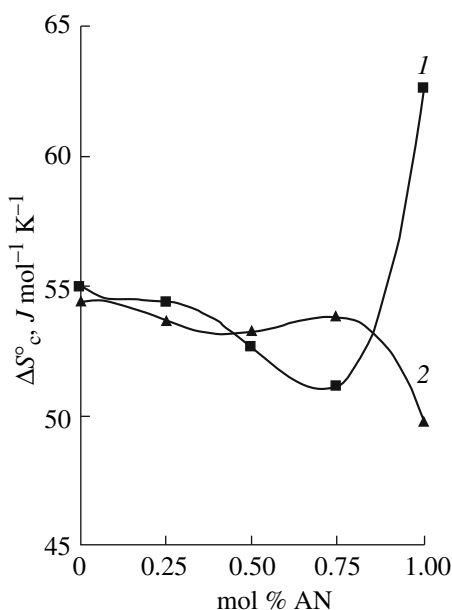


Fig. 7. Changes of ΔS_c° of (4'-nitrobenzo-15C5.Mg) $^{2+}$ and (4'-nitrobenzo-15C5.Ca) $^{2+}$ complexes with the mole fraction of AN at 25°C: 1 – (4'-nitrobenzo-15C5.Mg) $^{2+}$, 2 – (4'-nitrobenzo-15C5.Ca) $^{2+}$.

As seen from Fig. 7, the values of ΔS_c° for formation of (4'-nitrobenzo-15C5.Mg) $^{2+}$ and (4'-nitrobenzo-15C5.Ca) $^{2+}$ complexes in AN-MeOH binary solution changes non-monotonically with the composition of the mixed solvent. Since there are many factors which contribute to changes in complexation enthalpies and entropies, one should not expect a strict regularity between these parameters and the solvent composition of these binary mixtures of associated solvents.

CONCLUSIONS

The results obtained for complexation of Mg $^{2+}$, Ca $^{2+}$ and Sr $^{2+}$ cations with 4'-nitrobenzo-15C5 in AN-MeOH binary mixtures show that the stability and thermodynamics of complexation are governed by the solvent medium. The conductance data show that 4'-nitrobenzo-15C5 forms 1:1 complexes with Mg $^{2+}$, Ca $^{2+}$ and Sr $^{2+}$ metal cations but in the case of Ba $^{2+}$ cation a 1:2 [ML $_2$] complex is formed in this solvent systems. The stability constants of (4'-nitrobenzo-15C5.Mg) $^{2+}$, (4'-nitrobenzo-15C5.Ca) $^{2+}$ and (4'-nitrobenzo-15C5.Sr) $^{2+}$ complexes decrease suddenly with increasing the concentration of the solvent with higher donicity (based on the Guttmann donicity scale) in the binary mixed solvents. Therefore, the electron donor ability of the solvent plays an important role in complexation process.

The changes in the stability constants ($\log K_f$) of the complexes versus the composition of the mixed solvents are non-linear. In addition, a non-linear behavior is observed between the ΔS_c° and the composition of the mixed solvents. These behaviors are probably due to a change in the structure of the binary solvents as the composition of the medium is varied.

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