A Thermodynamic Study of Complex Formation between 15-Crown-5 with Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} in Acetonitrile-Methanol Binary Mixtures Using Conductometric Method ☆

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ABSTRACT: *The complexation reactions between Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} metal cations with 15-crown-5 (15C5) were studied in acetonitrile (AN) - methanol (MeOH) binary mixtures at different temperatures using conductometric method. 15C5 forms 1:1 complexes with Mg^{2+}, Ca^{2+} and Sr^{2+} cations in solutions. The Ba^{2+} cation forms a 2:1 complex (ratio of ligand to cation) in solutions. A linear relation was observed for variation of $logK_f$ of 15C5-Ca^{2+} and 15C5-Sr^{2+} complexes vs the composition of AN-MeOH binary systems, but a non-linear behaviour was observed in the case of 15C5-Mg^{2+} complex in these binary mixtures. Selectivity of 15C5 for Mg^{2+}, Ca^{2+} and Sr^{2+} cations is sensitive to solvent composition. In some cases and in certain compositions of the mixed solvent systems, the selectivity order is changed. The values of thermodynamic parameters (ΔH^0_c, ΔS^0_c) for formation of 15C5-Mg^{2+}, 15C5-Ca^{2+} and 15C5-Sr^{2+} complexes were obtained from temperature dependence of stability constants and the results show that the thermodynamics of complexation reactions is affected by the nature and composition of the mixed solvents.*

KEY WORDS: *15-Crown-5, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} cations, AN-MeOH binary mixtures, Conductometry.*

INTRODUCTION

The first macrocyclic polyethers were reported by Luttringhaus in 1937[1]. However, the importance of these compounds begins from 1967 with the synthesis of dibenzo-18-crown-6 (DB18C6) by Pedersen and the observation that this compound and its homologues form very strong complexes with alkali and alkaline earth metal cations [2] . The values of stability constants, as well as the values of enthalpy changes (ΔH), entropy changes (ΔS) and heat capacity changes (ΔC_p) of various crown ether complexes are summarized in two reviews by Christensen and et al. [3,4].

An important part of cyclic polyethers chemistry deals with alkali and alkaline earth metal ion complexes, because of the vital role of these cations in biological

systems [5]. Naturally occuring macrocycles were shown to be capable of actively transport metal ions across membrans. Macrocyclic crown ethers which are similar to antibiotic ligands can be used as models for investigation of ion transport through membranes in biological systems[6]. 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 [7,8].

A large number of physico-chemical techniques such as potentiometry [9,10],calorimetry [11,12], conductometry [13,14], polarography [15-17], NMR spectrometry [18-20], spectrophotometry [21,22] and ion exchange membrane [23] have been used to study the complexation reactions between crown ethers with different metal cations in solutions. Most of these techniques still have problems, i.e., measurements in non-ideal solutions and association between cations and anions. Therefore, it is difficult to determine accurate complex formation constants under such conditions.

The advantage of conductometry is that measurements can be carried out with high precision at extremely low solution concentrations, where the interactions between cations and anions are known to be very small. In addition, conductometry is a highly sensitive and inexpensive technique with a simple experimental arrangement.

In this paper we report the results of thermodynamic study for complexation reaction between 15-crown-5 with Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} cations in AN-MeOH binary mixtures at different temperatures using conductometric method.

EXPERIMENTAL

Reagents and Solvents

15C5 (Aldrich, Milwaukee, WI, USA), magnesium nitrate (Riedel, Sleeze-Hannover, Germany), calcium nitrate (Riedel), strontium nitrate (Merck, Darmstadt, Germany) and barium perchlorate (Merck) were used without further purification. The solvents acetonitrile and methanol (Merck) were used with the highest purity.

Apparatus

The conductance measurements were performed on a digital AMEL conductivity apparatus, model 60, in a water bath thermostated with a constant temperature 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 0.79 cm^{-1} was used throughout the studies.

Methods

The experimental procedure to obtain the formation constants of complexes is as follow: a solution of metal salt (5×10^{-4} M) was placed in a titration cell and the, conductance of the solution was measured, then a step-by-step increase in the crown ether concentration was performed by rapid transfer from crown ether solutions prepared in the same solvent (2.5×10^{-2} M) to the titration cell using a microburet and the conductance, of the solution in the cell was measured after each addition at the desired temperature.

RESULTS

The variations of molar conductance (Λ) versus the ligand to the cation molar ratio ($[L]_t/[M]_t$) for complexation of 15C5 with Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} cations in AN-MeOH binary system were studied at different temperatures. The variations of Λ versus ($[L]_t/[M]_t$) for 15C5-Mg^{2+} in neat AN, 15C5-Ca^{2+} and 15C5-Ba^{2+} in AN-MeOH binary systems are shown in Figs. 1-3, respectively.
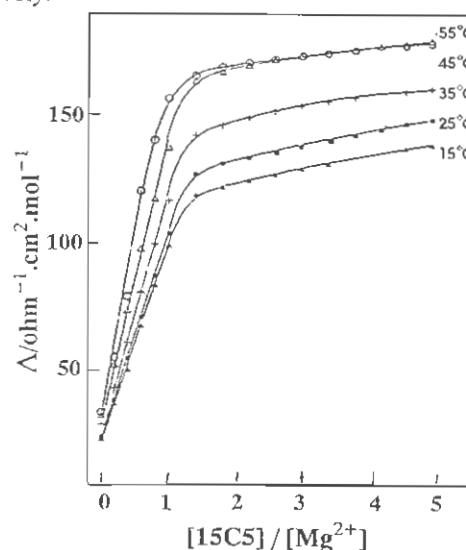

Fig. 1: Molar conductance - mole ratio plots for 15C5-Mg^{2+} complex in neat acetonitrile at different temperatures
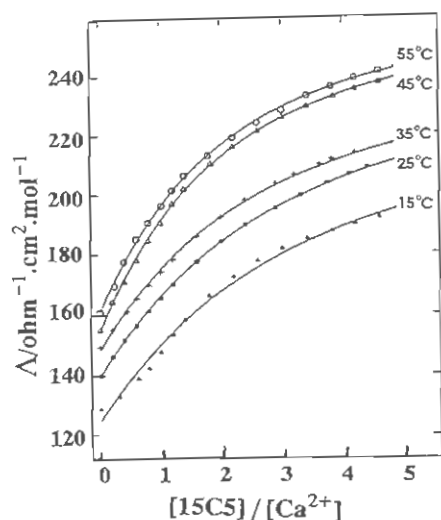
Fig. 2 : *Molar conductance - mole ratio plots for 15C5-Ca $^{2+}$ complex in AN-MeOH(mol% AN=75) at different temperatures*
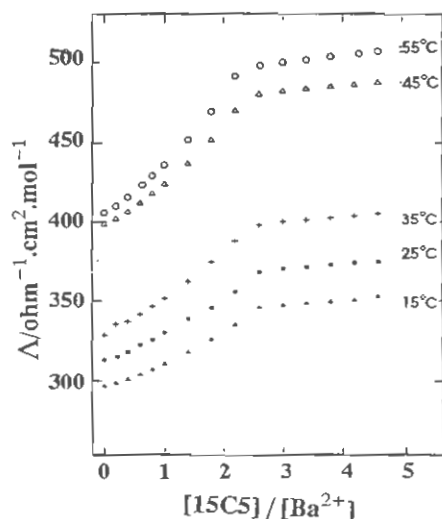

Fig. 3 : *Molar conductance - mole ratio plots for 15C5-Ba $^{2+}$ complex in AN-MeOH(mol% AN=75) at different temperatures*

The stability constants of 15C5 crown ether complexes at each temperature were calculated from variation of molar conductance as a function of Ligand /M^{2+} mole ratios using a GENPLOT computer program [24]. The details of calculation of the stability constant of complexes by conductometric method has been described elsewhere [15]. The stability constants ($logK_f$) for 15C5-M^{n+} (M^{n+} = Mg $^{2+}$, Ca $^{2+}$, and Sr $^{2+}$) complexes in various solvent systems are listed in Table 1. Assuming that the activity cofficients of cation and complex have the same

value, K_f , is a thermodynamic equilibrium constant on the molar concentration scale. Plots of $logK_f$ versus 1/T in all cases were linear. Two typical examples of these plots are shown in Figs. 4 and 5.
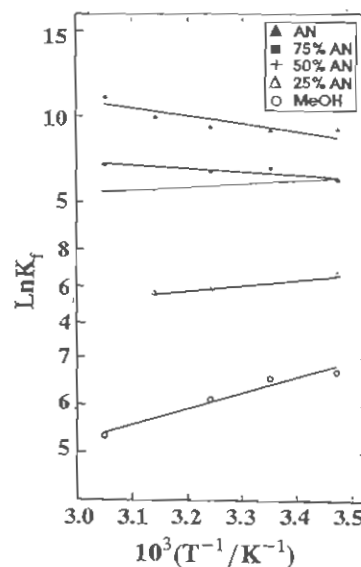

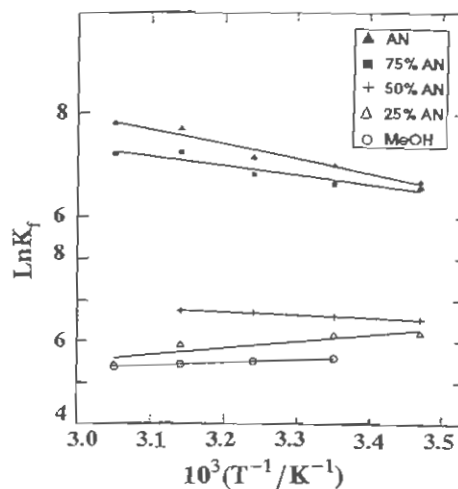Fig.4: *van't Hoff plots for 15C5-Mg $^{2+}$ complex in AN-MeOH binary systems*

Fig. 5: *van't Hoff plots for 15C5-Ca $^{2+}$ complex in AN-MeOH binary systems*

The changes in the standard enthalpy (ΔH°_c) for complexation reactions were obtained from slope of the van't Hoff plots and the changes in standard entropy (ΔS°_c) were calculated from the relationship $\Delta G^\circ_{c\ (298\ 15)} = \Delta H^\circ_c - 298.15\ \Delta S^\circ_c$. The thermodynamic data are summarized in Table 2.

Table 1: Log K_f values of 15C5-Mg^{2+}, 15C5-Ca^{2+} and 15C5-Sr^{2+} complexes in AN-MeOH binary mixtures at different temperatures

Medium	Log $K_f \pm$ SD[a]				
	15^0C	25^0C	35^0C	45^0C	55^0C
15C5-Mg^{2+} [b]					
Pure AN	3.99 ± 0.09	3.95 ± 0.08	4.05 ± 0.09	4.21 ± 0.07	5.00 ± 0.20
75%AN-25%MeOH[c]	2.70 ± 0.04	3.00 ± 0.01	2.94 ± 0.02	3.14 ± 0.02	3.11 ± 0.01
50%AN-50%MeOH	2.74 ± 0.06	2.70 ± 0.04	2.56 ± 0.06	2.48 ± 0.07	2.44 ± 0.08
25%AN-75%MeOH	2.88 ± 0.04	2.60 ± 0.03	2.53 ± 0.06	2.44 ± 0.09	2.42 ± 0.08
Pure MeOH	2.92 ± 0.05	2.85 ± 0.03	2.66 ± 0.04	2.80 ± 0.03	2.45 ± 0.09
15C5-Ca^{2+} [b]					
Pure AN	2.90 ± 0.09	3.04 ± 0.09	3.10 ± 0.09	3.34 ± 0.06	3.39 ± 0.07
75%AN-25%MeOH[c]	2.86 ± 0.09	2.88 ± 0.02	2.96 ± 0.04	3.14 ± 0.01	3.13 ± 0.02
50%AN-50%MeQH	2.83 ± 0.02	2.86 ± 0.02	2.91 ± 0.01	2.92 ± 0.02	2.80 ± 0.02
25%AN-75%MeOH	2.68 ± 0.02	2.66 ± 0.02	2.46 ± 0.01	2.56 ± 0.02	2.36 ± 0.04
Pure MeOH	2.38 ± 0.06	2.42 ± 0.03	2.39 ± 0.09	2.36 ± 0.05	2.33 ± 0.07
		(2.18 ± 0.05)[e]			
15C5-Sr^{2+} [b]					
PureAN	d	d	d	d	d
50%AN-50%MeOH[c]	2.26 ± 0.07	2.28 ± 0.07	2.32 ± 0.06	2.16 ± 0.06	1.98 ± 0.09
25%AN-75%MeOH	2.65 ± 0.04	2.58 ± 0.05	2.48 ± 0.02	2.42 ± 0.05	2.38 ± 0.05
Pure MeOH	2.70 ± 0.04	2.69 ± 0.01	2.56 ± 0.01	2.62 ± 0.02	2.63 ± 0.05
		(2.63 ± 0.03)[e]			

(a) SD = standard deviation.

(b) The concentration of each metal cation was 5×10^{-4}M.

(c) The composition of binary mixtures is expressed in mol% for each solvent.

(d) The salt is not dissolved.

(e) From reference 26.

The variation of log K_f versus the mole fraction of MeOH for 15C5-Mg^{2+} and 15C5-Ca^{2+} complexes in AN-MeOH binary systems at different temperatures is shown in Figs. 6-8, and the variation of stability constant (log K_f)of 15C5-Mg^{2+}, 15C5-Ca^{2+} and 15C5-Sr^{2+} complexes as a function of cationic radii in various AN-MeOH binary systems is shown in Fig. 9.

DISCUSSION

As is evident from Fig.1-3, addition of 15C5 to cation solutions causes an increase in the molar counductivity which indicates that 15C5 forms complexes with Mg^{2+}, Ca^{2+} and Ba^{2+} cations and the complexes are more mobile

than the corresponding alkaline earth metal ions. It is clear from Fig. 1 that the slope of each curve changes sharply at the point where ([L]$_t$/[M]$_t$)=1 which is an evidence for formation of a relatively stable 1:1 complex between 15C5 and Mg^{2+} ion in solution. In the case of mixed solvents (Fig. 2), however, a gradual increase in molar conductance of Ca^{2+} ion on addition of the ligand is observed, which does not show a considerable change in curvature at a mole ratio of ca.1, indicating that a weaker 1:1 complex is formed in solution. Somewhat similar behaviour was observed for Ca^{2+} and Sr^{2+} ions in binary mixed solvents, but in the case of Ba^{2+} cation, the slope of molar coductance mole ratio curves changes at the
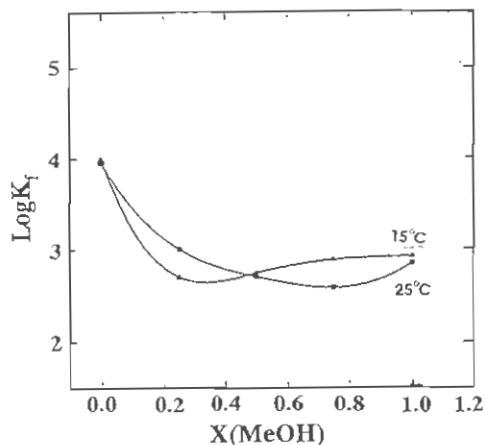
Fig. 6: Variation of stability constant of 15C5-Mg $^{2+}$ complex with the composition of the AN-MeOH binary systems at 25°C and 15°C
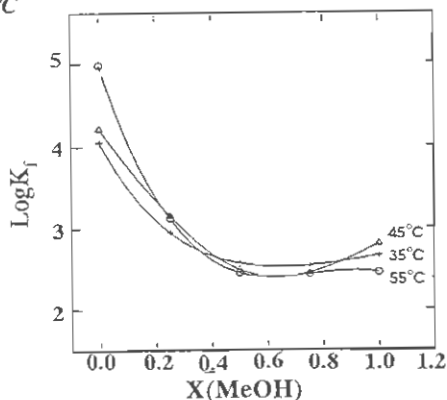

Fig. 7: Variation of stability constant of 15C5-Mg $^{2+}$ complex with the composition of the AN-MeOH binary systems at 35°C, 45°C and 55°C

point where $([L]_t/[M]_t) = 2$ which indicates the formation of a 2:1 (ligand : metal) complex in solution (Fig 3). Similar results have been obtained for complexation of Ba $^{2+}$ with 15C5 in nitrobenzene [25] and methanol solutions [26].

The variation of stability constant of 15C5-Ca $^{2+}$ complex as a function of solvent composition in AN-MeOH binary system is shown in Fig. 8. There is a linear relationship between $\log K_f$ values and the mole fraction of methanol in mixed solvent system. It seems reasonable to assume that in this case, it is the preferential solvation of Ca $^{2+}$ cation by methanol molecules that is responsible for this monotonic dependence of stability constant on the solvent composition. In methanol with a relatively high
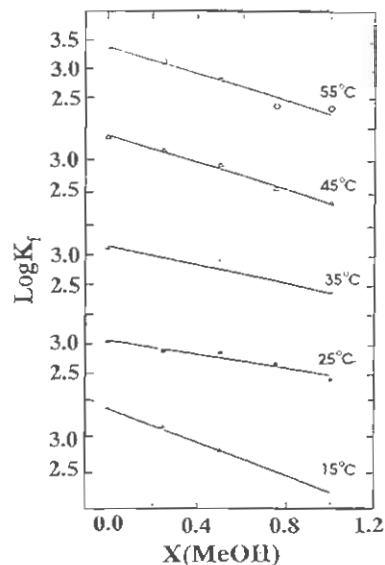

Fig. 8: Variation of stability constant of 15C5-Ca $^{2+}$ complex with the composition of the AN-MeOH binary system at different temperatures
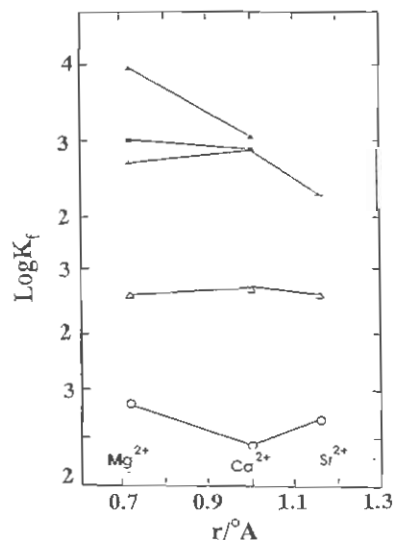

Fig. 9: Variation of $\log K_f$ for 15C5-Mg $^{2+}$, 15C5-Ca $^{2+}$ and 15C5-Sr $^{2+}$ complexes vs cationic radii in various solvent systems at 25°C: (▲) neat AN, (■)mol% AN=75, (+) mol% AN=50, (Δ) mol% AN=25, (o) neat MeOH

Gutmann Donor Number(DN=20), the solvation of the Ca $^{2+}$ ion should be stronger than acetonitrile of lower solvating ability (DN=14), therefore, the stability of 15C5-Ca $^{2+}$ complex increases as the concentration of methanol is lowered in mixed binary systems.

Table 2: Thermodynamic parameters for 15C5-Mg $^{2+}$, 15C5-Ca $^{2+}$ and 15C5-Sr^{2+} complexes in AN-MeOH binary mixtures

Medium	Log K_f±SD[a] (25°C)	$-\Delta G^o_c$±SD[a] Kcal.mol^{-1}	ΔH^o_c±SD[a] Kcal.mol^{-1}	ΔS^o_c+SD[a] Cal.mol^{-1}.K^{-1}
15C5-Mg^{2+}				
Pure AN	3.95 ± 0.08	5.4 ± 0.1	9 ± 4	50 ± 10
75%AN-25%MeOH[b]	3.00 ± 0.01	4.1 ± 0.3	4 ± 2	27 ± 7
50%AN-50%MeOH	2.70 ± 0.04	3.69 ± 0.05	-3.5 ± 0.4	c
25%AN-75%MeOH	2.60 ± 0.03	3.53 ± 0.04	-6 ± 1	-8 ± 3
Pure MeOH	2.85 ± 0.03	3.90 ± 0.04	-6.7 ± 0.9	-9 ± 3
15C5-Ca^{2+}				
Pure AN	3.04 ± 0.09	4.2 ± 0.1	5.6 ± 0.7	32 ± 2
75%AN-25%MeOH[b]	2.88 ± 0.02	3.93 ± 0.03	3.5 ± 0.7	25 ± 2
50%AN-50%MeOH	2.86 ± 0.02	3.91 ± 0.02	1.3 ± 0.1	17.5 ± 0.3
25%AN-75%MeOH	2.66 ± 0.02	3.64 ± 0.02	-3 ± 1	c
Pure MeOH	2.42 ± 0.03	3.31 ± 0.04	-1.39 ± 0.02	6.4 ± 0.1
15C5-Sr^{2+}				
50%AN-5O%MeOH[b]	2.28 ± 0.07	3.1 ± 0.1	-3 ± 1	c
25%AN-75%MeOH	2.58 ± 0.05	3.53 ± 0.07	-3.0 ± 0.2	1.8 ± 0.6
Pure MeOH	2.69 ± 0.01	3.67 ± 0.02	-0.9 ± 0.2	9.3 ± 0.7

(a) SD = standard deviation.

(b) The composition of binary mixtures is expressed in mol% of each solvent.

(c) With high uncertainty.

As illustrated in Table 1, for Sr^{2+} complexation by 15C5, in spite of the lower donor ability of acetonitrile relative to methanol, the stability of 15C5-Sr^{2+} complex increases with increasing concentration of MeOH in binary systems. Although the solvation of the cation is an important factor in complexation reactions, solvation of the ligand and the resulting complex has also been documented to contribute to the overal free energy of complex formation [27]. In the case of complexation of Sr^{2+} ion, the solvation of the complex may destabilize it when passing from acetonitrile to methanol. As is evident from Table 1, the values of stability constants of 15C5-Ca^{2+} and 15C5-Sr^{2+} complexes in neat methanol which were obtained in this work are in agreement with the results reported in references [26] and [28].

It is interesting to note that while the stability constant of 15C5-Ca^{2+} varies nearly monotonically and linearly

with the solvent composition in AN-MeOH binary mixtures. a very different behavior is observed for 15C5-Mg $^{2+}$ complex (Figs. 6 and 7). As is shown in Figs.6 and 7, the change in the stability constant at various temperatures is certainly not monotonic. As the concentration of MeOH increases, the complex stability decreases suddenly to a minimum value at about 0.6 - 0.7 mole fraction of methanol and then increases gradually until the mole fraction of methanol is reached to 1. This behavior is probably due to some kind of solvent- solvent interactions between these two solvents and changing the structure of solvent system when they are mixed. Prasad and co-workers have studied the interaction between acetonitrile and methanol molecules by excess adiabatic compressibility (β^E) and excess inter-molecular free lenght (L_f^E) measurements at 303.15 K and showed that these parameters become increasingly negative with increasing strength

of interaction between the component molecules [29]. In addition, 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 [30].

The variation of $\log K_f$ for formation of 15C5-Mg^{2+}, 15C5-Ca $^{2+}$ and 15C5-Sr $^{2+}$ complexes vs the ionic radii in various AN-MeOH binary mixtures is shown in Fig. 9. Some reversals of stability can be observed, e.g. the 15C5-Ca $^{2+}$ complex is more stable compared to the other two complexes in 25-75 mol% and 50-50 mol% of AN-MeOH binary mixtures than neat MeOH, neat AN and 75-25 mol% of AN-MeOH binary system. Although the reversals of stabilities shown in Fig. 9 are not large, one can suggest that more changes in stabilites and reversal of cation selectivities may be obtained with better optimized mixed solvent systems.

As illustrated in Table 2, the calculated thermodynamic parameters for 15C5-Mg $^{2+}$, 15C5-Ca $^{2+}$ and 15C5-Sr $^{2+}$ complexes in AN-MeOH binary systems show that the ΔH°_c and ΔS°_c values are influenced by the solvent and vary with the solvent composition and both values generally become less positive in methanol rich mixtures. In most cases, positive values of ΔS°_c characterize the formation of these complexes . It seems reasonable to assume that the increase in entropy on complexation is due to additional solvent molecules which may be released from solvation shell of the cation upon complexation. It should be stressed, however, that the complexation reaction involves not only a change in the solvation of cation, but also that of the ligand.

The data in Table 2, show that the values of enthalpy for complexation reactions between 15-crown-5 and Mg $^{2+}$, Ca $^{2+}$ and Sr $^{2+}$ cations in AN-MeOH binary mixtures, do not vary monotonically with the solvent composition. 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.

Acknowledgment

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