

A Thermodynamic Study Between 18-Crown-6 with Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} Cations in Water–Methanol and Water–Ethanol Binary Mixtures Using The Conductometric Method

MOHAMMAD ANSARIFARD and GHOLAMHOSSEIN ROUNAGHI*

Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran

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Abstract

The complexation reactions between Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} cations with the macrocyclic ligand, 18-Crown-6 (18C6) in water–methanol (MeOH) binary systems as well as the complexation reactions between Ca^{2+} and Sr^{2+} cations with 18C6 in water–ethanol (EtOH) binary mixtures have been studied at different temperatures using conductometric method. The conductance data show that the stoichiometry of all the complexes is 1:1. It was found that the stability of 18C6 complexes with Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} cations is sensitive to solvent composition and in all cases, a non-linear behaviour was observed for the variation of $\log K_f$ of the complexes *versus* the composition of the mixed solvents. In some cases, the stability order is changed with changing the composition of the mixed solvents. The selectivity order of 18C6 for the metal cations in pure methanol is: $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$. The values of thermodynamic parameters (ΔH_c° and ΔS_c°) for formation of 18C6– Mg^{2+} , 18C6– Ca^{2+} , 18C6– Sr^{2+} and 18C6– Ba^{2+} complexes were obtained from temperature dependence of the stability constants. The obtained results show that the values of ΔH_c° and ΔS_c° for formation of these complexes are quite sensitive to the nature and composition of the mixed solvent, but they do not vary monotonically with the solvent composition.

Introduction

The discovery of the complexing properties of macrocyclic polyethers (crown ethers) by Pedersen [1] has sparked a wide range of activity in the fields ranging from synthesis of compounds to various analytical applications [2–4]. An important property of the crown ethers is their ability in formation of stable complexes with metal ions specially with the alkali and alkaline-earth ions [1]. In a typical complex, the metal ion occupies a site in the center of the crown ether with ligating donor atoms from the ring providing a full or partial inner coordination sphere for the metal ion. The studies of macrocyclic polyethers, mainly deal with the stability and selectivity of metal ion complexes of crown compounds [5,6] and also with the kinetics and thermodynamic of complex formation in solutions [7, 8].

While macrocyclic complexes of the alkali and alkaline-earth metal cations have been extensively investigated in aqueous solutions and in a wide variety of pure non-aqueous solvents [9–12], the complexation reactions of these complexes in mixed solvent systems have been investigated only to a very limited extent [13–15]. In the present study, we investigated the dependence of com-

plex stabilities on the nature and the composition of dipolar protic binary solvent systems in order to examine the effect of the solvent composition on the stability and selectivity of complexation. In order to achieve appropriate solvent properties, we may use mixed solvents.

Various physico-chemical techniques such as spectrophotometry [16], polarography [17], NMR spectrometry [18], calorimetry [19], potentiometry [20] and conductometry [21–23] have been used to study the complex formation between macrocyclic polyethers (crown ethers) and various metal ions in solutions. Among these various methods, the conductometric technique is a sensitive and inexpensive method with a simple experimental arrangement for such investigations.

In the present study, the stability constants of 18C6– Mg^{2+} , 18C6– Ca^{2+} , 18C6– Sr^{2+} and 18C6– Ba^{2+} complexes in water–methanol binary systems as well as the stability constants of 18C6– Ca^{2+} and 18C6– Sr^{2+} complexes in water–ethanol binary mixtures were determined at different temperatures by the conductometric method.

Materials and method

18-Crown-6 (Aldrich) was recrystallized from acetonitrile (Merck) and dried under vacuum for 72 h at room

* Author for correspondence. E-mail: ghrounaghi@yahoo.com

temperature. Extra pure methanol (MeOH) and ethanol (EtOH) were obtained from Merck company and were used without further purification. Extremely pure $\text{Ba}(\text{ClO}_4)_2$ (Merck), $\text{Sr}(\text{NO}_3)_2$ (Riedel), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Merck) and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Riedel) were used without further purification. The conductivity of each solvent was less than $3 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$ at 25 °C.

The experimental procedure used to obtain the stability constants of complexes is as follows: a solution of metal salt ($5 \times 10^{-4} \text{M}$) was placed in a titration cell thermostated at a given temperature, and the conductance of the solution was measured. For preparation of solutions with different ligand/cation mole ratios, a step by step increase in the crown ether concentration was carried out by a rapid transfer from crown ether solution prepared in the same solvent ($3 \times 10^{-2} \text{M}$) 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 Amel conductivity apparatus, model 60, in a water-bath thermostated at a constant temperature maintained within ± 0.03 °C. The conductance of the solutions 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 0.98cm^{-1} was used throughout the studies.

Results

The variation of molar conductivity with ligand/ M^{2+} molar ratios for metal ion complexes in various binary mixed solvents was studied at different temperatures. Two typical series of molar conductance values as a function of 18C6/ Sr^{2+} mole ratio in pure MeOH and 18C6/ Ba^{2+} mole ratio in H_2O -MeOH binary mixture (mol% MeOH = 60) are shown in Figures 1 and 2.

The stability constants of 18C6 complexes at each temperature were calculated from variation of molar conductance as a function of ligand/ M^{2+} mole ratios. The details of calculation of the stability constants of complexes by conductometric method has been described elsewhere [24].

The stability constants ($\log K_f$) for 18C6- M^{2+} ($\text{M}^{2+} = \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}$) complexes in various solvent systems are listed in Tables 1 and 2. Assuming that the activity coefficients of cation and complex have the same values, K_f is a thermodynamic equilibrium constant on the molar concentration scale, related to the Gibbs standard free energy of complexation reactions. The van't Hoff plots of $\log K_f$ versus $1/T$ for all of the systems investigated were constructed. A typical example of these plots is shown in Figure 3.

The changes in the standard enthalpy (ΔH_c°) for complexation reactions were determined in the usual manner from the slope of the van't Hoff plots assuming that ΔC_p is equal to zero over the entire temperature range

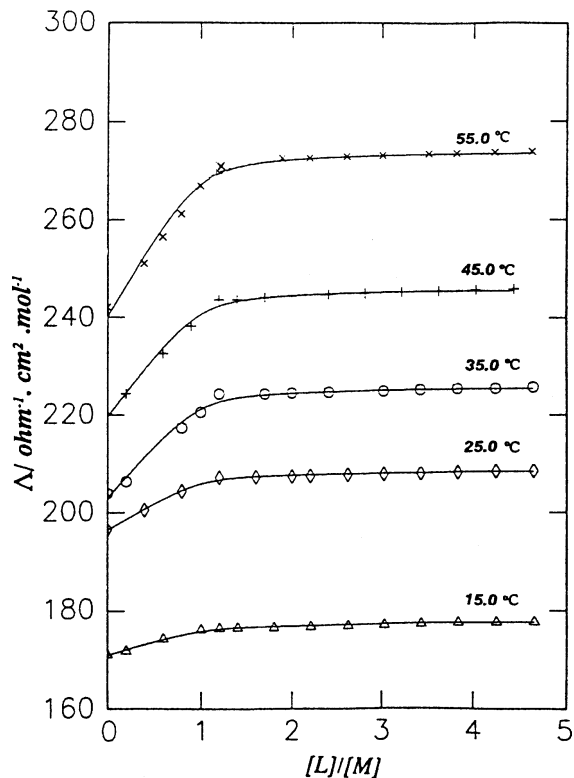


Figure 1. Molar conductance–mole ratio plots for 18C6- Sr^{2+} complex in pure methanol at different temperatures.

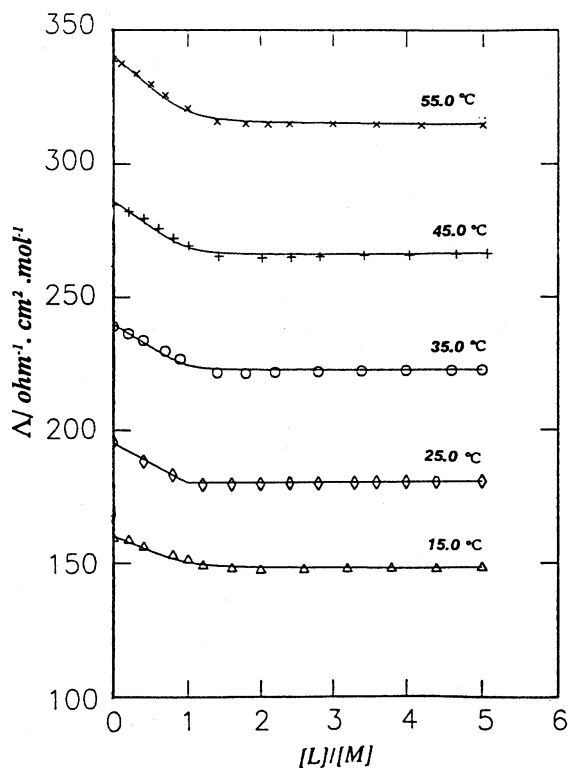


Figure 2. Molar conductance–mole ratio plots for 18C6- Ba^{2+} complex in H_2O -MeOH (mol% MeOH = 60) at different temperatures.

investigated. The changes in standard entropy (ΔS_c°) were calculated from the relationship $\Delta G_{c,298.15}^\circ = \Delta H_c^\circ - 298.15\Delta S_c^\circ$. The results are summarized in Table 3.

Table 1. $\log K_f$ values of $18C6-Mg^{2+}$, $18C6-Ca^{2+}$, $18C6-Sr^{2+}$ and $18C6-Ba^{2+}$ complexes in $H_2O-MeOH$ binary mixtures at different temperatures

Medium	$\log K_f \pm SD^a$				
	15 °C	25 °C	35 °C	45 °C	55 °C
<i>18C6-Mg²⁺</i> ^b					
Pure water	3.2 ± 0.2	3.3 ± 0.2	– ^c	3.1 ± 0.2	3.1 ± 0.2
70% H_2O –30% $MeOH$ ^d	3.6 ± 0.1	3.54 ± 0.09	– ^c	3.40 ± 0.08	3.3 ± 0.1
40% H_2O –60% $MeOH$	3.2 ± 0.2	3.38 ± 0.08	– ^c	– ^c	3.3 ± 0.1
20% H_2O –80% $MeOH$	3.5 ± 0.1	– ^c	3.45 ± 0.09	3.1 ± 0.2	3.0 ± 0.2
Pure $MeOH$	3.3 ± 0.1	3.4 ± 0.1	3.3 ± 0.1	3.3 ± 0.1	3.2 ± 0.1
<i>18C6-Ca²⁺</i> ^b					
Pure water	3.3 ± 0.1	3.2 ± 0.1	3.3 ± 0.1	– ^c	3.4 ± 0.1
70% H_2O –30% $MeOH$ ^d	3.5 ± 0.1	3.45 ± 0.08	3.3 ± 0.1	3.6 ± 0.1	3.4 ± 0.1
40% H_2O –60% $MeOH$	3.1 ± 0.2	3.3 ± 0.1	3.2 ± 0.1	3.4 ± 0.1	3.4 ± 0.1
20% H_2O –80% $MeOH$	– ^c	3.7 ± 0.3	3.45 ± 0.07	3.4 ± 0.1	3.1 ± 0.1
Pure $MeOH$	3.76 ± 0.06	3.74 ± 0.06	3.69 ± 0.07	3.63 ± 0.07	3.60 ± 0.07
<i>18C6-Sr²⁺</i> ^b					
Pure water	3.42 ± 0.08	3.41 ± 0.08	3.35 ± 0.08	3.34 ± 0.08	3.32 ± 0.08
70% H_2O –30% $MeOH$ ^d	3.81 ± 0.08	4.09 ± 0.06	3.84 ± 0.04	3.85 ± 0.07	3.81 ± 0.05
40% H_2O –60% $MeOH$	4.3 ± 0.1	4.6 ± 0.2	4.5 ± 0.1	4.5 ± 0.2	4.6 ± 0.1
Pure $MeOH$	4.48 ± 0.07	4.70 ± 0.06	4.7 ± 0.1	4.68 ± 0.07	4.7 ± 0.1
<i>18C6-Ba²⁺</i> ^b					
Pure water	4.21 ± 0.05	4.02 ± 0.04	3.87 ± 0.06	3.93 ± 0.05	3.80 ± 0.05
80% H_2O –20% $MeOH$ ^d	4.2 ± 0.1	4.1 ± 0.1	4.4 ± 0.1	4.13 ± 0.06	4.03 ± 0.05
60% H_2O –40% $MeOH$	4.73 ± 0.09	4.77 ± 0.08	4.8 ± 0.2	4.32 ± 0.09	4.36 ± 0.08
40% H_2O –60% $MeOH$	5.7 ± 0.5	6.0 ± 0.4	5.0 ± 0.3	4.8 ± 0.2	4.6 ± 0.1
20% H_2O –80% $MeOH$	>6	>6	>6	>6	>6
Pure $MeOH$	>6	>6	>6	>6	>6

^aSD = standard deviation.

^bThe concentration of each metal cation was 5.0×10^{-4} M.

^cSD of $\log K_f$ is high.

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

Table 2. $\log K_f$ values of $18C6-Ca^{2+}$ and $18C6-Sr^{2+}$ complexes in $H_2O-EtOH$ binary mixtures at different temperatures

Medium	$\log K_f \pm SD^a$				
	15 °C	25 °C	35 °C	45 °C	55 °C
<i>18C6-Ca²⁺</i> ^b					
74.90% H_2O –25.1% $EtOH$ ^d	– ^c	3.2 ± 0.2	– ^c	– ^c	3.61 ± 0.9
50.0% H_2O –50.0% $EtOH$	3.9 ± 0.2	4.03 ± 0.04	3.37 ± 0.08	3.4 ± 0.1	– ^c
24.6% H_2O –75.4% $EtOH$	3.2 ± 0.1	3.2 ± 0.1	3.2 ± 0.1	2.9 ± 0.2	– ^c
Pure $EtOH$	4.33 ± 0.04	4.37 ± 0.02	4.46 ± 0.04	4.48 ± 0.05	4.41 ± 0.03
<i>18C6-Sr²⁺</i> ^b					
74.90% H_2O –25.1% $EtOH$ ^d	4.22 ± 0.06	4.21 ± 0.04	4.13 ± 0.06	4.03 ± 0.06	4.07 ± 0.04
50.0% H_2O –50.0% $EtOH$	5.4 ± 0.4	5.0 ± 0.2	4.73 ± 0.06	5.2 ± 0.1	4.30 ± 0.06
24.6% H_2O –75.4% $EtOH$	3.2 ± 0.2	3.3 ± 0.2	3.0 ± 0.2	3.63 ± 0.08	3.6 ± 0.1

^aSD = standard deviation.

^bThe concentration of each metal cation was 5.0×10^{-4} M.

^cSD of $\log K_f$ is high.

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

Discussion

As is evident from Figure 1, addition of $18C6$ ligand to a solution of strontium ion in pure methanol at different temperatures shows an increase in molar conductivity with an increase in the ligand concentration. This

indicates that the $18C6-Sr^{2+}$ complex in pure methanol is more mobile than free solvated Sr^{2+} ion. Similar behaviour was observed for $18C6-Mg^{2+}$ and $18C6-Ca^{2+}$ in pure methanol as well as for $18C6-Ca^{2+}$ in pure ethanol. The slope of the corresponding molar conductivity *versus* ligand/cation mole ratio plots changes

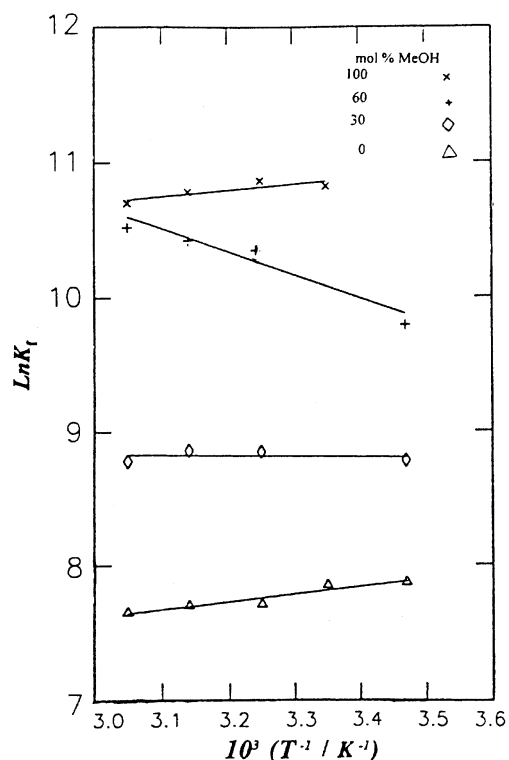


Figure 3. Van't Hoff plots for 18C6-Sr²⁺ in H₂O-MeOH binary systems.

Table 3. Thermodynamic parameters for 18C6-Mg²⁺, 18C6-Ca²⁺, 18C6-Sr²⁺ and 18C6-Ba²⁺ complexes in H₂O-MeOH and 18C6-Ca²⁺, 18C6-Sr²⁺ complexes in H₂O-EtOH binary mixtures

Medium	$-\Delta G_c^\circ \pm SD^a$ (25 °C) (KJ/mol)	$-\Delta H_c^\circ \pm SD^a$ (KJ/mol)	$-\Delta S_c^\circ \pm SD^a$ (J/mol K)
18C6-Mg²⁺			
Pure water	18.8 ± 4.2	-5.9 ± 0.8	33 ± 13
70%H ₂ O-30%MeOH ^b	20.1 ± 3.3	-15.1 ± 2.5	17 ± 8
20%H ₂ O-80%MeOH	19.2 ± 2.1	-25.9 ± 1.7	-21 ± 4
Pure MeOH	19.2 ± 2.1	-7.1 ± 1.7	42 ± 4
18C6-Ca²⁺			
40%H ₂ O-60%MeOH ^b	18.0 ± 2.9	18.0 ± 2.1	121 ± 8
20%H ₂ O-80%MeOH	21 ± 8	-33 ± 4	-42 ± 17
18C6-Sr²⁺			
Pure water	19.2 ± 1.3	-4.6 ± 0.8	49.4 ± 2.9
70%H ₂ O-30%MeOH ^b	17.6 ± 2.1	4.6 ± 0.8	75 ± 4
40%H ₂ O-60%MeOH	25 ± 4	13 ± 4	134 ± 13
Pure MeOH	26.8 ± 2.5	-3.8 ± 1.7	79 ± 4
18C6-Ca²⁺			
Pure water	25 ± 4	-17 ± 4	21 ± 13
80%H ₂ O-20%MeOH ^b	23.8 ± 3.3	-6.3 ± 2.1	59 ± 8
40%4H ₂ O-60%MeOH	29 ± 4	-52.7 ± 2.9	-75 ± 8
18C6-Ca²⁺			
50.0%H ₂ O-50.0%EtOH ^b	21 ± 13	-33 ± 8	-42 ± 29
Pure EtOH	25 ± 4	5.4 ± 2.9	100 ± 8
18C6-Sr²⁺			
74.9%H ₂ O-25.1%EtOH ^b	23.8 ± 2.9	-9.2 ± 2.1	50 ± 4
50.0%H ₂ O-50.0%EtOH	29 ± 4	-47.7 ± 2.9	-63 ± 8
24.6%H ₂ O-75.4%EtOH	17 ± 8	21 ± 4	134 ± 17

^aSD = standard deviation.

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

^cSD of log K_f is high.

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

sharply at the point where the ligand to cation mole ratio is 1, which is an evidence for formation of a relatively stable 1:1 complex. As is shown in Figure 2, addition of the ligand to a solution of barium ion in H₂O-MeOH (mol% MeOH = 60) mixed solvent at various temperatures indicates a decrease in molar conductivity with increasing the ligand concentration. This shows that the 18C6-Ba²⁺ complex in this mixed solvent is less mobile than free solvated Ba⁺ ion.

It is obvious from Figure 1 as the temperature increases, the curvature of the plots of 18C6-Sr²⁺ complex increases which indicates the formation of a stronger complex at higher temperatures. Therefore, there is an endothermic reaction between Sr²⁺ ion with 18C6. Similar behaviour was observed for 18C6-Ca²⁺ in H₂O-MeOH (mol% MeOH = 60) and 18C6-Sr²⁺ complex in H₂O-EtOH (mol% EtOH = 75.4) binary mixtures as well as for 18C6-Ca²⁺ complex in pure ethanol.

It is seen from Table 1 that for 18C6-Ba²⁺ and 18C6-Sr²⁺ complexes as the concentration of water is increased in H₂O-MeOH binary mixtures, the stability of these complexes decreases. This behaviour reflects the much stronger cation solvation by water molecules compared with the methanol molecules, with which the ligand has to challenge. Water with a relatively high

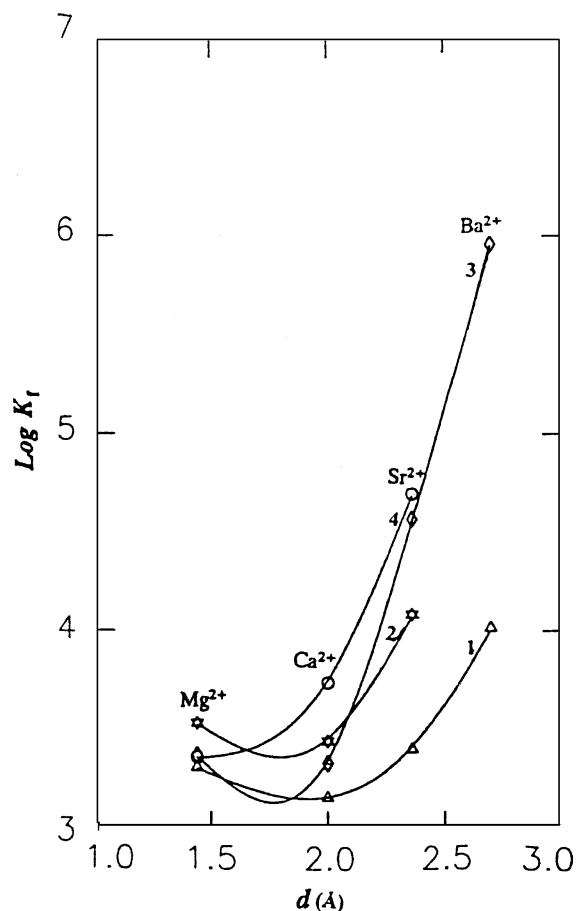


Figure 4. Variation of $\log K_f$ of 18C6 complexes of Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} versus cationic diameter in (1) pure water, (2) 30 mol% MeOH, (3) 60 mol% MeOH and (4) pure MeOH at 25 °C.

Gutmann donor number ($\text{DN} = 33$) solvates the metal cations more strongly than methanol and, therefore, compete with the polyether for the metal ions. As a consequence, the formation of complexes is weakened with increasing the concentration of water in these mixed binary solvents. In addition, as is evident from Tables 1 and 2, in most of the mixed solvent systems used in these studies, the stability of complexes of the alkaline earth cations with 18C6 decreases in the order: $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$. The Ba^{2+} ion forms the most stable complex with 18C6. This result is expected, since its ionic size (2.70 Å) is very close to the size of the 18C6 cavity (2.76 Å). The ionic size of the Sr^{2+} ion (2.36 Å) is relatively close to the cavity size of the 18C6, but since the sizes of Ca^{2+} (ionic size = 2.00 Å) and Mg^{2+} (ionic size = 1.44 Å) cations are smaller than the 18C6 cavity, they form less stable complexes with 18C6.

The variation of $\log K_f$ of 18C6 complexes with Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} cations versus cationic diameter in some water–methanol binary systems at 25 °C is shown in Figure 4. As is evident from this Figure, several reversals of stability are observed in some solvent systems. These reversal of stabilities indicate the possibility of changes in stabilities and,

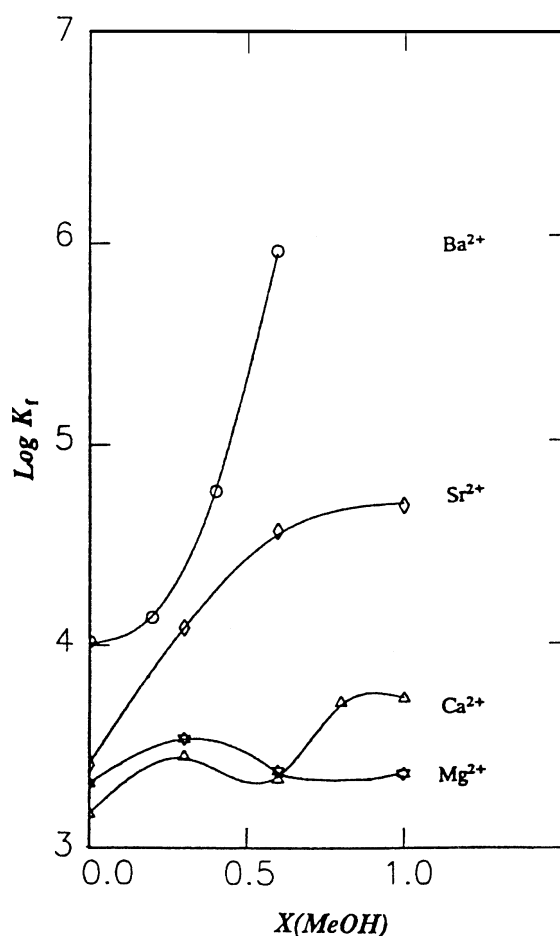


Figure 5. Variation of stability constant of 18C6– Mg^{2+} , 18C6– Ca^{2+} , 18C6– Sr^{2+} and 18C6– Ba^{2+} complexes with the composition of the H_2O –MeOH binary system at 25 °C.

therefore, reversals of cation selectivities which may be obtained in certain selected mixed solvent systems.

The variation of stability constants ($\log K_f$) of 18C6– Mg^{2+} , 18C6– Ca^{2+} , 18C6– Sr^{2+} and 18C6– Ba^{2+} complexes with the composition of H_2O –MeOH binary system at 25 °C is shown in Figure 5. It is interesting to note that while the formation constants of 18C6– Sr^{2+} and 18C6– Ba^{2+} complexes increase, with concentration of methanol in H_2O –MeOH binary solutions, this trend is not followed for 18C6– Mg^{2+} and 18C6– Ca^{2+} complexes.

The water–methanol and water–ethanol data are compared in Tables 1 and 2. The change in stability constant of 18C6– Sr^{2+} complex at various temperatures versus the composition of H_2O –EtOH is not monotonic. As the concentration of EtOH increases, the complex stability increases to a maximum value at 0.5 mole fraction of ethanol and then decreases. This behaviour is probably due some kind of solvent–solvent interactions between these two solvents and changing the structure of solvent system and, therefore, changing the solvation properties of the solvents. The solvation number is probably strongly influenced by the structure of the solvent. The maximum which is observed in variation of $\log K_f$ of 18C6– Sr^{2+} complex versus the composition of

H₂O–EtOH binary systems seems to be attributable to a difference in the structure of the solvent before and after of 0.5 mole fraction of ethanol. Some of the physico-chemical properties of water–alcohol binary mixtures such as viscosity have maxima in certain composition [25]. A non-linear behaviour was also observed for variation of $\log K_f$ of 18C6–Ca²⁺ complex *versus* the composition of H₂O–EtOH mixed solvents.

As is evident from Table 3, the values of thermodynamic parameters for complexation reactions vary with the nature and composition of the mixed solvents. The experimental values of ΔH_c° and ΔS_c° show that in most cases, the complexes are both enthalpy and entropy stabilized, therefore, the enthalpies and the entropies of complexation reactions are the principal driving forces for formation of these complexes.

The data collected in Table 3, show that the values of enthalpy and entropy for complexation reactions between 18C6 and Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺ cations in H₂O–MeOH and H₂O–EtOH binary mixtures, do not vary monotonically with the solvent composition. Since there are many parameters which contribute to changes in complexation enthalpies and entropies, therefore, we should not expect a regularity between these parameters and the solvent composition of these binary mixtures of associated dipolar protic solvents.

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