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ORIGINAL ARTICLE

# Conductometric study of complexation reaction between 15-crown-5 and $Cr^{3+}$, $Mn^{2+}$ and $Zn^{2+}$ metal cations in pure and binary mixed organic solvents

**Gholamhossein Rounaghi · Massoumeh Mohajeri · Zahra Atashi · Roya Mohammadzadeh kakhki**

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**Abstract** The stability constants ($K_f$) for the complexation reactions of $Cr^{3+}$, $Mn^{2+}$ and $Zn^{2+}$ metal cations with macrocyclic ligand, 15-crown-5 (15C5), in acetonitrile (AN), ethanol (EtOH) and also in their binary solutions (AN–EtOH) were determined at different temperatures, using conductometric method. 15C5 forms 1:1 complexes with $Cr^{3+}$, $Mn^{2+}$ and $Zn^{2+}$ cations in solutions. A non-linear behaviour was observed for changes of $\log K_f$ of the metal ion complexes versus the composition of the mixed solvent. The order of stability of the metal–ion complexes in pure AN and in a binary solution of AN–EtOH (mol% AN = 52) at 25 °C was found to be: $(15C5Zn)^{2+} > (15C5{\cdot}Mn)^{2+} > (15C5{\cdot}Cr)^{3+}$, but in the case of pure EtOH at the same temperature, it changes to: $(15C5{\cdot}Zn)^{2+} > (15C5{\cdot}Cr)^{3+} > (15C5{\cdot}Mn)^{2+}$. The results also show that the stability sequence of the complexes in the other binary solutions of AN–EtOH (mol% AN = 26 and mol% AN = 76) varies in order: $(15C5{\cdot}Cr)^{3+} \sim (15C5{\cdot}Zn)^{2+} > (15C5{\cdot}Mn)^{2+}$. The values of the standard thermodynamic quantities ($\Delta H_C°$, $\Delta S_C°$) for formation of ($15C15\text{-}Cr^{3+}$), ($15C5\text{-}Mn^{2+}$) and ($15C5\text{-}Zn^{2+}$) complexes were obtained from the temperature dependence of the stability constants and the results show that the thermodynamics of complexation reactions is affected by nature and composition of the solvent systems and in most solution systems, the complexes are enthalpy stabilized but entropy destabilized.

**Keywords** 15-Crown-5 · $Cr^{3+}$ · $Mn^{2+}$ and $Zn^{2+}$ cations · Acetonitrile-ethanol binary mixture · Conductometry

## Introduction

From the discovery of complexing properties of macrocyclic polyetheres (crown ethers) in the mid-1960s by Pedersen [1], these macrocyclic ligands have played a leading role in the development of host–guest and supramolecular chemistry. These complexes appeared to be salt-polyether complexes formed by ion–dipole interaction between the cation and the electronegative oxygen atoms which are symmetrically placed in the crown ether ring [1].

The factors which influence the stability of the metal cation-crown ether complexes include: the relative size of the cation and the cavity of the crown ether, the number of oxygen atoms in the ring, the coplanarity of the oxygen atoms, the symmetrical placement of the oxygen atoms, the basicity of the oxygen atoms, steric hindrance in the polyether ring, the nature of the cation and the electrical charge on the cation [2, 3]. The ability of the solvent molecules to compete with the donor atoms of the ligand towards the coordination sites of the cation and also the solvation of the ligand and the resulting complex are another factors that can thermodynamically influence the complexation process between such macrocyclic ligands and the metal cations [4, 5].

Over the years, these heteromacrocyclic ligands have been used for the construction of new materials and devices, such as: organic synthesis [6], in construction of ion-selective electrodes[7, 8], separation of metal cations [9–12], as solid phase in chromatography columns [13–16], in the design of fiber optic chemical sensors [17], in ion exchange membranes [18], recognition of isomers [19] and also in chemical analysis [20, 21]. Most of the applications of the crown compounds are based on their complexing ability to the metal cations. Therefore, study of crown ether complexation is very important. Among the various

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G. Rounaghi (✉) · M. Mohajeri · Z. Atashi · R. Mohammadzadeh kakhki
Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran
e-mail: ronaghi0970i@mashdiau.ac.ir

methods, which have been used for study of complexation processes between the macrocyclic ligands and the metal cations, the conductometry is a very sensitive and inexpensive method with a simple experimental arrangement. In addition, in this method, the measurements can be carried out at low solution concentrations, where the interactions between the cations and anions are to be negligible.

The thermodynamic studies of such complexation reactions result in a better understanding of high selectivity of these ligands towards different metal cations. We are especially interested in study of the thermodynamics of complexation and selectivity profiles of crown compounds towards the various metal cations [22, 23].

In solution, the metal ion, the crown ether and also the metal ion–crown ether complex would be surrounded by solvent molecules that might play a significant role in shifting the preference for one metal ion over another. Thus, it is of great importance to study the effect of solvent on the complexation of metal ions to crown ethers.

The combination of pure solvents as mixed solvents substantially increases the diversity of reaction media. Investigation of solvent effects on thermodynamic and kinetic functions is interesting both experimentally and theoretically in chemical and biochemical analysis. The study of solvent effects on chemical and physical processes in binary mixtures is more complicated than in pure solvents, because the solute–solvent and solvent–solvent interactions can create new solvent properties leading to preferential solvation.

While the complexation of crown compounds with metal cations have been studied in aqueous solutions and in pure organic solvents but a little attention has been paid to complexation of these macrocyclic ligands with metal cations in mixed binary organic solvents. The goal of the present investigation, is to study the effect of the nature of the cation, especially the solvent properties on the stability, selectivity and of thermodynamic parameters of 15-crown-5 (Fig. 1) complexes with $Cr^{3+}$, $Mn^{2+}$ and $Zn^{2+}$ metal cations in pure acetonitrile and pure ethanol and also their binary solutions (AN–EtOH) at different temperatures, using the conductometric method.

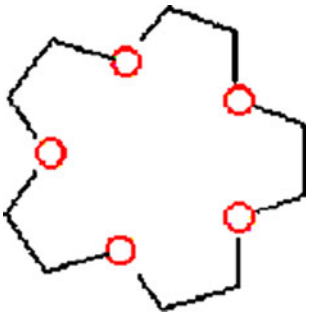

**Fig. 1** Structure of 15-crown-5

## Experimental

### Reagent and solvents

15-crown-5 (Fluka), chromium (III) nitrate (Merck), manganese (II) nitrate (Merck) and zinc (II) nitrate (Merck) were used without further purification. The solvents: acetonitrile and ethanol (both from Merck) were used with highest purity. All reagents were purchased from Merck company.

### Procedure

The experimental procedure to obtain the formation constants of complexes was as follows: a solution of metal salt ($1.00 \times 10^{-4}$ M) was placed in a titration cell and the conductance of solution was measured, then 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 ($2.00 \times 10^{-3}$ M) to the titration cell using a micropipette 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 Metrohm conductivity apparatus (model 712) in a water bath Julabo (model F12) thermostated with a constant temperature maintained within ±0.01 °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 $1.25\ \mathrm{cm}^{-1}$ was used throughout the studies.

### Theory

When a crown compound forms a $M_aL_b^{m+}$ complex with a metal cation, the equilibrium equation can be written as:

$$aM^{m+} + bL \leftrightarrow M_aL_b^{m+} \qquad (1)$$

$$\alpha C_M \; C_L - (1-\alpha)C_M \; (1-\alpha)C_M$$

where $M^{m+}$, L and α are the metal cation, crown compound and the fraction of free cation, respectively. Thus, the equilibrium constant, $K_e$, in different ratios of complex formation are calculated using the following equations:

$$K_e = \left[M_aL_b^{m+}\right]/\left[M^{m+}\right]^a[L]^b \qquad (2)$$

$$C_M/C_L = 1 \qquad (3)$$

$$C_M = [M_a]^{m+} + [\,M_aL_b]^{m+} \qquad (4)$$

$$C_L = [L_b] + [\,M_aL_b]^{m+} \qquad (5)$$

$$\alpha = [M_a]^{m+}/\,C_M \qquad (6)$$

$$P = [M_aL_b]^{m+}/C_M = K_e[L_b]/1 + K_e[L_b] \qquad (7)$$

The observed conductivity, $\kappa$, is given by

$$\kappa = \kappa^{m+}_{(Ma)} + \kappa^{m+}_{(MaLb)} \tag{8}$$

The molar conductivities are given by the following equations:

$$\Lambda^{m+}_{(Ma)} = \kappa^{m+}_{(Ma)}/[M_a]^{m+} \tag{9}$$

$$\Lambda^{m+}_{(MaLb)} = \kappa^{m+}_{(MaLb)}/[M_aL_b]^{m+} \tag{10}$$

$$\Lambda = \kappa/C_M \tag{11}$$

$$\Lambda = \alpha\Lambda^{m+}_{(Ma)} + (1-\alpha)\,\Lambda^{m+}_{(MaLb)} \tag{12}$$

As a result of Eqs. (12) and (2) can be transformed into:

$$K_e = \Lambda^{m+}_{(Ma)} - \Lambda/(\Lambda - \Lambda^{m+}_{(MaLb)})[L_b] \tag{13}$$

Where

$$[L_b] = C_L - C_M \cdot P$$

and

$$[L_b] = C_L - C_M \cdot (\Lambda^{m+}_{(Ma)} - \Lambda)\,/\,(\Lambda^{m+}_{(Ma)} - \Lambda^{m+}_{(MaLb)})$$

$C_M$, $C_L$ are the total concentrations of the metal cation and crown ether, respectively; $[M_a]^{m+}$, $[L_b]$ and $[M_aL_b]^{m+}$ are the concentrations of uncomplexed cation, uncomplexed crown ether and complexed cation, respectively; P is the experimental mole fraction of the complexed cation or the ligand, for a 1:1 complex, and a and b are the complexing degrees of both sides in the case of several degrees of complexing (Eqs 1–13), $\kappa^{m+}_{(Ma)}$ and $\kappa^{m+}_{(MaLb)}$, are the observed conductivities of the cation and the crown-cation complex, respectively; $\Lambda^{m+}_{(Ma)}$ and $\Lambda^{m+}_{(MaLb)}$ are the molar conductivities of the cation and the crown -cation complex, respectively.

## Results and discussion

The changes of molar conductance ($\Lambda_m$) versus the ligand to cation molar ratio ($[L]_t/[M]_t$) for complexation of 15C5 with $Cr^{3+}$, $Mn^{2+}$ and $Zn^{2+}$ metal cations in pure AN and EtOH and their binary systems were studied at different temperatures. $[L]_t$ is the total concentration of 15C5 and $[M]_t$ is the total concentration of each metal cation in solution.

Two typical series of molar conductance values as a function of ligand to metal cation mole ratios for the formation of $(15C5{\cdot}Zn)^{2+}$ complex in pure AN and in AN–EtOH (mol% AN = 52) binary system are shown in Figs. 2 and 3, respectively. As seen from these Figures, addition of 15C5 to a solution of $Zn^{2+}$ cation in pure acetonitrile at different temperatures results in an increase in molar conductivity. This indicates that the $(15C5{\cdot}Zn)^{2+}$ complex is more mobile than free solvated $Zn^{2+}$ cation. Since the size of the cation is smaller and its charge density is much higher than the complexed cation, therefore, it is much more solvated than the bulky complexed cation and therefore, the complex is more mobile than free solvated $Zn^{2+}$ cation, so that the molar conductivity increases upon addition of the ligand to the $Zn^{2+}$ cation solution. Also it seems that in lower temperatures the structure of the solvent become more rigid, therefore, the solvation of the species reduces and their mobility increases, which results in increasing the molar conductivity with decreasing the temperature.

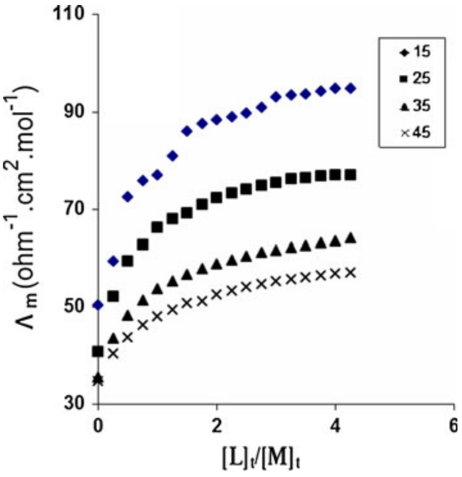

**Fig. 2** Molar conductance-mole ratio plots for $(15C5{\cdot}Zn)^{2+}$ complex in pure acetonitrile at different temperatures (*filled diamond* 15 °C, *filled square* 25 °C, *filled triangle* 35 °C, *times* 45 °C)

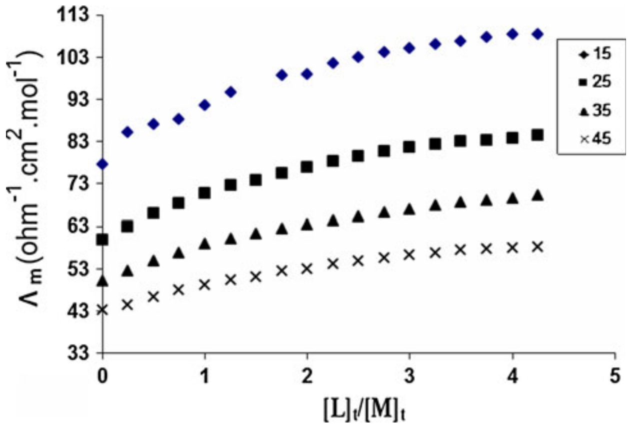

**Fig. 3** Molar conductance-mole ratio plots for $(15C5{\cdot}Zn)^{2+}$ complex in acetonitrile-ethanol binary system (mol% AN = 52) at different temperatures (*filled diamond* 15 °C, *filled square* 25 °C, *filled triangle* 35 °C, *times* 45 °C)

The slope of the corresponding molar conductivity versus ligand/metal cation plots changes at the point where the ligand to cation mole ratio is about 1, which is an evidence for formation of a relatively stable 1:1 complex between $Zn^{2+}$ cation and 15C5 in these solvent systems.

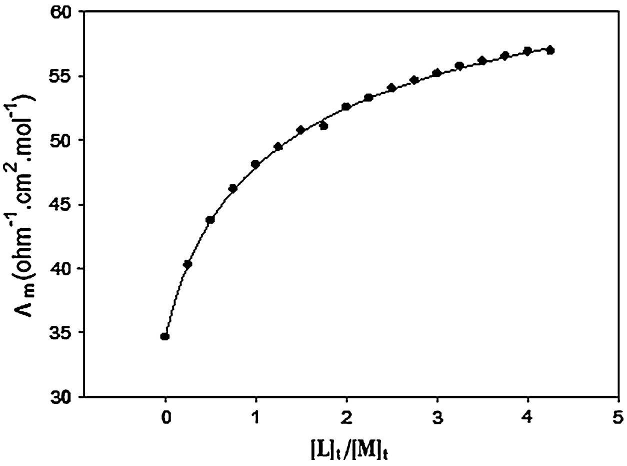

**Fig. 4** The fitting and experimental (*filled diamond*) curves for $(15C5{\cdot}Zn)^{2+}$ at 25 °C complex in pure acetonitrile

In order to make more clear the 1:1 [M:L] complexation model, the fitting and experimental curves for $(15C5{\cdot}Zn)^{2+}$ complex (at 45 °C in pure AN) are shown in Fig. 4. As is evident in this figure, there is a good agreement between the fitting and experimental data. Somewhat similar behavior was observed for $Cr^{3+}$ and $Mn^{2+}$ cations in the binary mixed solvents.

The stability constants of the 15C5 complexes at each temperature were calculated (Table 1) from the changes of molar conductance as a function of $[L]_t/[M]_t$ molar ratio using a GENPLOT computer program [24]. The details of the calculation of the stability constants of complexes by conductometric method has been described elsewhere [25].

Ion–solvent interactions play a very important role in the studies of stoichiometry, structure, and the stability of metal cation complexes with crown ethers. Knowledge of the ionophore solvation properties enables one to choose a suitable solvent for complexation studies and to obtain detailed information on the solvent effect. Also in the complexation process of 15C5 with $Cr^{3+}$, $Mn^{2+}$ and $Zn^{2+}$ the solvent plays a critical role [26–28]. In this work we investigated on the complexation of 15C5 with these three metal cations in acetonitrile, ethanol and their binary solutions. The stability constants ($\log K_f$) for $(15C5\text{-}M)^{n+}$ ($M^{n+} = Cr^{3+}$, $Mn^{2+}$ and $Zn^{2+}$) complexes in acetonitrile are bigger than in EtOH. Since the donor ability of EtOH

**Table 1** $\log K_f$ values of $(15C5{\cdot}Cr)^{3+}$, $(15C5{\cdot}Mn)^{2+}$ and $(15C5{\cdot}Zn)^{2+}$ complexes in AN–EtOH binary mixtures at different temperatures

| Medium | $\log K_f \pm SD$ | | | |
|---|---|---|---|---|
| | 15 °C | 25 °C | 35 °C | 45 °C |
| $(15C5{\cdot}Cr)^{3+}$[a] | | | | |
| Pure AN | [b] | [b] | [b] | [b] |
| 90%AN–10%EtOH[c] | 4.55 ± 0.13 | 4.05 ± 0.19 | 3.01 ± 0.11 | 3.67 ± 0.14 |
| 75%AN–25%EtOH | 4.18 ± 0.09 | 3.33 ± 0.07 | 3.28 ± 0.12 | 3.50 ± 0.09 |
| 50%AN–50%EtOH | [d] | 2.88 ± 0.16 | 2.83 ± 0.07 | 2.99 ± 0.06 |
| 25%AN–75%EtOH | 3.12 ± 0.17 | 3.50 ± 0.15 | 3.00 ± 0.14 | [d] |
| Pure EtOH | 3.42 ±0.43 | 3.05 ± 0.10 | 3.77 ± 0.15 | 2.85 ± 0.18 |
| $(15C5{\cdot}Mn)^{2+}$[a] | | | | |
| Pure AN | 4.53 ± 0.15 | 4.46 ± 0.12 | 4.78 ± 0.30 | 5.33 ± 0.30 |
| 75%AN–25%EtOH[c] | 3.74 ± 0.05 | 2.98 ± 0.16 | [d] | 2.73 ± 0.30 |
| 50%AN–50%EtOH | 3.10 ± 0.14 | 3.12 ± 0.12 | 3.41 ± 0.18 | 3.21 ± 0.11 |
| 25%AN–75%EtOH | 3.48 ± 0.14 | 2.84 ± 0.26 | 3.24 ± 0.12 | 3.34 ± 0.07 |
| Pure EtOH | 3.04 ± .0.20 | [d] | 3.34 ± 0.12 | [d] |
| $(15C5{\cdot}Zn)^{2+}$[a] | | | | |
| Pure AN | 4.52 ± 0.10 | 4.64 ± 0.11 | 4.43 ± 0.09 | 4.36 ± 0.08 |
| 75%AN–25%EtOH[c] | 3.71 ± 0.09 | 3.28 ± 0.06 | 3.24 ± 0.03 | 3.45 ± 0.20 |
| 50%AN–50%EtOH | 3.80 ± 0.10 | 3.76 ± 0.02 | 3.65 ± 0.03 | 3.62 ± 0.04 |
| 25%AN–75%EtOH | 3.14 ± 0.08 | 3.45 ± 0.50 | 3.19 ± 0.08 | 3.12 ± 0.13 |
| Pure EtOH | 3.91 ± 0.14 | 3.68 ± 0.11 | 3.33 ± 0.09 | 3.5 ± 0.10 |

*SD* standard deviation

[a] The concentration of each metal cation was $1.0 \times 10^{-4}$ M

[b] The salt is not dissolved in pure AN

[c] Composition of binary mixtures is expressed in mol% for each solvent system

[d] The data cannot be fitted to the equation

(DN = 19) as expressed by the Gutmann donocity [29] is higher than AN (DN = 14.0), therefore, it competes more strongly with the ligand for the metal cations than AN.

The complexation reaction between a metal cation with a ligand in solution, which is an exchange process can be written as:

$$(\mathrm{Metal}^{n+})\mathrm{S_x} + (\mathrm{ligand})\mathrm{S_y} \leftrightarrow (\mathrm{metal-ligand})^{n+}\mathrm{S_z} + (\mathrm{x}+\mathrm{y}-\mathrm{z})\mathrm{S}$$

in which S is the solvent molecule, x, y, z, are the solvation numbers of the metal cation, ligand and the resulting complex, respectively. Therefore, the change of free energy of this reaction, depends on the difference in affinity of ligand and solvent for the metal cation and also the difference in affinity of the metal cation and solvent molecules for the ligand. In addition, the solvation of the resulting complex is effective in the free energy of complexation process. Therefore, in addition of solvation of the metal cation, the solvation of the ligand and the resulting complex contribute to the overall free energy of complex formation in solutions [30].

The thermodynamic characteristics ($\Delta H°_C$ and $\Delta S°_C$) of the complex formation, calculated from the temperature dependences of the stability constants, are given in Table 2. The Gibbs energy of the complex formation non-monotonically varies with the composition of the binary organic solvents and this indicates on interparticle interactions because of the entropy enthalpy compensation [31]. Physically this means that the enthalpy and entropy components of the Gibbs energy directly reflect specifics of reagent-solvent interactions and characterize qualitative and quantitative distinctions of systems and processes under comparison [32].

For all investigated systems, the van′t Hoff plots of log $K_f$ versus 1/T were constructed. The changes in standard enthalpy ($\Delta H°_C$) were obtained from the slope of the van′t Hoff plots and the changes in standard entropy ($\Delta S°_C$) were calculated from the relationship $\Delta G°_{C298.15} = -RT\ln K_f = \Delta H°_C - 298.15\Delta S°_C$. A typical of these plots for $(15C5\cdot Mn)^{2+}$ complex formation is shown in Fig. 5.

As is evident from Table 2, the overall free Gibbs energy ($\Delta G°_C$) in pure acetonitrile for formation of $(15C15\cdot Cr)^{3+}$, $(15C5\cdot Mn)^{2+}$ and $(15C5\cdot Zn)^{2+}$ complexes is more appropriate and more stable complexes are formed in this solvent compared to the other solvent systems. As expected, the enthalpy and entropy values for complexation reactions vary with the nature and composition of the mixed solvents. Since the values of standard entropy and

**Table 2** Thermodynamic parameters for $(15C5\cdot Cr)^{3+}$, $(15C5\cdot Mn)^{2+}$ and $(15C5\cdot Zn)^{2+}$ complexes in AN–EtOH binary mixtures

| Medium | $\Delta G°_C$ ± SD (25 °C) | $\Delta H°_C$ ± SD | $\Delta S°_C$ ± SD |
|---|---|---|---|
| $(15C5\cdot Cr)^{3+a}$ | | | |
| Pure AN | [b] | [b] | [b] |
| 90%AN–10%EtOH[c] | −23.12 ± 0.10 | −64.1 ± 0.04 | 137.2 ± 3.62 |
| 75%AN–25%EtOH | −19.01 ± 0.14 | −39.13 ± 0.03 | −67.48 ± 1.02 |
| 50%AN–50%EtOH | −16.48 ± 0.94 | −4.77 ± 0.01 | 39.27 ± 3.16 |
| 25%AN–75%EtOH | −17.79 ± 0.84 | −8.50 ± 0.00 | −31.66 ± 2.79 |
| Pure EtOH | −17.22 ± 0.59 | −16.4 ± .0.04 | 3.38 ± 0.00 |
| $(15C5\cdot Mn^{)2+a}$ | | | |
| Pure AN | −25.5 ± 0.68 | 34.71 ± 0.03 | 201.84 ± 2.20 |
| 75%AN–25%EtOH[d] | −17.00 ± 0.92 | −54.62 ± 0.02 | −126.18 ± 3.09 |
| 50%AN–50%EtOH | −17.84 ± 0.70 | 29.84 ± 0.06 | 159.80 ± 2.20 |
| 25%AN–75%EtOH | −18.50 ± 0.50 | −1.63 ± 0.03 | 48.83 ± 0.50 |
| Pure EtOH | [d] | [d] | [d] |
| $(15C5\cdot Zn)^{2+a}$ | | | |
| Pure AN | −26.48 ± 0.60 | −11.73 ± 0.08 | 49.45 ± 4.13 |
| 75%AN–25%EtOH[c] | −18.75 ± 0.33 | −15.36 ± 0.17 | 11.36 ± 1.11 |
| 50%AN–50%EtOH | −21.50 ± 0.03 | −11.63 ± 0.01 | 33.02 ± 0.45 |
| 25%AN–75%EtOH | −19.71 ± 0.28 | −4.81 ± 0.04 | 49.96 ± 0.94 |
| Pure EtOH | −21.00 ± 0.64 | −28.03 ± 0.01 | −24.30 ± 2.20 |

*SD* standard deviation

[a] The concentration of each metal cation was $1.0 \times 10^{-4}$ M

[b] The salt is not dissolved in pure AN

[c] Composition of binary mixtures is expressed in mol% for each solvent system

[d] With high uncertainly

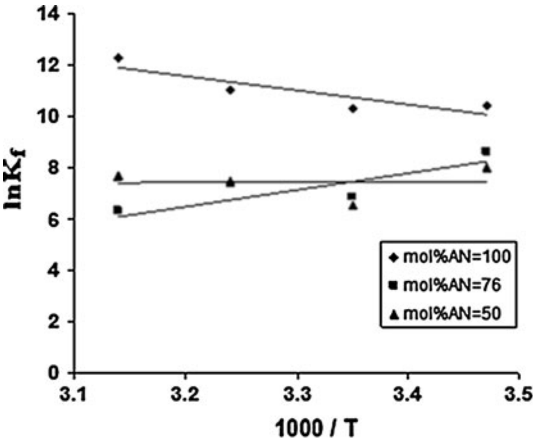

**Fig. 5** van,t Hoff plots for $(15C5{\cdot}Mn)^{2+}$ complex in acetonitrile-ethanol binary systems(mol% AN: *filled triangle* 50.0, *filled square* 76.0, *filled diamond* 100)

standard enthalpy for formation of the metal cation-crown ether complex in solution, vary with different parameters such as changes in the flexibility of the macrocyclic ligand during the complexation process, and also with the extent of cation–solvent, ligand–solvent and complex–solvent interactions and even with the solvent solvent interactions, therefore, these thermodynamic quantities change non-monotonically with the composition of the binary mixed solvent system. Also it obvious from this table that, in the most cases, the complexation reactions between 15C5 and the studied metal cations in AN–EtOH binary solutions are enthalpy stabilitized but entropy destabilized.

The changes of logK$_f$ versus the mole fraction of AN for $(15C5{\cdot}Cr)^{3+}$ complex in AN–EtOH binary system at different temperatures are shown in Fig. 6. As is obvious from this figure, a non-linear relationship is observed between the stability constant of the $(15C5{\cdot}Cr)^{3+}$ complex versus the mole fraction of AN in AN–EtOH binary system. Similar behavior was observed for $(15C5{\cdot}Zn)^{+2}$ and $(15C5{\cdot}Mn)^{+2}$ complexes in AN–EtOH binary system. This behavior may be related to ethanol-acetonitrile molecular interactions that lead to changes occurring in the structure of the solvent mixtures and, therefore, changing in the solvation properties of the cyclic polyether, cation and even the resulting complexes in these solvent mixtures. Some structural changes probably occur in the structure of the solvents when they mixed with one another. These structural changes may result in changing the interactions of those solvents with the solutes. In addition, the preferential solvation of the cation, anion and the ligand and the character of its changes with the composition of the mixed solvent and temperature may be effective in these complexation processes. Somewhat similar behaviors have been observed for some of the complexation reactions of crown ethers and aza-crown ethers with metal cations in various binary mixed solvent solutions [33, 34].

The changes of logK$_f$ of the $(15C5{\cdot}Cr)^{+3}$, $(15C5{\cdot}Mn)^{+2}$ and $(15C5{\cdot}Zn)^{2+}$ complexes versus the ionic radii of the metal cations in various AN–EtOH binary mixtures is shown in Fig. 7. Also 15C5 has a cavity size of 1.7–2.2 Å, and the $Mn^{2+}$ (1.8 Å) has the optimized diameter for the complex $(15C5{\cdot}Mn^{2+})$. However, logK$_f$ indicated in Fig. 7 show no relation with metal diameter even in pure solvent. The size of the cavity isn't the only factor that effect on the complexation process. But other factors such as the type of the solvent can be effective in complexation process. Therefore, only based on the size of the crown ether cavity,

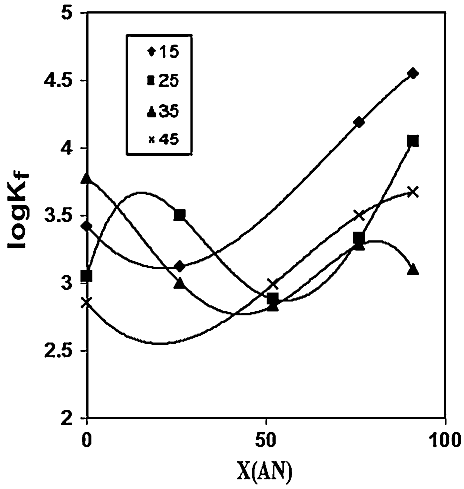

**Fig. 6** Changes of stability constant (logK$_f$) of $(15C5{\cdot}Cr)^{3+}$ complex with the mole fraction of acetonitrile at different temperatures (*filled diamond* 15 °C, *filled square* 25 °C, *filled triangle* 35 °C, *times* 45 °C)

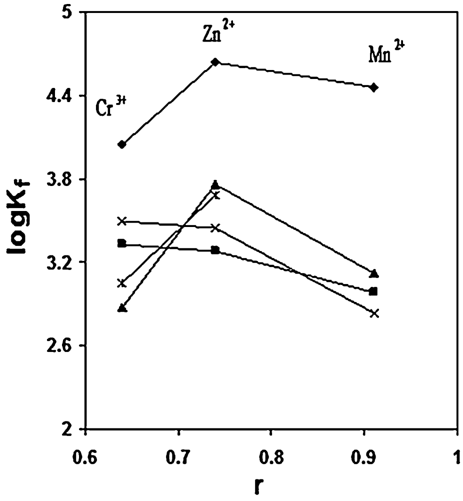

**Fig. 7** Variation of logK$_f$ for $(15C5{\cdot}Cr)^{3+}$, $(15C5{\cdot}Zn)^{2+}$ and $(15C5{\cdot}Mn)^{2+}$ complexes vs cationic radii in acetonitrile-ethanol binary systems at 25 °C: (mol% AN: *asterisk* 0, *filled square* 26.0, *times* 50.0, *filled triangle* 76.0, *filled diamond* 100 [for $Cr^{3+}$ *filled diamond* 90])

we cannot always predict about the stability of the crown ether complexes for example, although the $K^+$ ion has a very good condition for the cavity size of 18C6, but the $Na^+$ ion in MeOH forms a stronger complex with respect to $K^+$ ion.

Some reversals of the stabilities can be observed which show that the selectivity order of the ligand for these metal cations is affected by the nature and composition of the solvent systems. As is evident from Fig. 7, the order of selectivity of the metal–ion complexes in pure AN and in a binary solution of AN–EtOH (mol% AN = 52) at 25 °C is : $(15C5{\cdot}Zn)^{2+} > (15C5{\cdot}Mn)^{2+} > (15C5{\cdot}Cr)^{3+}$, but in pure EtOH it changes to: $(15C5{\cdot}Zn)^{2+} > (15C5{\cdot}Cr)^{3+} > (15C5{\cdot}Mn)^{2+}$. It is interesting to note that the selectivity order of the complexes in the other binary mixtures of AN–EtOH (mol% AN = 26 and mol% AN = 76) varies as : $(15C5{\cdot}Cr)^{3+} \sim (15C5{\cdot}Zn)^{2+} > (15C5{\cdot}Mn)^{2+}$. The results obtained in this study show that the selectivity of the macrocyclic ligands for metal cations may be changed with the composition of the binary mixed solvents.

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