J Incl Phenom Macrocycl Chem (2012) 73:67–73
DOI 10.1007/s10847-011-0021-8

ORIGINAL ARTICLE

Thermodynamics of ZrO^{2+} cation complexation with dibenzo-18-crown-6 in mixed non-aqueous solvents

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Received: 27 February 2011 / Accepted: 19 July 2011 / Published online: 18 August 2011

Abstract The complexation reaction of dibenzo-18-crown-6 (DB18C6) with ZrO^{2+} cation was studied in some binary solvent solutions of acetonitrile (AN), 1,2 dichloroethane (DCE), nitromethane (NM) and ethylacetate (EtOAc) with methanol (MeOH), at different temperatures by conductometry method. The stability constant of the resulting 1:1 complex at each temperature was determined using a computer fitting conductance-mole ratio data. The results revealed that, the $(DB18C6{\cdot}ZrO)^{2+}$ complex is more stable in the EtOAc–MeOH binary mixed solvents compared with the other binary mixed solvent solutions. A non-linear relationship was observed for changes of log K_f of $(DB18C6{\cdot}ZrO)^{2+}$ complex versus the composition of the binary mixed solvents. The corresponding standard thermodynamic parameters (ΔH°_{c}, ΔS°_{c}) were obtained from temperature dependence of the stability constant. The results show that the $(DB18C6{\cdot}ZrO)^{2+}$ complex is enthalpy destabilized but entropy stabilized and the values along with the sign of these parameters are influenced by the nature and composition of the mixed solvents.

Keywords Dibenzo-18-crown-6 · ZrO^{2+} cation · Mixed non-aqueous solvents · Conductometry

Introduction

Since the time Pedersen published the first report on crown compounds in 1967, [1] these compounds have been considered for a wide range of applications including enzyme models, biophysics, and medicine [2]. Crown ethers are noted for their remarkable selectivity towards specific cations, making them excellent choices for the separation of desired metal ions from their mixtures by solvent extraction and membrane transport [3, 4].

The binding ability and selectivity of crown ethers to metal ions depend on several factors: such as the size of the crown ether cavity, metal ion radius, type of donor atom, conformation of the crown ether, the nature of the solvent and etc. Solvent plays a crucial role in the binding selectivity of the crown ethers for metal ions [5, 6].

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.

Knowledge of the thermodynamic functions for crown ether complex formation with cations or organic molecules in various pure or mixed solvents may be used in model planning of various processes such as extraction or drug design [7, 8]. Many data concerning the complex formation process in non-aqueous solvents and mixed solvent systems can be found in the literature [9–11].

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The study of complexation reactions of crown ethers with metal cations in non-aqueous matrices could be used as an efficient strategy to design the analytical systems such as, potentiometric sensors, bulk liquid membrane transport, optical sensors, solid phase extraction and biochemistry fields. Thus, thermodynamic studies of macrocyclic complexation reactions with metal cations not only provide relevant information on the binding process, but also lead to a better understanding of the selective behavior of these ligands toward different metal cations.

It is of interest to us, therefore, to investigate the influence of the nature and also the composition of the solvent on the interactions between metal cations with crown ethers in binary mixed non-aqueous solutions. In continuation of our previous works [12–15], here, we report the results of conductometric study for determination of the stoichiometry, stability and thermodynamic parameters of dibenzo-18-crown-6 complex with ZrO^{2+} cation in acetonitrile–methanol (AN–MeOH), 1,2 dichloroethane–methanol (DCE–MeOH), nitromethane–methanol (NM–MeOH) and ethylacetate–methanol (EtOAc–MeOH) binary solvent solutions.

Experimental

Reagents and apparatus

Reagent-grade $ZrO(NO_3)_2$, DB18C6 with the highest purity were purchased from Merck (>99% purity) and were used without any further purification. The organic solvents (all from Merck, >99% purity) were used without further purification. The conductivity of each solvent was less than 3.0×10^{-7} S^{-1} cm^{-1} at 298.15 K. The water content of solvents was checked by Karl Fischer titration and was always less than 100 ppm. Conductance measurements were performed using a digital Metrohm conductometer (model 712) in a water bath thermostated at a constant temperature which maintained within ±0.01 °C. The electrolytic conductance was measured using a dip-type conductivity cell consisting of two platinum electrodes to which an alternating potential was applied. The calibration of conductometric cell was made with the use of aqueous KCl solution and cell constant was found to be of 0.89 cm^{-1}.

Procedure

The experimental procedure to obtain the stability constant of $(DB18C6{\cdot}ZrO)^{2+}$ complex by conductometric procedure was as follows: A solution of metal salt (1.0×10^{-4} mol L^{-1}, 20 mL) was placed in a titration cell, thermostated at a given temperature, and the conductance of the solution was measured. The ligand (2×10^{-3} mol L^{-1}) was transferred step-by-step to the titration cell using a precalibrated microburette and the conductance of the solution was measured after each transfer at the desired temperature. Addition of the ligand solution was continued until the total concentration of the DB18C6 was approximately five times higher than that of metal ion. The conductance of the solution was measured after each addition and the data were used for the calculation of the stability constant of the complex.

Result and discussion

Conductance studies

In order to study the influence of adding DB18C6 on the molar conductance of ZrO^{2+} cation in studied binary solvent mixtures, the conductivity of the solution at a constant salt concentration (1.0×10^{-4} mol L^{-1}) was monitored with increase of macrocycle concentration at various temperatures. The molar conductance versus ligand/cation mole ratio plots for $(DB18C6{\cdot}ZrO)^{2+}$ complex in EtOAc–MeOH (mol% EtOAc = 75%) binary solvent system at different temperatures are shown in Fig. 1. As is seen from this Figure, addition of DB18C6 to ZrO^{2+} cation solution shows an increase in molar conductivity, which indicates that the $(DB18C6{\cdot}ZrO)^{2+}$ complex in this system is more mobile than free solvated ZrO^{2+} cation.

Since the $(DB18C6{\cdot}ZrO)^{2+}$ complex is more bulky than ZrO^{2+}, therefore, it is much less solvated by the solvent molecules, and hence the complex is more mobile than free ZrO^{2+} solvated cation. Similar behavior was observed in all other solvent systems.

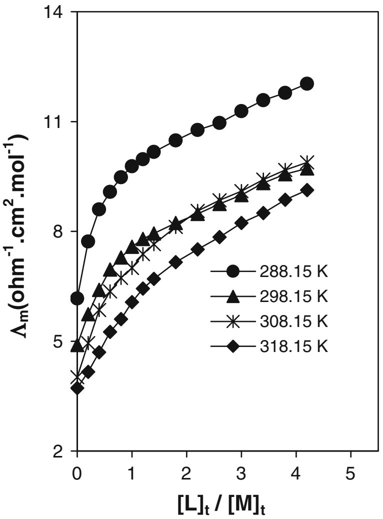

Fig. 1 Molar conductance–mole ratio plots for the $(DB18C6{\cdot}ZrO)^{2+}$ complex in EtOAc–MeOH(mol% EtOAc = 75%) binary solvent system at different temperatures

For the EtOAc–MeOH solvent systems, the slope of the corresponding molar conductivity versus $[L]_t/[M]_t$ plots changes sharply 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 in this binary solution. For the other solvent systems, the corresponding molar conductivity versus $[L]_t/[M]_t$ plots does not show a considerable change in their slopes at a mole ratio of about 1, emphasizing the formation of a weak 1:1 complex (see Fig. 2, in pure MeOH). Moreover, the entire resulting molar conductance-mole ratio data were fitted by [M:L] program, which further supports the formation of $(DB18C6{\cdot}ZrO)^{2+}$ complex in solution.

In order to make more clear the 1:1 [M:L] complexation model, the fitting and experimental curves for $(DB18C6{\cdot}ZrO)^{2+}$ complex in pure MeOH at 298.15 K are shown in Fig. 3. As is evident in this Figure, there is a very good agreement between the fitting and experimental data.

Theoretical calculations of complex formation constants

The reaction for a 1:1 complex formation can be expressed by Eq. 1 and the corresponding equilibrium constant, K_f, is given by Eq. 2:

$$M^{n+} + L \leftrightarrow ML^{n+} \tag{1}$$

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} \times \frac{f_{ML^{n+}}}{f_{M^{n+}} f_L} \tag{2}$$

where $[ML^{n+}]$, $[M^{n+}]$, [L] and f, represent the equilibrium molar concentrations of the complex, cation, ligand and the activity coefficient of the species indicated, respectively. In this paper, L = DB18C6 and $M = ZrO^{2+}$. Under the highly dilute experimental conditions which we used in this study, the activity coefficient of the uncharged ligand, f_L, can be reasonably assumed as unity [16]. The use of Debye–Huckel limiting law leads to the conclusion that, $f_{M^{n+}} \sim f_{ML^{n+}}$, therefore, the activity coefficients in Eq. 2 could be canceled.

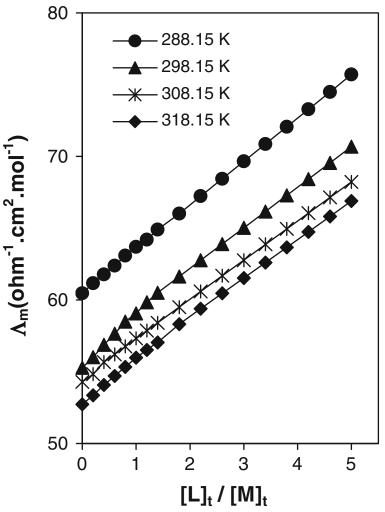

Fig. 2 Molar conductance–mole ratio plots for the $(DB18C6{\cdot}ZrO)^{2+}$ complex in pure MeOH at different temperatures

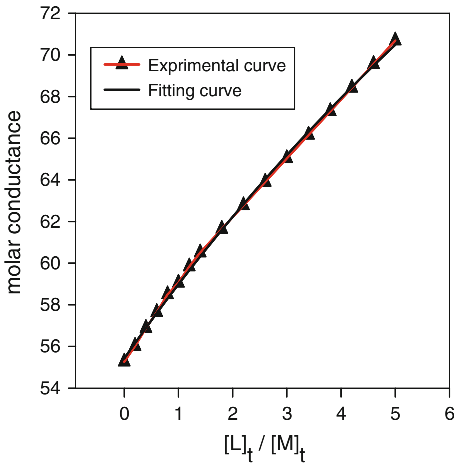

Fig. 3 The fitting and experimental curves for $(DB18C6{\cdot}ZrO)^{2+}$ complex in pure MeOH at 298.15 K

The complex formation constant in terms of the molar conductance can be expressed as [16, 17]:

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} = \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[L]} \tag{3}$$

where

$$[L] = C_L - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_M - \Lambda_{ML})} \tag{4}$$

Here, Λ_M is the molar conductance of the metal nitrate before addition of the ligand, Λ_{obs} the molar conductance of solution during titration and Λ_{ML} the molar conductance of the complexed ion. C_L is the analytical concentration of the ligand added and C_M is the analytical concentration of the metal nitrate.

The complex stability constant, K_f, was evaluated by computer fitting of Eqs. 3 and 4 to the molar conductance-mole ratio data using a non-linear least-squares program GENPLOT [18]. It should be noted that, under the highly dilute experimental conditions used in this study, in the process of calculation of formation constant, the association of ions into ion-pairs in solutions was considered to be negligible. Since the ligand concentration was kept below 2.0×10^{-3} mol L^{-1} during the experiments, correction for the viscosity changes was also neglected. The obtained values of stability constant ($\log K_f$) are given in Table 1.

Effect of solvent composition

Comparison of the data given in Table 1, reveals that, the $(DB18C6{\cdot}ZrO)^{2+}$ complex is more stable in the EtOAc–

MeOH binary mixed systems compared with other binary mixed solvent solutions. This can be attributed to the lower dielectric constant of EtOAc ($\varepsilon = 6.02$) compared with AN ($\varepsilon = 36$), NM ($\varepsilon = 38.6$) and DCE ($\varepsilon = 10.4$) and, therefore, an increase in electrostatic interaction between DB18C6 and ZrO^{2+}cation in solution.

In addition, in the case of EtOAc–MeOH binary solutions, the stability of the resulting complex increases with increasing the concentration of EtOAc in the solvent mixture. It is well known that the solvating ability of the solvent, as expressed by the Gutmann donor number [19], plays an important role in different complexation reactions [20]. There is actually an inverse relationship between the stabilities of the complexes and the solvating abilities of the solvents. EtOAc has a lower donicity (DN = 17.1) than MeOH (DN = 20.0) and, therefore, shows less competition than MeOH for ZrO^{2+} cation, therefor, the $(DB18C6{\cdot}ZrO)^{2+}$ complex becomes more stable as the concentration of EtOAc increases in EtOAc–MeOH binary solvent solutions.

The stability constants of crown ether-cation complexes in solutions could be interpreted as representing the overall equilibrium constants of a series of reactions including: (i) partial or complete desolvation of the cation, (ii) partial or complete desolvation of the crown ether, (iii) conformational change of the crown ether, (iv) formation of the crown-cation complex, and (v) solvation of the resulting charged complex. As is evident, the solvent molecules are

Table 1 Stability constant (log K_f) values for the $(DB18C6{\cdot}ZrO)^{2+}$ complex in AN–MeOH, DCE–MeOH, NM–MeOH and EtOAc–MeOH binary mixtures

Medium	Log k_f ± SD			
	288.15 K	298.15 K	308.15 K	318.15 K
AN–MeOH				
Pure AN	b	b	b	b
75% AN–25% MeOH[a]	2.69 ± 0.13	2.69 ± 0.13	2.7 ± 0.13	2.7 ± 0.13
65% AN–35% MeOH	2.74 ± 0.10	2.71 ± 0.14	2.71 ± 0.14	2.71 ± 0.13
50% AN–50% MeOH	2.69 ± 0.13	2.69 ± 0.10	2.69 ± 0.12	2.7 ± 0.12
25% AN–75% MeOH	2.69 ± 0.14	2.69 ± 0.13	2.7 ± 0.13	2.7 ± 0.13
Pure MeOH	2.7 ± 0.12	2.69 ± 0.07	2.73 ± 0.11	2.81 ± 0.08
DCE–MeOH				
Pure DCE	b	b	b	b
75% DCE–25% MeOH[a]	2.82 ± 0.10	2.79 ± 0.11	2.79 ± 0.09	2.78 ± 0.11
65% DCE–35% MeOH	3.11 ± 0.04	2.73 ± 0.09	2.97 ± 0.07	2.79 ± 0.08
50% DCE–50% MeOH	2.81 ± 0.08	2.81 ± 0.07	2.81 ± 0.07	2.72 ± 0.11
25% DCE–75% MeOH	2.72 ± 0.12	2.70 ± 0.13	2.70 ± 0.13	2.70 ± 0.12
Pure MeOH	2.70 ± 0.12	2.69 ± 0.07	2.73 ± 0.11	2.81 ± 0.08
NM–MeOH				
Pure NM	b	b	b	b
75% NM–25% MeOH[a]	2.74 ± 0.10	2.69 ± 0.13	2.73 ± 0.11	2.70 ± 0.12
65% NM–35% MeOH	2.72 ± 0.08	2.77 ± 0.09	2.82 ± 0.10	2.72 ± 0.14
50% NM–50% MeOH	2.69 ± 0.13	2.71 ± 0.12	2.80 ± 0.11	2.76 ± 0.09
25% NM–75% MeOH	2.69 ± 0.13	2.70 ± 0.13	2.70 ± 0.12	2.70 ± 0.12
Pure MeOH	2.70 ± 0.12	2.69 ± 0.07	2.73 ± 0.11	2.81 ± 0.08
EtOAc–MeOH				
Pure EtOAc	b	b	b	b
75% EtOAc–25% MeOH[a]	4.16 ± 0.14	3.98 ± 0.10	3.97 ± 0.06	3.72 ± 0.04
65% EtOAc–35% MeOH	3.91 ± 0.10	3.61 ± 0.11	3.87 ± 0.04	3.64 ± 0.05
50% EtOAc–50% MeOH	2.76 ± 0.11	2.79 ± 0.11	2.82 ± 0.14	2.87 ± 0.09
25% EtOAc–75% MeOH	2.77 ± 0.09	2.77 ± 0.10	2.78 ± 0.09	2.79 ± 0.08
Pure MeOH	2.70 ± 0.12	2.69 ± 0.07	2.73 ± 0.11	2.81 ± 0.08

SD standard deviation

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

[b] The salt is not completely dissolved

directly involved in three of the five possible equilibria. Thus, it is expected that the solvent properties such as dielectric constant, solvating ability and potential for hydrogen bonding will affect the selectivity order of the formed complexes considerably.

As is seen from Fig. 4, the change of the stability constant (logK_f) of $(DB18C6{\cdot}ZrO)^{2+}$ complex with the composition of EtOAc–MeOH binary solvent system is not linear. This behavior may be due to the interaction between the EtOAc and MeOH molecules via hydrogen bonding in their binary mixtures which results in changing the structure of the mixed solvents and, therefore, changing the solvation of the cation, the ligand and the resulting complex in EtOAc–MeOH binary solutions. In addition, the preferential solvation of the cation, anion and ligand and the characteristics of its changes with the composition of the mixed solvents and temperature may be effective in the complexation processes. In addition, this non-monotonic behavior, probably reflects a balance between the solvation properties, donicity, hydrogen bonding ability, etc. of the solvent systems. A non-linear behavior was also observed for the other binary solvent systems.

Thermodynamic calculations

In order to have a better understanding of thermodynamics of complexation reactions of the metal ions with the ligands, it is useful to determine the contribution of enthalpy and entropy of the reactions. The ΔH_c^o and ΔS_c^o values for complexation process between DB18C6 and ZrO^{2+} cation were determined from the temperature dependence of the stability constant using the van't Hoff plots. In all cases, the plots of LnK_f vs. 1/T were linear, and a typical example of these plots is shown in Fig. 5. The values of standard enthalpies 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 investigated. The values of the standard entropies were calculated from relationship: $\Delta G^{\mathrm{o}}_{\mathrm{c},298.15} = \Delta H^{\mathrm{o}}_{\mathrm{c}} - 298.15\Delta S^{\mathrm{o}}_{\mathrm{c}}$. The results are summarized in Table 2.

The thermodynamic data given in Table 2, reveal that in most cases, the sign of the enthalpy values for formation of $(DB18C6{\cdot}ZrO)^{2+}$ complex is positive and, therefore, the complexation process is endothermic (unfavorable). The results in Table 1 show that in some of the solvent systems, the stability constants (log K_f) do not change with the temperature and, therefore, the changes of standard enthalpy is negligible, therefore, the complexation reactions in these systems seems to be athermic.

In all cases, the positive values of ΔS_c^o characterize the formation of this complex. Hence, the $(DB18C6{\cdot}ZrO)^{2+}$ complex is stabilized from entropy viewpoint. The two main factors, which affect the ΔS_c^o values, are (i) the loss of conformational entropy of ligand upon complexation and (ii) the randomness of the solvent molecules in bulk solvent after being released during desolvation of metal cation and the ligand. It has been reasonably assumed that the positive entropy changes upon complexation are related to the release of some solvent molecules after desolvation process of the cation and the ligand [21, 22].

As is obvious from Table 2, the standard thermodynamic quantities (ΔH_c^o, ΔS_c^o) are quite sensitive to the nature and composition of the mixed solvents and a non-monotonic behavior is observed between these thermodynamic functions and the composition of the binary

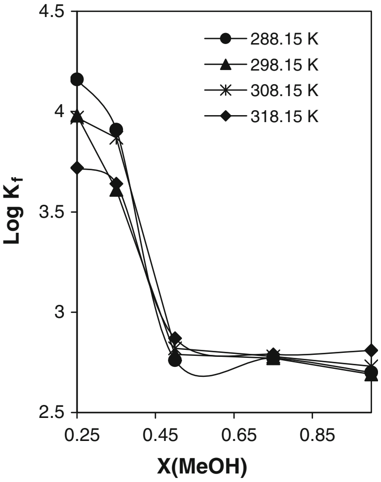

Fig. 4 Changes of the stability constant (logK_f) of the $(DB18C6{\cdot}ZrO)^{2+}$ complex with the composition of the EtOAc–MeOH binary solvent system at different temperatures

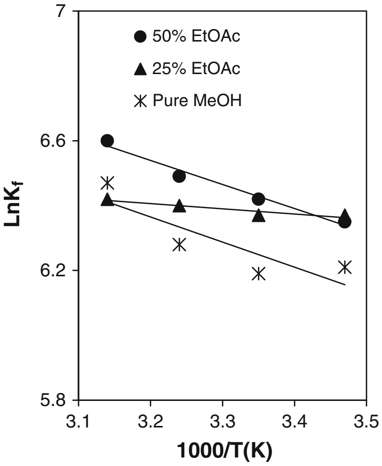

Fig. 5 van't Hoff plots for the $(DB18C6{\cdot}ZrO)^{2+}$ complex in pure MeOH and the EtOAc–MeOH(mol% EtOAc = 25%, 50%) binary solvent systems

Table 2 Thermodynamic parameters for the $(DB18C6{\cdot}ZrO)^{2+}$ complex in AN–MeOH, DCE–MeOH, NM–MeOH and EtOAc–MeOH binary mixtures

Medium	ΔG°c ± SD (298.15 K) (kJ mol^{-1})	ΔH°c ± SD (kJ mol^{-1})	ΔS°c ± SD (J mol^{-1} K^{-1})
AN–MeOH			
75% AN–25% MeOH[a]	−15.38 ± 0.65	0.31 ± 0.05	52.63 ± 0.16
65% AN–35% MeOH	−15.48 ± 0.67	−1.67 ± 0.62	46.48 ± 2.04
50% AN–50% MeOH	−15.36 ± 0.65	1.24 ± 0.67	55.76 ± 2.23
25% AN–75% MeOH	−15.37 ± 0.65	0.56 ± 0.12	53.47 ± 0.40
Pure MeOH	−15.36 ± 0.35	5.98 ± 2.52	72.11 ± 8.35
DCE–MeOH			
75% DCE–25% MeOH[a]	−15.94 ± 0.44	−2.57 ± 0.64	45.06 ± 2.12
65% DCE–35% MeOH	−15.61 ± 0.41	b	b
50% DCE–50% MeOH	−16.04 ± 0.27	b	36.98 ± 9.07
25% DCE–75% MeOH	−15.43 ± 0.64	b	49.27 ± 1.18
Pure MeOH	−15.36 ± 0.35	5.98 ± 2.52	72.11 ± 8.35
NM–MeOH			
75% NM–25% MeOH[a]	−15.36 ± 0.65	−47.16 ± 5.81	47.53 ± 6.96
65% NM–35% MeOH	−15.80 ± 0.38	b	57.30 ± 14.84
50% NM–50% MeOH	−15.47 ± 0.58	b	70.39 ± 10.35
25% NM–75% MeOH	−15.41 ± 0.64	0.34 ± 0.02	52.84 ± 0.06
Pure MeOH	−15.36 ± 0.35	5.98 ± 2.52	72.11 ± 8.35
EtOAc–MeOH			
75% EtOAc–25% MeOH[a]	−22.71 ± 0.02	−23.61 ± 5.24	b
65% EtOAc–35% MeOH	−20.58 ± 0.07	b	b
50% EtOAc–50% MeOH	−15.93 ± 0.44	6.16 ± 0.44	23.61 ± 5.24
25% EtOAc–75% MeOH	−15.83 ± 0.42	1.39 ± 0.20	57.75 ± 0.66
Pure MeOH	−15.36 ± 0.35	5.98 ± 2.52	72.11 ± 8.35

SD standard deviation

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

[b] With high uncertainty

solutions. This is due to variation in the extent of the contribution of such important parameters as solvation-desolvation of the species involved in the complexation reaction (i.e., cation, macrocycle and the resulting complex), as well as, the conformational changes of the macrocyclic ligand with the composition of solutions. Therefore, we should not expect a monotonic relationship between these thermodynamic quantities and the solvent composition. Similar behaviors have already been reported for various metal cation-crown ether complexes in different binary mixed solvents [12–18, 23].

Acknowledgments We gratefully acknowledge the support of this work by Ferdowsi University of Mashhad, Mashhad, Iran.

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