

## Determination of Stability Constants of Dibenzo-18-Crown-6 Complexes with $Ce^{3+}$ , $Y^{3+}$ , $UO_2^{2+}$ and $Sr^{2+}$ Cations in Acetonitrile-Dimethylformamide Binary Solutions

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(Received: 30 August 2012;

Accepted: 29 January 2013)

AJC-12767

The complexation reactions between  $Ce^{3+}$ ,  $Y^{3+}$ ,  $UO_2^{2+}$  and  $Sr^{2+}$  cations with dibenzo-18-crown-6 (DB18C6) was studied in acetonitrile-dimethyl formamide binary mixtures at different temperatures using conductometry method. The stability constants of the resulting 1:1 complexes were calculated from computer fitting of the molar conductance-mole ratio data. A non-linear relationship was observed between the stability constants ( $\log K_f$ ) of these complexes with the composition of acetonitrile-dimethyl formamide binary solutions, which was explained on the basis of changes occurring in the structure of the mixed solvents and also the preferential solvation of the cations, ligand and the resulting complexes in solutions. The results show that the selectivity order of dibenzo-18-crown-6 for the metal ions in pure DMF at 25 °C is:  $UO_2^{2+} > Sr^{2+} > Ce^{3+} > Y^{3+}$ , but this selectivity order is changed with the composition of the mixed solvents. The corresponding thermodynamic parameters ( $\Delta H^{\circ}_c$ ,  $\Delta S^{\circ}_c$ ) were obtained from temperature dependence of the stability constants using the van't Hoff plots. The results show that both parameters are affected by the nature and composition of the solvent systems.

**Key Words:** Dibenzo-18-crown-6, Mixed non-aqueous solvents, Conductometry.

### INTRODUCTION

Pedersen published the first report on crown compounds in 1967<sup>1</sup>. These compounds have been considered for a wide range of applications including enzyme models, biophysics and medicine<sup>2</sup>. Crown ethers are noted for their remarkable selectivity towards specific cations, making them excellent choices for the separation of desired ions from mixtures by solvent extraction and membrane transport<sup>3,4</sup>. It has been found that the selectivity of the macrocyclic ligands for metal cations depends on several factors such as macrocyclic cavity size, the type of the donor atoms in polyether ring, shape and topology of the ligand, substituent effects, conformational flexibility/rigidity of the ligand and solvation effect. Among these factors, the solvent has a dramatic effect on cation selectivity with crown ethers<sup>5,6</sup>.

Studies of crown ethers complexation in different solvents show that the thermodynamic and kinetic parameters are affected by the nature and the composition of the solvent system<sup>7,8</sup>. 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 behaviour of these ligands toward different metal cations. Although cation complexation studies involving macrocycles have been investigated in a wide variety of solvents<sup>9,10</sup>, very limited information is available in

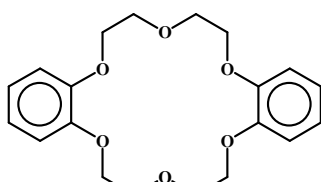
mixed non-aqueous solvents<sup>11</sup>. The widespread use of non-aqueous solvents, especially dipolar aprotic solvents in various fields of pure and applied chemistry has contributed greatly to advances in chemical sciences technologies<sup>12</sup>. Using non-aqueous solutions plays an important role in exploring new chemical possibilities, as well as, in providing the methods to evaluate static solvent effects on various chemical processes.

Various techniques have been used to study the complexation of a range of ligands with different cations in a variety of nonaqueous and mixed solvents<sup>13-15</sup>. In recent years, we have employed conductance measurements as a sensitive and inexpensive method for such investigations<sup>16-18</sup>. In this paper, we report the stability constants and thermodynamic quantities of the resulting complexes of dibenzo-18-crown-6 (**Scheme-I**) with  $Ce^{3+}$ ,  $Y^{3+}$ ,  $UO_2^{2+}$  and  $Sr^{2+}$  cations in acetonitrile-dimethyl formamide (AN-DMF) binary mixtures at various temperatures which are obtained by the conductometric method.

### EXPERIMENTAL

The ligand, dibenzo-18-crown-6 (Merck) was of the highest purity available and used as received. The salts:  $Ce(NO_3)_3 \cdot 6H_2O$  (Merck),  $Y(NO_3)_3 \cdot 6H_2O$  (Riedel),  $UO_2(NO_3)_2 \cdot 6H_2O$  (Riedel) and  $Sr(NO_3)_2$  (Merck) were used as purchased. The organic solvents acetonitrile and dimethyl

formamide obtained from Merck were used without further purification. The conductance measurements were carried out with a digital Metrohm conductivity meter (model 712). A dip-type conductivity cell made of platinum black, with a cell constant of  $0.75 \text{ cm}^{-1}$  was used. The cell constant was obtained from calibration and checked by an aqueous potassium chloride solution according to the manufacture procedure. In all measurements, the cell was thermostated at the desired temperature  $\pm 0.1 \text{ }^\circ\text{C}$  using a Julabo model F12 thermostat circulator water bath.



**Scheme-I:** Dibenzo-18-crown-6

**Procedure:** The experimental procedure to obtain the stability constant of dibenzo-18-crown-6 (DB18C6) complexes with  $\text{Ce}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{UO}_2^{2+}$  and  $\text{Sr}^{2+}$  cations by conductometric procedure was as follows: a solution of metal nitrate ( $1.25 \times 10^{-4} \text{ M}$ , 20 mL) was placed in a titration cell, thermostated at a given temperature and the conductance of the solution was measured. The ligand ( $6.25 \times 10^{-3} \text{ M}$ ) was transferred step-by-step to the titration cell using a pre-calibrated micropipette and the conductance of the solution was measured after each transfer. Addition of the ligand solution was continued until the total concentration of the studied ligand was approximately five times higher than that of the metal cation. The conductance of the solution was measured after each addition and the data were used for the calculation of the stability constant of the complexes in  $\text{CH}_3\text{CN}$ -DMF mixtures.

## RESULTS AND DISCUSSION

The changes of molar conductance ( $\Lambda_m$ ) versus the ligand to the cation molar ratio, ( $[\text{L}]_i/[\text{M}]_i$ ), for complexation of dibenzo-18-crown-6 with  $\text{Ce}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{UO}_2^{2+}$  and  $\text{Sr}^{2+}$  cations in acetonitrile-dimethylformamide ( $\text{CH}_3\text{CN}$ -DMF) binary systems were studied at different temperatures. A typical example of molar conductance-mole ratio plots for complexation of DB18C6 with  $\text{Sr}^{2+}$  cation in pure  $\text{CH}_3\text{CN}$  is shown in Fig. 1. The stability constants of the complexes at each temperature were obtained from variation of molar conductance as a function of  $[\text{L}]_i/[\text{M}]_i$  molar ratio plots using a GENPLOT computer program<sup>19</sup>. The details of calculation of the stability constants of complexes by conductometric method have been described in reference<sup>20</sup>. The values of the stability constants ( $\log K_f$ ) for (DB18C6. $\text{M}^{n+}$ ) ( $\text{M}^{n+}$ :  $\text{Ce}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{UO}_2^{2+}$  and  $\text{Sr}^{2+}$ ) complexes in various solvent systems are listed in Table-1. Plots of  $\ln K_f$  versus  $1/T$  in all cases were linear and a typical example of these plots is shown in Fig. 2. The changes of the standard enthalpy ( $\Delta H^\circ_c$ ) for complexation reactions were determined in the usual manner from the slope of the van't Hoff plots assuming that  $\Delta C_p$  is equal to zero over the entire temperature range investigated. The changes of standard entropy ( $\Delta S^\circ_c$ ) were calculated from the relationship  $\Delta G^\circ_{c,298.15}$

$= \Delta H^\circ_c - 298.15 \Delta S^\circ_c$ . The results are summarized in Table-2. The changes of  $\log K_f$  of (DB18C6. $\text{Ce}$ )<sup>3+</sup> complex versus the mole fraction of acetonitrile in AN-DMF binary system at different temperatures are shown in Fig. 3. The changes of stability constants ( $\log K_f$ ) versus the ionic radii in various solvent systems are shown in Fig. 4.

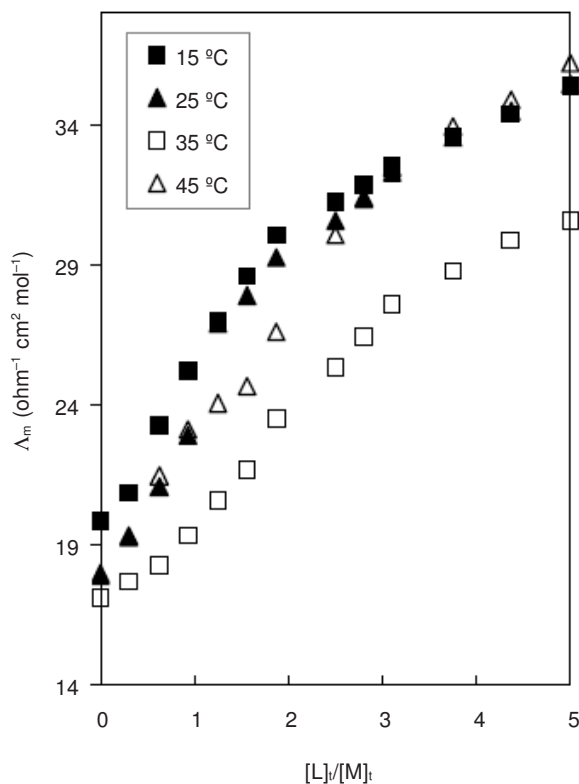


Fig. 1. Molar conductance–mole ratio plots for (DB18C6. $\text{Sr}$ )<sup>2+</sup> complex in pure  $\text{CH}_3\text{CN}$  at different temperatures

Cation	Mol % $\text{CH}_3\text{CN}$	$\log K_f \pm \text{SD}^a$			
		15 °C	25 °C	35 °C	45 °C
$\text{Ce}^{3+}$	0	$3.50 \pm 0.08$	$3.21 \pm 0.04$	$3.09 \pm 0.03$	$3.16 \pm 0.04$
	25	$3.21 \pm 0.06$	$3.18 \pm 0.07$	$3.20 \pm 0.05$	$3.22 \pm 0.10$
	50	$3.05 \pm 0.07$	$3.07 \pm 0.07$	$3.20 \pm 0.06$	$3.28 \pm 0.04$
	75	$3.20 \pm 0.10$	$3.14 \pm 0.04$	$3.15 \pm 0.05$	$3.06 \pm 0.09$
	100	b	b	b	b
$\text{Y}^{3+}$	0	$3.24 \pm 0.07$	$2.90 \pm 0.10$	$2.97 \pm 0.09$	$2.77 \pm 0.06$
	25	$2.70 \pm 0.10$	$3.14 \pm 0.08$	$3.26 \pm 0.05$	$3.20 \pm 0.10$
	50	$3.40 \pm 0.10$	$3.20 \pm 0.10$	$3.20 \pm 0.04$	$3.08 \pm 0.09$
	75	$3.10 \pm 0.10$	$4.18 \pm 0.07$	$2.90 \pm 0.07$	$3.00 \pm 0.10$
	100	b	b	b	b
$\text{UO}_2^{2+}$	0	$3.22 \pm 0.07$	$3.35 \pm 0.06$	$3.28 \pm 0.04$	$3.21 \pm 0.07$
	25	$3.25 \pm 0.03$	$3.23 \pm 0.06$	$3.13 \pm 0.06$	$3.11 \pm 0.05$
	50	$3.27 \pm 0.07$	$3.44 \pm 0.03$	$3.47 \pm 0.03$	$2.81 \pm 0.09$
	75	$3.08 \pm 0.03$	$3.31 \pm 0.06$	$3.18 \pm 0.04$	$3.00 \pm 0.04$
	100	b	b	b	b
$\text{Sr}^{2+}$	0	$3.19 \pm 0.05$	$3.24 \pm 0.04$	$3.26 \pm 0.06$	$3.24 \pm 0.05$
	25	$3.47 \pm 0.08$	$3.56 \pm 0.10$	$2.80 \pm 0.10$	$2.60 \pm 0.10$
	50	$3.10 \pm 0.10$	$2.60 \pm 0.10$	$2.50 \pm 0.10$	$3.12 \pm 0.07$
	75	$3.14 \pm 0.04$	$3.08 \pm 0.06$	$3.01 \pm 0.04$	$3.13 \pm 0.04$
	100	$3.77 \pm 0.05$	$3.76 \pm 0.07$	$3.10 \pm 0.10$	$3.30 \pm 0.10$

<sup>a</sup>SD = standard deviation. <sup>b</sup>The data can not be fitted in equation

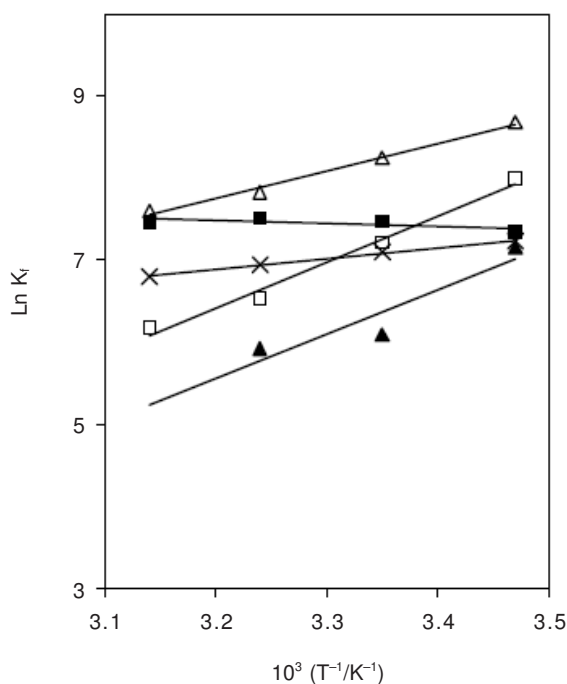


Fig. 2. Van't Hoff plots for (DB18C6.Sr)<sup>2+</sup> complex in CH<sub>3</sub>CN–DMF binary systems: mol % CH<sub>3</sub>CN: (■) 0.0, (□) 25, (▲) 50, (△) 75, (×) 100

TABLE-2  
THERMODYNAMIC PARAMETERS FOR (DB18C6.Ce)<sup>3+</sup>,  
(DB18C6.Y)<sup>3+</sup>, (DB18C6.UO<sub>2</sub>)<sup>2+</sup> AND (DB18C6.Sr)<sup>2+</sup>  
COMPLEXES IN CH<sub>3</sub>CN-DMF BINARY MIXTURES

Cation	Mol % CH <sub>3</sub> CN	-ΔG °C ± SD <sup>a</sup> (25 °C) (kJ mol <sup>-1</sup> )	ΔH °C ± SD <sup>a</sup> (kJ mol <sup>-1</sup> )	ΔS °C ± SD <sup>a</sup> (J mol <sup>-1</sup> K <sup>-1</sup> )
Ce <sup>3+</sup>	0	18.34 ± 0.06	-34.51 ± 0.06	b
	25	18.20 ± 0.10	-50.86 ± 0.10	-109.54 ± 26.19
	50	17.53 ± 0.10	11.88 ± 0.58	98.64 ± 1.91
	75	17.93 ± 0.07	-9.02 ± 1.85	29.88 ± 6.20
Y <sup>3+</sup>	0	16.95 ± 0.2	-26.38 ± 1.96	-31.62 ± 6.53
	25	17.97 ± 0.10	10.73 ± 1.75	96.26 ± 5.85
	50	18.72 ± 0.10	-17.35 ± 2.24	b
	75	23.88 ± 0.01	-21.54 ± 4.90	b
UO <sub>2</sub> <sup>2+</sup>	0	19.13 ± 0.06	-13.03 ± 0.08	20.45 ± 0.17
	25	18.46 ± 0.08	-11.57 ± 3.40	b
	50	19.65 ± 0.02	17.50 ± 6.20	124.60 ± 20.79
	75	16.40 ± 0.02	-27.36 ± 2.62	-36.76 ± 8.76
Sr <sup>2+</sup>	0	18.52 ± 0.05	9.85 ± 1.41	95.15 ± 4.72
	25	20.36 ± 0.57	-47.05 ± 5.29	-89.51 ± 17.74
	50	15.10 ± 0.57	-36.65 ± 10.47	b
	75	17.59 ± 0.34	-10.45 ± 0.88	23.94 ± 2.93
	100	21.47 ± 0.03	-26.99 ± 1.30	-18.51 ± 4.35

<sup>a</sup>SD = standard deviation. <sup>b</sup>With high uncertainty

In order to evaluate the influence of adding DB18C6 on the molar conductance of Ce<sup>3+</sup>, Y<sup>3+</sup>, UO<sub>2</sub><sup>2+</sup> and Sr<sup>2+</sup> cations in acetonitrile-dimethylformamide (CH<sub>3</sub>CN-DMF) binary solutions, the molar conductance at a constant salt concentration (1.25 × 10<sup>-4</sup> M) was monitored while increasing the crown ether concentration at various temperatures. In all cases, there is an increase in the molar conductance as a result of complex formation. This is expected due to the lower mobility of the solvated cations compared to the complexed ones. In all cases, the slope of corresponding molar conductivity *versus* [L]<sub>t</sub>/[M]<sub>t</sub> 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 DB18C6 with Ce<sup>3+</sup>, Y<sup>3+</sup>, UO<sub>2</sub><sup>2+</sup> and Sr<sup>2+</sup> cations. As an example, the molar conductivity plots for (DB18C6.Sr)<sup>2+</sup> complex in pure CH<sub>3</sub>CN at different temperatures are shown in Fig. 1.

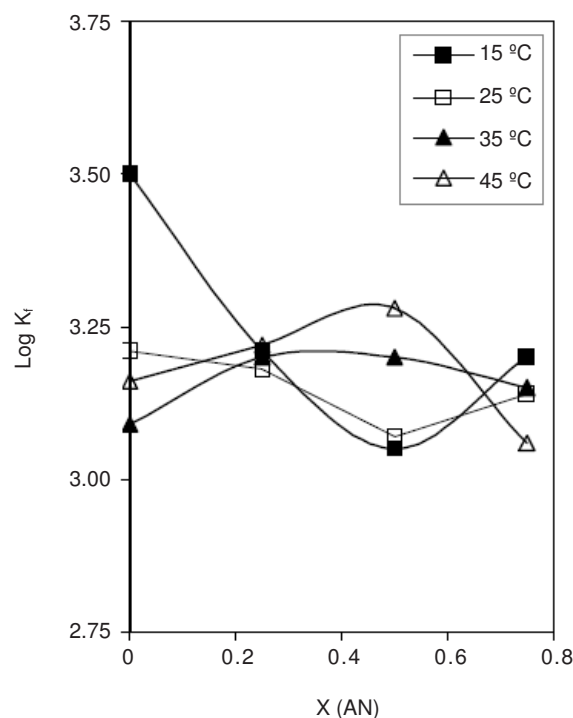


Fig. 3. Changes of the stability constant (log K<sub>f</sub>) of (DB18C6.Ce)<sup>3+</sup> complex with the composition of CH<sub>3</sub>CN–DMF binary system at different temperatures

Fig. 3 showed that the changes of stability constants (log K<sub>f</sub>) of (DB18C6.Ce)<sup>3+</sup> complex with the composition of CH<sub>3</sub>CN-DMF binary system is not linear. A non-linear behaviour was also observed for other complexes. This behaviour may be related 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 complex in these solvent mixtures. Some structural changes probably occur in the structure of the solvents when they mix 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 ligand and the characteristics of its changes with the composition of the mixed solvents and temperature may be effective in this complexation process. In this regard, the interactions between some binary mixed solvents have been studied<sup>21</sup>. The acetonitrile and dimethyl formamide solvents both are dipolar aprotic liquids with large but nearly equal dipole moments. Thus mixing of DMF with CH<sub>3</sub>CN will induce the mutual destruction of dipolar structures of the component liquids and releasing free dipoles. As a result, strong dipolar interaction between CH<sub>3</sub>CN and DMF molecules is expected. The observed negative values of excess adiabatic compressibility (β<sub>E</sub>) and excess intermolecular free length (L<sub>f</sub><sup>E</sup>) over the complete range of composition of CH<sub>3</sub>CN-DMF binary mixtures support the above observation<sup>22</sup>.

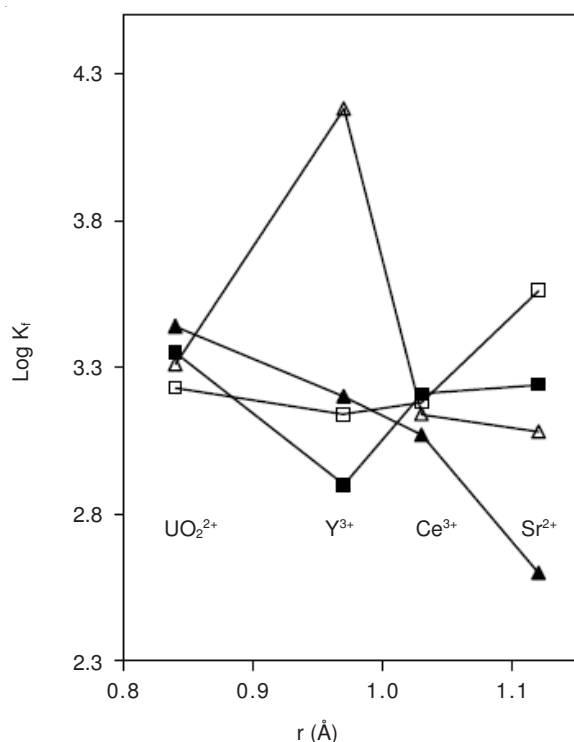


Fig. 4. Changes of  $\log K_f$  for (DB18C6.Ce)<sup>3+</sup>, (DB18C6.Y)<sup>3+</sup>, (DB18C6.UO<sub>2</sub>)<sup>2+</sup> and (DB18C6.Sr)<sup>2+</sup> complexes vs. cationic radii in various solvent systems at 25 °C: mol% AN: (■) 0.0, (□) 25, (▲) 50, (△) 75

The changes of stability constants ( $\log K_f$ ) of (DB18C6.M<sup>n+</sup>) (M<sup>n+</sup>: Ce<sup>3+</sup>, Y<sup>3+</sup>, UO<sub>2</sub><sup>2+</sup> and Sr<sup>2+</sup>) complexes versus the ionic radii in CH<sub>3</sub>CN-DMF binary systems is shown in Fig. 4. The order of selectivity of DB18C6 for these cations in pure DMF at 25 °C is UO<sub>2</sub><sup>2+</sup> > Sr<sup>2+</sup> > Ce<sup>3+</sup> > Y<sup>3+</sup>. A comparison of the cavity size of DB18C6 (1.3-1.6 Å)<sup>23</sup> and the ionic size of the studied cations shows that the optimal spatial fit is reached for the Sr<sup>2+</sup> (r:1.12 Å) cation, but DB18C6 does not exhibit the best selectivity for this cation in DMF solution. From this result it can be concluded that the size-fit concept is not a dominant factor in complexation of these cations with DB18C6 in DMF solution.

It is interesting to note that the selectivity of the ligand for the studied cations varies with the composition of CH<sub>3</sub>CN-DMF binary mixtures in the sequences of: Y<sup>3+</sup> > UO<sub>2</sub><sup>2+</sup> > Ce<sup>3+</sup> > Sr<sup>2+</sup> in 75 mol % of CH<sub>3</sub>CN and as: UO<sub>2</sub><sup>2+</sup> > Y<sup>3+</sup> > Ce<sup>3+</sup> > Sr<sup>2+</sup> in 50 mol % of CH<sub>3</sub>CN and as: Sr<sup>2+</sup> > UO<sub>2</sub><sup>2+</sup> > Ce<sup>3+</sup> > Y<sup>3+</sup> in 25 mol % of CH<sub>3</sub>CN of this binary mixed solvent. A remarkable change in the selectivity sequence of the ligand for the cations takes place when the composition of mixed solvents is varied. The results show that the solvent effect is important in complexation processes of crown ethers with metal cations and this effect can be understood in terms of differences in cations solvation, which plays a dominant role in solution media.

The thermodynamic data (Table-2) reveal that, in most of the cases, the complexes are enthalpy stabilized. The negative values of  $\Delta H^{\circ}_c$  indicate that the corresponding complexation processes are exothermic and, therefore, favourable at lower

temperatures. However, depending on the nature and composition of the mixed solvents, some of the complexes are entropy destabilized and some are entropy stabilized. Similar results have been obtained for formation of different macrocyclic complexes which have been frequently reported in the literature<sup>3,4</sup>.

The results obtained in this study, show that the standard enthalpy and entropy values for complexation reactions vary with the nature and composition of the mixed solvents, but they do not vary monotonically with the solvent composition (Table-2). This behaviour is due to the variations 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) and also the conformational changes of the macrocyclic ligand in the binary solutions, therefore, we should not expect a monotonic relationship between these thermodynamic quantities and the solvent composition.

#### ACKNOWLEDGEMENTS

The authors gratefully acknowledged the support of this work by Mashhad Branch, Islamic Azad University, Mashhad, Iran.

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