



## ORIGINAL ARTICLE

# Study of complex formation process between 4'-nitrobenzo-18-crown-6 and yttrium(III) cation in some binary mixed non-aqueous solvents using the conductometry method



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4'-Nitrobenzo-18-crown-6;  
Yttrium(III) cation;  
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Conductometry

**Abstract** The complexation reaction between  $Y^{3+}$  cation and macrocyclic ligand, 4'-nitrobenzo-18-crown-6 (4'NB18C6), was studied in acetonitrile–methanol (AN–MeOH), acetonitrile–1,2-dichloroethane (AN–DCE), acetonitrile–dimethylformamide (AN–DMF) and acetonitrile–ethylacetate (AN–EtOAc) binary mixed solvent solutions at different temperatures using the conductometric method. The conductance data show that in most cases, the stoichiometry of the complex formed between 4'NB18C6 and  $Y^{3+}$  cation is 1:1 [M:L], but in the case of AN–DCE binary solution (mol% DCE = 50) at 15, 25 and 35 °C, a 2:1 [M<sub>2</sub>:L] and also a 2:2 [M<sub>2</sub>:L<sub>2</sub>] complexes are formed in solution. The results show that the stoichiometry of the complex formed between 4'NB18C6 and  $Y^{3+}$  cation changes with the composition of the mixed solvents and even with temperature. The stability constant of the 1:1 complex was determined using a computer program, GENPLOT. The stability order of (4'NB18C6.Y)<sup>3+</sup> complex in pure studied solvents at 25 °C was found to be: EtOAc > AN > MeOH > DMF and in the case of the mixed solvent solutions with 25 mol percent of AN at 25 °C was: AN–DCE > AN–EtOAc > AN–MeOH ~ AN–DMF. The values of stability constant (log  $K_f$ ) of (4'NB18C6.Y)<sup>3+</sup> complex which were obtained from conductometric data, show that the stability of the complex is not only affected by the nature and composition of the solvent system, but it is also influenced by the temperature. In all cases, a non-linear behavior is observed for changes of log  $K_f$  of the (4'NB18C6.Y)<sup>3+</sup> complex versus the composition of the binary mixed solvents. The values of standard thermodynamic quantities ( $\Delta H^\circ_c$  and  $\Delta S^\circ_c$ ) for

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the complexation process which were obtained from temperature dependence of the stability constant of  $(4'NB18C6.Y)^{3+}$  complex, show that depending on the solvent system, in most cases, the complex is enthalpy and also entropy stabilized, but in some cases, it is stabilized or destabilized from these view points.

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## 1. Introduction

Crown ethers are known for their ability to strongly solvate the metal cations. In other words, the equilibrium is strongly towards the formation of complex. The oxygen atoms in the polar ring, are ideally situated to coordinate with a cation in the interior of the ring, whereas the exterior of the ring is hydrophobic. The result is that the complexed cations are soluble in nonpolar solvents. Due to their ability to bind strongly and selectively to the metal cations and substrate molecules, macrocyclic polyethers and their derivatives can find use in many diverse processes such as construction of ion-selective electrodes (Sendil et al., 2009; Han et al., 2008; Shim et al., 2007), phase transfer catalysts (Pozzi et al., 2008), extraction of metal ions (Alivertis et al., 2009; Zamani et al., 2009; Tu et al., 2008), chiral separation (Yongzhu et al., 2006) and membrane separation process (Rawat et al., 2006).

It has been suggested that the formation of a complex between an alkali metal cation and a macrocyclic polyether is due to ion-dipole interactions (Pedersen, 1968) and is, therefore, similar in nature to ordinary solvation, although more favorable because of the appropriate configuration and the polydentate character of the ligand. The specificity of the complexation is due to the required fit between the ionic size and the size of the macrocyclic ring, nevertheless, it may be affected by the medium (Wong et al., 1970), as the macrocyclic polyether must compete with the surrounding solvent for the cation. Complexing of alkali cations by neutral molecules is an uncommon phenomenon, however, it has now been observed not only with the cyclic polyethers, but also with a number of antibiotics, such as valinomycin, nonactin, and monactin which have macrocyclic structures containing ester, ether and peptide groups. Stability constants for several antibiotic alkali cation systems have been reported (Wipf et al., 1968; Prestegard and Chan, 1970). The formation constants for complexation between  $\text{NaClO}_4$  and various coumestano-crown ethers in acetonitrile at 25 °C have been determined by conductance measurement (Abdurrahmanoglu et al., 2005), and the structure of crown compound-cation complexes has been estimated from the conductance data. Also a complementary theoretical and experimental approach for providing important information on oxo-thiocrown ethers with various metal cations has been demonstrated (Cicek and Yildiz, 2011).

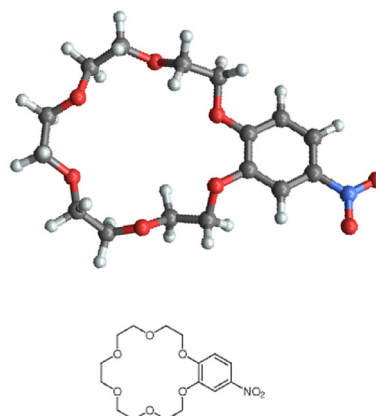
Yttrium was discovered by Johan Gadolin, while analyzing the composition of the mineral gadolinite ((Ce, La, Nd, Y)<sub>2</sub>FeBe<sub>2</sub>Si<sub>2</sub>O<sub>10</sub>) in 1789. Today, yttrium is primarily obtained through an ion exchange process from monazite sand ((Ce, La, Th, Nd, Y)PO<sub>4</sub>), a material rich in rare earth elements. Although metallic yttrium is not widely used, but some of its compounds such as yttrium oxide (Y<sub>2</sub>O<sub>3</sub>) and yttrium orthovanadate (YVO<sub>4</sub>) are both combined with europium to produce the red phosphor which is used in color televisions.

Garnets made from yttrium and iron (Y<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>) are used as microwave filters in microwave communication equipment. Garnets made from yttrium and aluminum (Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>) are used in jewelry as simulated diamond. They are also used in the production of electrodes, electrolytes, electronic filters, lasers and superconductors; various medical applications; and the tracing of various materials to enhance their properties. Yttrium has no known biological role, but exposure to yttrium compounds can cause lung disease in humans. The thermodynamics of the formation of some ionic complexes of some macrocyclic ligands with Y<sup>3+</sup> cation in mixed non-aqueous solutions, has previously been studied (Rounaghi et al., 2009, 2011; Rounaghi and Deiminiat, 2012). The data in mixed non-aqueous solutions especially for complexation of small crown ethers with metal cations are scarce (Khayatian et al., 2008; Khayatian and Karoonian, 2008; Rounaghi and Razavipanah, 2008; Razghandi et al., 2012; Rounaghi et al., 2009).

In this paper, we report the results of a conductance study of the thermodynamics of Y<sup>3+</sup> cation complexation with 4'-nitrobenzo-18-crown-6 (Scheme 1) in acetonitrile-methanol (AN-MeOH), acetonitrile-1,2-dichloroethane (AN-DCE), acetonitrile-dimethylformamide (AN-DMF) and acetonitrile-ethylacetate (AN-EtOAc) binary mixtures at different temperatures. The aim of the present work, is to study the influence of the nature and composition of the non-aqueous solvent systems in the mechanism and thermodynamics of complexation processes between yttrium(III) cation and macrocyclic ligand, 4'-nitrobenzo-18-crown-6.

## 2. Experimental and apparatus

4'NB18C6 (Merck) and Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Merck) were used without further purification. The solvents: acetonitrile,

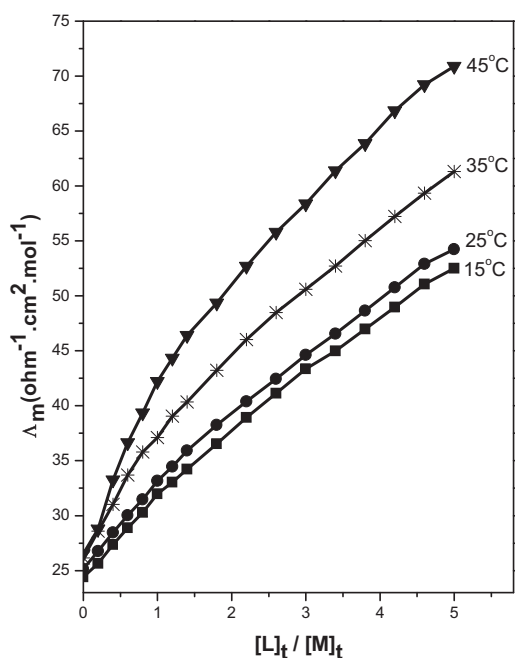


**Scheme 1** Structure of 4'-nitrobenzo-18-crown-6.

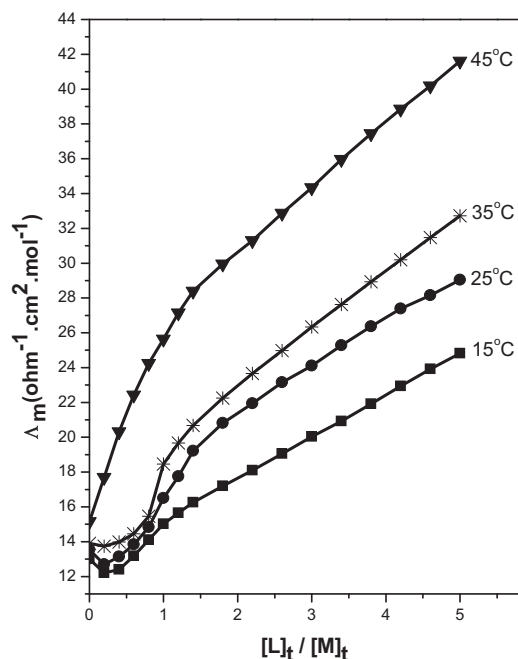
methanol, dimethylformamide, ethylacetate and 1,2-dichloroethane all from Merck were used with highest purity. The experimental procedure to obtain the formation constant of  $(4'\text{NB18C6.Y})^{3+}$  complex was as follows: a solution of metal salt ( $1.0 \times 10^{-4}$  M) was placed in a titration cell and the conductance of the solution was measured, then a step-by-step increase of the crown ether solution prepared in the same solvent ( $2.0 \times 10^{-3}$  M) was carried out by a rapid transfer to the titration cell, using a microburette and the conductance of the resulted solution was measured after each step at the desired temperature. The conductance measurements were performed on a digital AMEL conductivity apparatus, model 60, in a water bath thermostated at a constant temperature maintained within  $\pm 0.1$  °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  $0.73 \text{ cm}^{-1}$  was used throughout the studies.

### 3. Results

The changes of molar conductivity ( $\Lambda_m$ ) versus the ligand to the cation molar ratio,  $([L]_t/[M]_t)$ , for complexation of 4'NB18C6 with  $\text{Y}^{+3}$  cation were measured in pure EtOAc, DMF, MeOH, AN and DCE and also in AN–MeOH, AN–DCE, AN–DMF and AN–EtOAc binary solvent systems at different temperatures.  $[L]_t$  is the total concentration of the ligand and  $[M]_t$  is the total concentration of the metal cation. Two typical series of molar conductance values as a function of  $[L]_t/[M]_t$  in pure AN and AN–DCE (mol% DCE = 50) binary mixture are shown in Figs. 1 and 2, respectively. The stability constant of  $(4'\text{NB18C6.Y})^{3+}$  complex at each temperature was calculated from changes of the molar conductance as a function of  $[4'\text{NB18C6}]/[\text{Y}^{+3}]$  molar ratio using a GENPLOT computer program (Genplot, 1989). The details of



**Figure 1** Molar conductance-mole ratio plots for  $(4'\text{NB18C6.Y})^{3+}$  complex in pure AN at different temperatures.



**Figure 2** Molar conductance-mole ratio plots for  $(4'\text{NB18C6.Y})^{3+}$  complex in AN–DCE (mol% DCE = 50) binary solution at different temperatures.

calculation of the stability constants of complexes by conductometric method have been described in reference (Rounaghi et al., 1997). The values of stability constant ( $\log K_f$ ) for  $(4'\text{NB18C6.Y})^{3+}$  complex in various solvent systems are listed in Table 1.

The changes in the standard enthalpy ( $\Delta H^\circ_c$ ) for complexation of 4'NB18C6 with  $\text{Y}^{+3}$  cation were obtained from the slope of the van't Hoff plots assuming that  $\Delta C_p$  is equal to zero over the entire temperature range investigated. In most cases, the van't Hoff plots of  $\ln K_f$  versus  $1/T$  were linear and a typical example of these plots is shown in Fig. 4. The changes in 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 thermodynamic data are summarized in Table 2. The changes of  $\log K_f$  versus the solvent composition for  $(4'\text{NB18C6.Y})^{3+}$  complex in AN–DMF binary system at different temperatures is shown in Fig. 3.

### 4. Discussion

As is seen from Fig. 1, addition of 4'NB18C6 to a solution of yttrium(III) cation in pure AN at different temperatures shows a gradual increase in molar conductivity with an increase in the ligand concentration. This behavior indicates that the  $(4'\text{NB18C6.Y})^{3+}$  complex is more mobile than free solvated  $\text{Y}^{+3}$  cation. A similar behavior was observed in most solution systems. The slope of the corresponding molar conductivity versus  $[4'\text{NB18C6}]/[\text{Y}^{+3}]$  mole ratio plots changes at the point where the ligand to cation mole ratio is about one, which is an evidence for the formation of a relatively stable 1:1 [M:L] complex between 4'NB18C6 and  $\text{Y}^{+3}$  in these non aqueous solvents. In order to make more clear the 1:1 [M:L] complexation model, the fitting and experimental curves for  $(4'\text{NB18C6.Y})^{3+}$  complex in pure AN at 25 °C are shown in Fig. 5. As is evident

**Table 1** Log  $K_f$  values of  $(4'NB18C6.Y)^{3+}$  complex in binary mixed non-aqueous solvents at different temperatures.

Medium	Log $K_f \pm SD^a$			
	15 °C	25 °C	35 °C	45 °C
<i>AN-MeOH</i>				
Pure AN	2.93 ± 0.04	2.96 ± 0.05	3.24 ± 0.05	3.41 ± 0.06
75% AN–25% MeOH <sup>b</sup>	3.38 ± 0.04	3.03 ± 0.08	2.62 ± 0.07	2.57 ± 0.07
50% AN–50% MeOH	2.88 ± 0.07	2.82 ± 0.08	2.75 ± 0.13	2.72 ± 0.12
25% AN–75% MeOH	2.89 ± 0.08	2.87 ± 0.07	2.79 ± 0.10	2.73 ± 0.12
Pure MeOH	3.04 ± 0.06	2.89 ± 0.06	2.74 ± 0.10	2.63 ± 0.07
<i>AN-DMF</i>				
75% AN–25% DMF <sup>b</sup>	2.73 ± 0.06	2.83 ± 0.05	2.90 ± 0.07	2.98 ± 0.07
50% AN–50% DMF	2.68 ± 0.05	2.88 ± 0.05	3.09 ± 0.06	2.92 ± 0.07
25% AN–75% DMF	2.80 ± 0.08	2.73 ± 0.11	2.70 ± 0.12	2.69 ± 0.14
Pure DMF	2.92 ± 0.06	2.79 ± 0.08	2.71 ± 0.12	2.54 ± 0.15
<i>AN-EtOAc</i>				
75% AN–25% EtOAc <sup>b</sup>	2.64 ± 0.16	2.45 ± 0.33	2.41 ± 0.43	2.44 ± 0.36
50% AN–50% EtOAc	2.69 ± 0.13	2.45 ± 0.35	2.46 ± 0.32	2.49 ± 0.24
25% AN–75% EtOAc	2.88 ± 0.10	3.23 ± 0.03	2.79 ± 0.09	2.70 ± 0.16
Pure EtOAc	3.11 ± 0.04	3.04 ± 0.03	2.72 ± 0.08	2.60 ± 0.10
<i>AN-DCE</i>				
75% AN–25% DCE <sup>b</sup>	3.48 ± 0.03	3.58 ± 0.08	3.64 ± 0.06	3.71 ± 0.07
50% AN–50% DCE	c	c	c	3.59 ± 0.08
25% AN–75% DCE	3.32 ± 0.05	3.34 ± 0.04	3.45 ± 0.08	3.50 ± 0.07
Pure DCE	d	d	d	d

<sup>a</sup> SD = standard deviation.

<sup>b</sup> The composition of binary solvents is expressed in mol% of each solvent.

<sup>c</sup> The data cannot be fitted in equations.

<sup>d</sup> The salt is not dissolved.

**Table 2** Thermodynamic parameters for the formation of  $(4'NB18C6.Y)^{3+}$  complex in binary mixed non-aqueous solvents.

Medium	$-\Delta G^\circ_c \pm SD^a$ (25 °C) kJ/mol	$\Delta H^\circ_c \pm SD^a$ kJ/mol	$\Delta S^\circ_c \pm SD^a$ J/mol k
<i>AN-MeOH</i>			
Pure AN	16.94 ± 0.12	40.51 ± 4.04	192.71 ± 13.54
75% AN–25% MeOH <sup>b</sup>	17.33 ± 0.20	–49.93 ± 9.16	–109.36 ± 30.72
50% AN–50% MeOH	16.13 ± 0.30	–9.42 ± 1.13	22.51 ± 3.66
25% AN–75% MeOH	16.37 ± 0.24	–9.91 ± 1.52	21.69 ± 5.05
Pure MeOH	16.51 ± 0.21	–24.75 ± 0.92	–27.64 ± 3.01
<i>AN-DMF</i>			
75% AN–25% DMF <sup>b</sup>	16.16 ± 0.17	14.46 ± 0.72	102.68 ± 2.33
50% AN–50% DMF	16.44 ± 0.16	29.54 ± 3.19	154.23 ± 10.69
25% AN–75% DMF	15.59 ± 0.53	–5.86 ± 1.44	32.62 ± 4.49
Pure DMF	15.96 ± 0.30	–21.45 ± 2.11	–18.40 ± 7.00
<i>AN-EtOAc</i>			
75% AN–25% EtOAc <sup>b</sup>	14.01 ± 2.89	–19.17 ± 6.69	c
50% AN–50% EtOAc	13.99 ± 3.06	3.67 ± 1.77	c
25% AN–75% EtOAc	18.45 ± 0.04	–10.09 ± 2.43	28.02 ± 8.14
Pure EtOAc	17.35 ± 0.06	–32.43 ± 6.00	c
<i>AN-DCE</i>			
75% AN–25% DCE <sup>b</sup>	20.44 ± 0.05	13.37 ± 0.87	113.41 ± 2.91
50% AN–50% DCE	d	d	d
25% AN–75% DCE	19.05 ± 0.05	11.61 ± 2.09	102.82 ± 7.03
Pure DCE	e	e	e

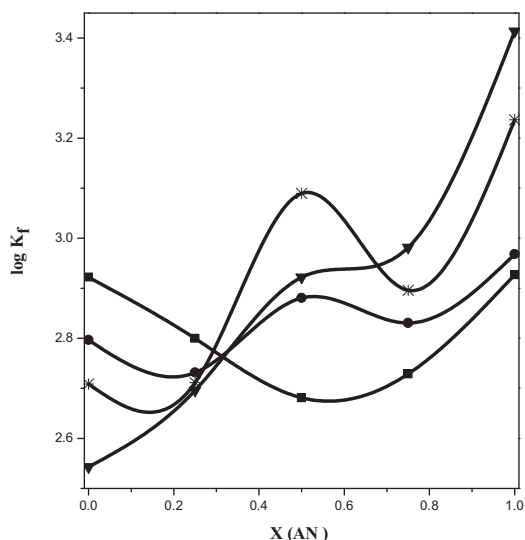
<sup>a</sup> SD = standard deviation.

<sup>b</sup> The composition of binary solvents is expressed in mol% of each solvent.

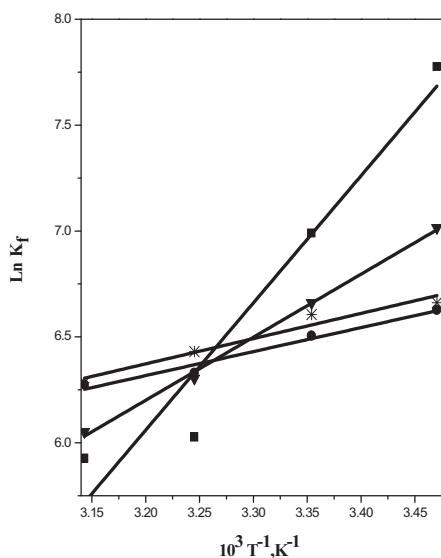
<sup>c</sup> With high uncertainty.

<sup>d</sup> The data cannot be fitted in equations.

<sup>e</sup> The salt is not dissolved.



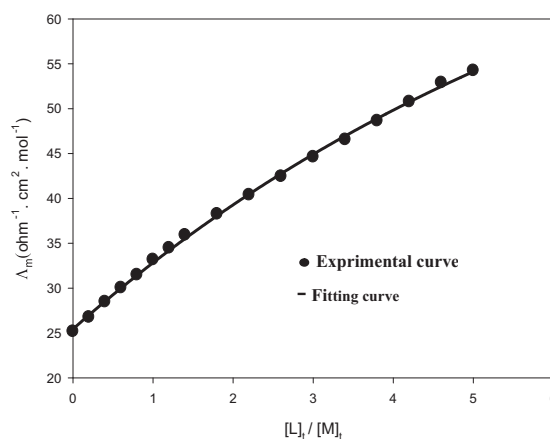
**Figure 3** Changes of the stability constant ( $\log K_f$ ) of  $(4'NB18C6.Y)^{3+}$  complex with the composition of AN-DMF binary system at different temperatures: (■) 15 °C, (●) 25 °C, \* 35 °C, (▼) 45 °C.



**Figure 4** van't Hoff plots for  $(4'NB18C6.Y)^{3+}$  complex in AN-MeOH binary systems: mol% AN: (■) (25), (●) (50), \* (75), (▼) (100.)

in this Figure, there is a good agreement between the fitting and experimental data.

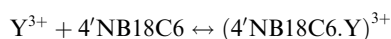
A different behavior was observed for complexation of  $Y^{3+}$  cation with 4'NB18C6 in AN-DCE binary system. As is clear from Fig. 2, addition of the ligand to  $Y^{3+}$  cation in AN-DCE (mol% DCE = 50) binary solution at 15, 25 and 35 °C, causes the molar conductivity to initially decrease until the mole ratio reaches to about  $\frac{1}{2}$  and then increases. The behavior observed in this solvent system, probably shows that a 2:1 [M2:L] complex is formed between 4'NB18C6 and  $Y^{3+}$  cation in the solution which is less mobile than the free solvated  $Y^{3+}$  cation. It seems that further addition of the ligand



**Figure 5** The fitting and experimental curves for  $(4'NB18C6.Y)^{3+}$  complex in pure AN at 25 °C.

to [M2:L] complex solution, causes the formation of a [M2:L2] complex in solution which is less solvated than [M2:L] complex and, therefore, the molar conductivity increases. Since the cavity size of 4'NB18C6 is not big enough to fit two  $Y^{3+}$  cations, but it may suggest that the second  $Y^{3+}$  cation probably interacts with the ligand via oxygen donor of the  $-NO_2$  group and also with the  $\pi$  electron system of benzo group and, therefore, it forms a 2:1 [M2:L] complex with the metal cation in the solution and further addition of 4'NB18C6 results in the formation a [M2:L2] complex with a club sandwich structure. It is interesting to note that at 45 °C, a relatively stable 1:1 [M:L] complex is formed in this solvent system. The results obtained in this study show that the stoichiometry of the complex formed between 4'NB18C6 and  $Y^{3+}$  cation changes with the composition of the binary mixed solvent solution and also with temperature.

The 1:1 complexation between 4'NB18C6 and  $Y^{3+}$  cation can be given by equation:



The corresponding equilibrium constant,  $K_f$ , is given by:

$$K_f = \frac{[(4'NB18C6.Y)^{3+}]}{[Y^{3+}][4'NB18C6]} \cdot \frac{f_{(4'NB18C6.Y)^{3+}}}{f_{Y^{3+}} \cdot f_{4'NB18C6}}$$

where  $[(4'NB18C6.Y)^{3+}]$ ,  $[Y^{3+}]$  and  $[4'NB18C6]$  denote the molar concentration of the complex, metal cation and crown ether and  $f$  indicates the activity coefficient of the species indicated. Under the highly dilute conditions which we employed in these experiments, the  $f_{(4'NB18C6.Y)^{3+}}$ ,  $f_{Y^{3+}}$  and  $f_{4'NB18C6}$  are essentially unity and, therefore, the equilibrium constants obtained in this study are thermodynamic equilibrium constants.

The values of the stability constant ( $\log K_f$ ) of  $(4'NB18C6.Y)^{3+}$  complex in various solvent systems are listed in Table 1. As is obvious from this Table, the stability constant of  $(4'NB18C6.Y)^{3+}$  complex in pure non-aqueous solvents at 25 °C decreases in the order: EtOAc > AN > MeOH > DMF, which is not consistent with the inverse order of their solvating abilities as expressed by the Gutmann donor number: DMF(DN = 26.6) > MeOH(DN = 20.0) > EtOAc(DN = 17.1) > AN(DN = 14.1).

Solvent properties are considered as the major factors influencing the formation constants of crown ether-cation com-



plexes. The reason is that the solvent and crown ether molecules compete in binding to the metal cation. When the donor properties of the solvent are low, the cation is poorly solvated and can easily be complexed by the crown ether molecule. The solvation of the crown ether also influences the formation constant of crown-cation complex in solution. The stability order of  $(4'NB18C6.Y)^{3+}$  complex in the mixed solvent solutions with 25 mol percent of AN at 25 °C was found to be:

AN-DCE > AN-EtOAc > AN-MeOH ~ AN-DMF

But in the case of the mixed solvents with 75 mol percent of AN at 25 °C it changes to:

AN-DCE > AN-MeOH > AN-DMF ~ AN-EtOAc

The results obtained in this study, reveal that the stability of  $(4'NB18C6.Y)^{3+}$  complex in the pure and also in the binary mixed non-aqueous solvent solutions, changes with the nature and composition of the solvent system. As is evident from Table 1, the stability of the complex also changes with temperature.

As is seen from Fig. 3, the change of the stability constant ( $\log K_f$ ) of  $(4'NB18C6.Y)^{3+}$  complex with the composition of AN-DMF binary system is not linear. A non-linear behavior was also observed in all other binary solvent solutions. This behavior may be related to changes occurring in the structure of the solvent mixtures and, therefore, change in the solvation properties of the ligand, 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 the ligand and the characteristics of its changes with the composition of the mixed solvents and temperature may be effective in this complexation process.

The thermodynamic data given in Table 2 reveal that, in most cases, the  $(4'NB18C6.Y)^{3+}$  complex is both enthalpy and entropy stabilized, therefore, both of these thermodynamic quantities are the driving force for the formation of this complex in these solutions. Since during the complexation of a metal cation by a macrocyclic ligand, most of the coordinated solvent molecules of the cation are replaced by the donor atoms of the ligand, even when the cation-macrocyclic binding is weak, the increased degree of freedom, due to desolvation of cation, may result in some positive entropic gain. In the cases where the macrocycle has also some interactions with the solvent molecules (Izatt et al., 1992), the release of some solvent molecules involved in interaction of the metal cation with the ligand, also contribute to the positive entropy values (Shamsipur and Pourtedal, 1999). The changes of the enthalpy of the ligand by complexation are mainly due to the changes of solvation, intermolecular ligand-ligand repulsion, the stacking of the aromatic residues and steric deformation of the ligand induced by the bound metal cation (Weber et al., 1989).

The experimental values of  $\Delta H^\circ_c$  and  $\Delta S^\circ_c$  (Table 2) show that, the values of standard enthalpy ( $\Delta H^\circ_c$ ) and standard entropy ( $\Delta S^\circ_c$ ) for complexation reaction between  $4'NB18C6$  and  $Y^{+3}$  cation in these solutions, do not vary monotonically with the solvent composition. A non-monotonic behavior has

also been observed for thermodynamic functions of several crown ether-metal ion complex formations in some binary mixed solvents (Rounaghi and Mofazzeli, 2005; Rounaghi et al., 2010; Rounaghi and Ghaemi, 2009). This behavior may be due to the strong interactions between the constituent solvent molecules which result in changes in some of the chemical and physical properties of each of the solvents and, therefore, changing their solvating ability towards the dissolved species. In addition, the heteroselective solvation of the cation and even the macrocyclic ligand may be effective in the complexation reactions (Rounaghi and Razavipanah, 2008). The solvation of crown ethers is of great importance during the complexation process of macrocyclic ligands with the metal cations and the relative enthalpy and entropy changes can be better understood if the ligand solvation is taken into consideration. Information on the interaction of macrocyclic ligands with the solvent molecules is distributed, and additional studies on the ligand-solvent interactions are necessary to investigate the thermodynamic behavior of macrocyclic complexes in solutions.

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