

## Complexation Ability of Dibenzo-24-crown-8 with Cs<sup>+</sup> Cation in Binary Mixed Non-Aqueous Solvents

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The complexation reaction of macrocyclic ligand, dibenzo-24-crown-8 (DB24C8) with Cs<sup>+</sup> cation was studied in acetonitrile-methanol (AN-MeOH), acetonitrile-ethanol (AN-EtOH), acetonitrile-dimethylformamide (AN-DMF) and nitromethane-methanol (NM-MeOH) binary mixtures at different temperatures using the conductometric method. The conductance data show that in all the solvent systems, the stoichiometry of the complex formed between DB24C8 and Cs<sup>+</sup> cation is 1:1 (ML). It was found that the stability of (DB24C8.Cs)<sup>+</sup> complex decreases with increasing temperature. The stability constant of the resulting 1:1 complex in pure non-aqueous solvents decreases in the order: EtOH > MeOH > DMF and in binary mixed solutions, it follows the order: AN-EtOH > AN-MeOH > AN-DMF. A non-linear behaviour was observed for changes of log K<sub>f</sub> of (DB24C8.Cs)<sup>+</sup> complex *versus* the composition of the binary mixed solvents. The obtained results show that the stability of the complex is quite sensitive to the composition of the mixed solvents. The values of thermodynamic quantities ( $\Delta H^\circ$  and  $\Delta S^\circ$ ) for formation of (DB24C8.Cs)<sup>+</sup> complex were obtained from temperature dependence of the stability constant using the van't Hoff plots. The results show that in all cases the complex is enthalpy stabilized but, in most cases entropy destabilized and both parameters are affected by the nature and composition of the mixed solvents.

**Key Words:** Dibenzo-24-crown-8, Cs<sup>+</sup>, Conductometry, Acetonitrile-methanol, Acetonitrile-ethanol, Acetonitrile-dimethylformamide, Nitromethane-methanol.

### INTRODUCTION

The metal-ion chemistry of macrocyclic ligands has been the subject of great interest since Pedersen first reported the synthesis of a crown ether in 1967<sup>1</sup>. These macrocyclic compounds are capable of forming complexes with alkali and alkaline earth metal ions by electrostatic attraction and encapsulation into the macrocyclic cavity<sup>2,3</sup>.

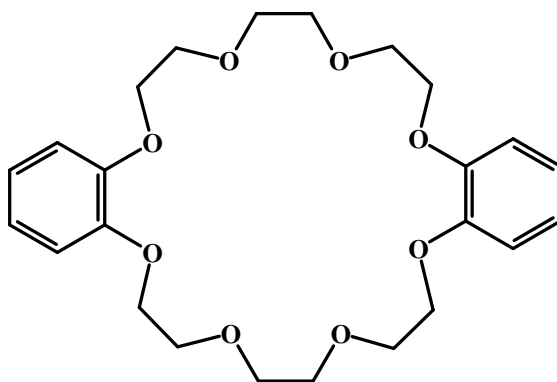
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Among the macrocyclic polyethers, large crown ethers (*i.e.*, larger than 18-crown-6) possess interesting properties. Some of these ligands are very flexible molecules with enough oxygen atoms in their rings to enable them to twist around a metal ion of suitable size to envelop it completely and form a "wrap around" complex in which all oxygen atoms of the ring are coordinated to the central cation. Evidence for the existence of such tri-dimensional structures both in solid state<sup>4,5</sup> and in solution<sup>6-10</sup> have been reported. Moreover, in some cases, the macrocyclic ring can accommodate two cations, if the repulsion forces are not so large, as in the cases, of Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup> complexes with dibenzo-24-crown-8<sup>11,12</sup> and dibenzo-30-crown-10<sup>6,13</sup>.

In these host-guest recognition processes, solvent plays a critical role in local structure optimization and complex stabilization. The effect of mixed solvent properties on the formation of crown ether-metal ion complexes is of interest due to the fact that solvation capacities of crown ether molecules and metal ions change with changing the composition of the mixed solvents. Contrary to the wide range of information about complex formation between crown compounds and metal cations in pure organic solvents, the data in mixed non-aqueous solvents are sparse<sup>14-16</sup>. It is worthwhile to extend such studies to some mixed binary non-aqueous systems in order to see how the thermodynamics of complexation are affected by the solvent composition. It should be noted that the solvating abilities of solvents in mixtures could be vary different from those of the neat solvent.

In this paper, we report the results obtained for thermodynamic study of complexation reaction between DB24C8 (**Scheme-I**), with Cs<sup>+</sup> metal cation in acetonitrile-methanol (AN-MeOH), acetonitrile-ethanol (AN-EtOH), acetonitrile-dimethylformamide (AN-DMF) and nitromethane-methanol (NM-MeOH) binary mixtures at different temperatures using the conductometric method. Conductance measurements can be carried out easily and with high precision at very low concentrations. As a consequence, precise data can be obtained for a wide variety of complexation systems at concentration for which theory is applicable.



**Scheme-I:** Dibenzo-24-crown-8

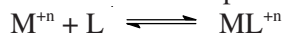
## EXPERIMENTAL

Dibenzo-24-crown-8 (DB24C8) and cesium chloride (Fluka) were used without further purification. The solvents *viz.*, acetonitrile, methanol, ethanol, nitromethane and dimethylformamide all from Merck were used with the highest purity. The experimental procedure to obtain the formation constant of the complex was as follows: a solution of metal salt ( $2.0 \times 10^{-4}$  M) was placed in a titration cell and the conductance of the solution was measured, then the crown ether concentration was increased by adding crown ether solution in the same solvent ( $1.0 \times 10^{-2}$  M) 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 Metrohm conductivity apparatus (model 712) in a thermostated water-bath with a constant temperature maintained within  $\pm 0.01$  °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  $0.75 \text{ cm}^{-1}$  was used throughout the studies.

## RESULTS AND DISCUSSION

The changes of molar conductance ( $\Lambda_m$ ) *versus* the ligand to the cation molar ratio, ( $[L]_t/[M]_t$ ), for complexation of DB24C8 with Cs<sup>+</sup> cation were measured in AN-MeOH, AN-EtOH, AN-DMF and NM-MeOH binary 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 *versus* the ligand/metal cation mole ratios in pure EtOH and AN-MeOH (mol % AN = 93.7) binary mixture are shown in Figs. 1 and 2, respectively.

The stability constant of (DB24C8.Cs)<sup>+</sup> complex at each temperature was calculated from variation of molar conductance as a function of ligand/metal cation mole ratios using a GENPLOT computer program<sup>17</sup>. The details of calculation of the stability constants of complexes by the conductometric method have been described elsewhere<sup>18</sup>. The values of the stability constant ( $\log K_f$ ) for the (DB24C8.Cs)<sup>+</sup> complex in various solvent systems are listed in Table-1. The 1:1 complexation of a metal cation, M<sup>n+</sup>, with a crown ether is represented by the following equilibrium:



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

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

where  $[ML^{n+}]$ ,  $[M^{n+}]$  and  $[L]$  denote the molar concentration of the complex, metal cation and crown ether and 'f' indicates the activity coefficient of the species indicated. In this paper, L = DB24C8 and M = Cs<sup>+</sup>. Under the highly dilute conditions which employed in these experiments, the  $f_{ML^{n+}}/f_{M^{n+}} f_L$  is essentially unity and, therefore, the equilibrium constants obtained in this study are thermodynamic equilibrium constants.

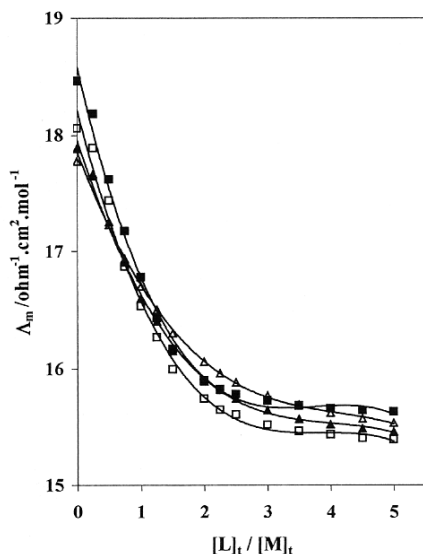


Fig. 1. Molar conductance-mole ratio plots for (DB24C8.Cs)<sup>+</sup> complex in pure EtOH at different temperatures (■ 15 °C, □ 25 °C, ▲ 35 °C, ▲ 45 °C)

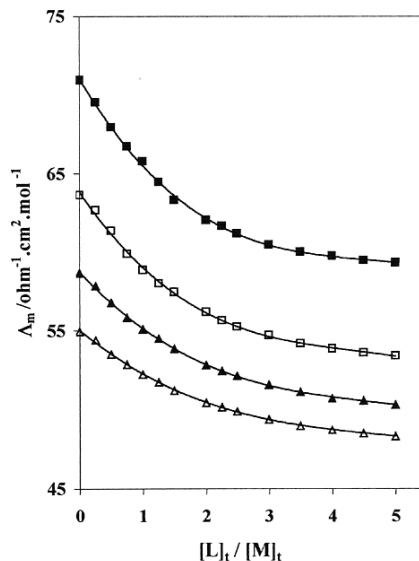


Fig. 2. Molar conductance-mole ratio plots for (DB24C8.Cs)<sup>+</sup> complex in AN-MeOH (mole % AN = 93.7) binary mixture at different temperatures: (■ 15 °C, □ 25 °C, ▲ 35 °C, ▲ 45 °C)

The thermodynamic equilibrium constant,  $K_f$ , is related to Gibbs standard free energy of complexation reaction,  $\Delta G_c^\circ$ . The van't Hoff plots of  $\ln K_f$  versus  $1/T$  in all cases were linear. A typical example of these plots is shown in Fig. 3. The changes in the standard enthalpy ( $\Delta H_c^\circ$ ) for complexation reaction 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. The changes in standard entropy ( $\Delta S_c^\circ$ ) were calculated from the relationship  $\Delta G_{c,298.15}^\circ = \Delta H_c^\circ - 298.15 \Delta S_c^\circ$ . The thermodynamic data are summarized in Table-3. The changes of  $\log K_f$  of (DB24C8.Cs)<sup>+</sup> complex versus the mole fraction of AN in AN-MeOH and AN-EtOH binary systems at different temperatures are shown in Figs. 4 and 5, respectively.

As is seen from Figs. 1 and 2, addition of DB24C8 to a solution of Cs<sup>+</sup> cation in pure EtOH and AN-MeOH (mol % AN = 93.7) binary mixture at different temperatures results in a decrease in molar conductivity with an increase in the ligand concentration, which indicates that the (DB24C8.Cs)<sup>+</sup> complex is less mobile than free solvated Cs<sup>+</sup> cation. Similar behaviour was observed in all other solvent systems. The slope of the corresponding molar conductivity versus ligand/metal cation mole ratio 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 [M:L] complex between DB24C8 with Cs<sup>+</sup> metal cation in solutions. As is evident in Table-1, the stability constant of (DB24C8.Cs)<sup>+</sup> complex decreases as the temperature

TABLE-1  
log K<sub>f</sub> VALUES OF (DB24C8.Cs)<sup>+</sup> COMPLEX IN AN–MeOH, AN–EtOH, AN–DMF  
AND NM–MeOH BINARY MIXTURES AT DIFFERENT TEMPERATURES

Medium	log K <sub>f</sub> ± SD <sup>a</sup>			
	15 °C	25 °C	35 °C	45 °C
<b>AN–MeOH</b>				
Pure AN	c	c	c	c
93.7 % AN–6.3 % MeOH <sup>b</sup>	3.74 ± 0.04	3.70 ± 0.03	3.57 ± 0.02	3.50 ± 0.02
70.0 % AN–30.0 % MeOH	3.77 ± 0.04	3.65 ± 0.03	3.48 ± 0.11	3.30 ± 0.07
43.8 % AN–56.2 % MeOH	3.61 ± 0.03	3.50 ± 0.04	3.40 ± 0.03	3.27 ± 0.03
20.6 % AN–79.4 % MeOH	3.54 ± 0.05	3.38 ± 0.03	3.29 ± 0.04	3.18 ± 0.05
Pure MeOH	3.88 ± 0.08	3.62 ± 0.06	3.50 ± 0.05	3.14 ± 0.05
<b>AN–EtOH</b>				
Pure AN	c	c	c	c
95.5 % AN–4.5 % EtOH <sup>b</sup>	3.83 ± 0.04	3.72 ± 0.03	3.61 ± 0.05	3.49 ± 0.04
77.0 % AN–20.3 % EtOH	3.80 ± 0.06	3.65 ± 0.04	3.52 ± 0.04	3.36 ± 0.05
52.8 % AN–47.2 % EtOH	3.63 ± 0.08	3.65 ± 0.04	3.51 ± 0.04	3.41 ± 0.04
27.2 % AN–73.8 % EtOH	3.94 ± 0.06	3.86 ± 0.05	3.68 ± 0.03	3.56 ± 0.03
Pure EtOH	4.23 ± 0.08	4.13 ± 0.09	3.95 ± 0.05	3.81 ± 0.05
<b>AN–DMF</b>				
Pure AN	c	c	c	c
93.0 % AN–7.0 % DMF <sup>b</sup>	3.54 ± 0.05	3.40 ± 0.05	3.33 ± 0.06	3.20 ± 0.07
81.6 % AN–18.4 % DMF	3.61 ± 0.06	3.39 ± 0.04	3.61 ± 0.08	3.41 ± 0.05
59.6 % AN–40.4 % DMF	2.81 ± 0.12	2.95 ± 0.06	2.75 ± 0.09	2.89 ± 0.07
33.0 % AN–67.0 % DMF	2.73 ± 0.07	2.72 ± 0.06	2.05 ± 0.14	2.59 ± 0.10
Pure DMF	2.76 ± 0.26	2.77 ± 0.16	2.74 ± 0.12	1.90 ± 0.33
<b>NM–MeOH</b>				
Pure NM	c	c	c	c
93.4 % NM–6.6 % MeOH <sup>b</sup>	3.88 ± 0.08	3.82 ± 0.06	3.73 ± 0.05	3.60 ± 0.06
69.1 % NM–30.9 % MeOH	3.84 ± 0.04	3.69 ± 0.03	3.56 ± 0.03	3.48 ± 0.03
43.7 % NM–57.3 % MeOH	3.78 ± 0.04	3.60 ± 0.03	3.47 ± 0.03	3.36 ± 0.05
20.0 % NM–80.0 % MeOH	3.81 ± 0.03	3.62 ± 0.04	3.48 ± 0.04	3.38 ± 0.04
Pure MeOH	3.88 ± 0.08	3.62 ± 0.06	3.50 ± 0.05	3.14 ± 0.05

<sup>a</sup>SD = Standard deviation; <sup>b</sup>Composition of binary mixtures is expressed in mol % for each solvent system; <sup>c</sup>The salt is not dissolved.

increases, which is an evidence for formation of a weaker complex at higher temperatures. Similar behaviour was observed in all solvent systems, therefore, the complexation reaction between Cs<sup>+</sup> cation and DB24C8 is exothermic in solutions.

Comparison of the data given in Table-1 reveals that the stability constant of (DB24C8.Cs)<sup>+</sup> complex in pure non-aqueous solvents decreases in the order: EtOH > MeOH > DMF. This behaviour reflects the much stronger cation solvation by DMF, compared with the other two solvents, with which the ligand has to challenge. Dimethylformamide with a high donor ability (DN = 26.6) relative to ethanol (DN

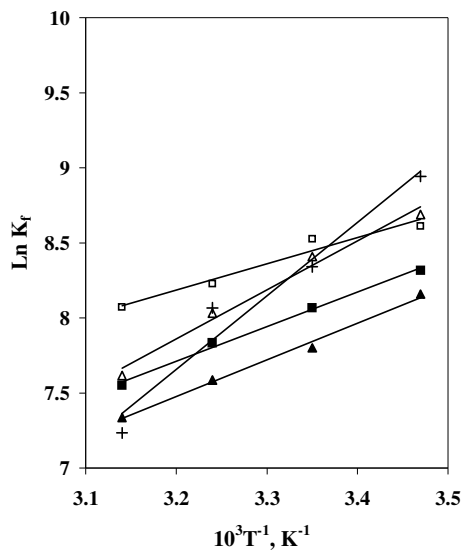


Fig. 3. Van't Hoff plots for (DB24C8.Cs)<sup>+</sup> complex in NM-MeOH binary systems: (mol % MeOH: ■ 6.6, ▲ 30.9, □ 57.3, + 80.0, +100)

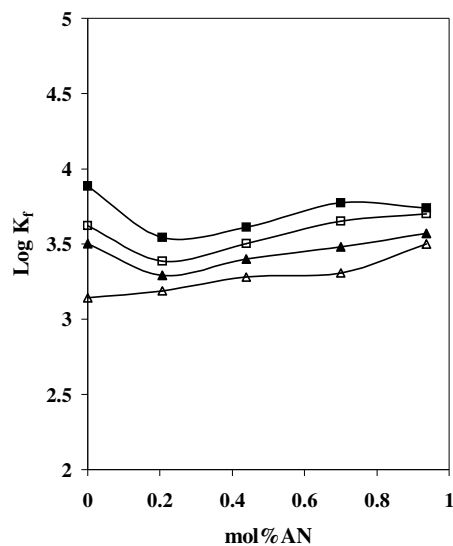


Fig 4. Changes of the stability constant ( $\log K_f$ ) of (DB24C8.Cs)<sup>+</sup> complex with the composition of the AN-MeOH binary systems at different temperatures: (■ 15 °C, □ 25 °C, ▲ 35 °C, △ 45 °C)

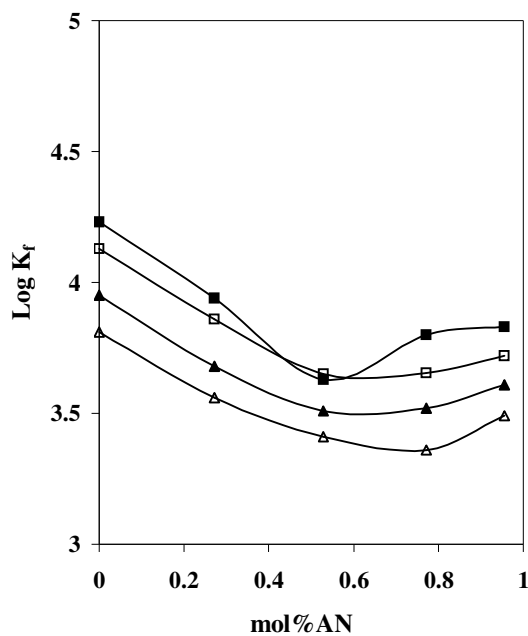


Fig. 5. Changes of the stability constant ( $\log K_f$ ) of (DB24C8.Cs)<sup>+</sup> complex with the composition of the AN-EtOH binary systems at different temperatures: (■ 15 °C, □ 25 °C, ▲ 35 °C, △ 45 °C)

= 19.0) and methanol, (DN = 20.0), can solvate the Cs<sup>+</sup> cation strongly and compete with the ligand for Cs<sup>+</sup> cation. In addition, the higher dielectric constant of DMF ( $\epsilon = 36.7$ ) compared with EtOH ( $\epsilon = 24.3$ ) and MeOH, ( $\epsilon = 32.6$ ) could also lead to a decrease in the electrostatic interactions between the ligand and cation, therefore, the formation of the (DB24C8.Cs)<sup>+</sup> complex is weakened in this solvent compared with the other two organic solvents.

Although, MeOH and EtOH have almost the same donor numbers, but the stability constant of the complex in EtOH is much higher than in MeOH. It seems that the dielectric constant of the solvent is a dominant factor for complexation process between DB24C8 and Cs<sup>+</sup> cation in these solvents. The lower dielectric constant of EtOH ( $\epsilon = 24.3$ ) in comparison with that of MeOH ( $\epsilon = 32.6$ ) would cause the electrostatic contribution to bond formation to increase in ethanolic solution, therefore, as is expected, the stability constant of (DB24C8.Cs)<sup>+</sup> complex varies inversely with the dielectric constants of these pure organic solvents.

The stability constants of crown-cation complexes in solution could be interpreted as representing the overall equilibrium constants of a series of reactions including<sup>19</sup>: (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 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 process of complexation considerably.

The complexation ability of DB24C8 with Cs<sup>+</sup> cation in some pure non-aqueous solvents has been studied by other research groups<sup>20-36</sup>. The values of stability constant ( $\log k_f$ ) for (DB24C8.Cs)<sup>+</sup> complex in two pure non-aqueous solvents obtained from the present work and also by some other research groups are given in Table-2. As is evident from this Table, there is a reasonable agreement between present experimental results and previous data.

TABLE-2  
REPORTED VALUES OF STABILITY CONSTANTS ( $\log K_f$ )  
FOR (DB24C8.Cs)<sup>+</sup> COMPLEX AT 25 °C

MeOH	DMF
3.62 [In this work]	2.77 [In this work]
3.60 [Ref. 7; <sup>133</sup> Cs NMR (30 °C)]	2.77 [Ref. 34; Potentiometry]
3.78 [Ref. 30; Potentiometry]	2.21 [Ref. 35; <sup>133</sup> Cs NMR (27 °C)]
3.84 [Ref. 31; Conductometry; Ref. 32, Calorimetry]	2.15 [Ref. 36; <sup>133</sup> Cs NMR (30 °C)]
3.76 [Ref. 33, Chromatography]	

As is evident in Table-1, the stability constant of (DB24C8.Cs)<sup>+</sup> complex in binary mixed solutions varies in the order: AN-EtOH > AN-MeOH > AN-DMF

which can be attributed to the inherent solvating ability of the pure solvents which form the mixture. The solvation of ligand and metal cation is influenced by the donor ability and dielectric constant of the solvent. Since the donor ability and dielectric constant of dimethylformamide molecule is higher than ethanol and methanol molecules, therefore, the complex formation is weakened in AN-DMF binary solutions compared to AN-EtOH and AN-MeOH binary mixed solvents. It is known that the donor ability and dielectric constant of the solvent, play an important role in different complexation reactions<sup>37,38</sup>.

As shown in Figs. 4 and 5, the change of the stability constant ( $\log K_f$ ) of (DB24C8.Cs)<sup>+</sup> complex with the composition of acetonitrile-methanol and acetonitrile-ethanol binary solutions, is not linear. Similar behaviour was also observed in other binary solutions. This behaviour is probably due some kinds of solvent-solvent interactions between these two solvents and changing the structure of the solvent mixtures and, therefore, changing in solvation properties of the cation, the cyclic polyether and even the resulting complex in solutions. It has been shown that there is an interaction between acetonitrile and methanol molecules ( $K_{\text{ass}} = 1.23$ ) *via* hydrogen bonding in their binary mixtures<sup>39</sup>. 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 data which are summarized in Table-3, show that in all cases, (DB24C8.Cs)<sup>+</sup> complex is enthalpy stabilized, but in most cases entropy destabilized, therefore, the enthalpy of the complexation reaction is the principal driving force for formation of this complex in solutions. As expected, the values of  $\Delta H^\circ_c$  and  $\Delta S^\circ_c$  depend strongly on the nature and composition of the mixed solvents. The value and the sign of the standard entropy changes are expected to vary with different parameters, such as changes in flexibility of the macrocyclic ligand during the complexation process and the extent of cation-solvent, ligand-solvent and also complex-solvent interactions. It is known that large macrocyclic ligands such as dibenzo-24-crown-8 are rather flexible in the uncomplexed states, therefore, the negative entropy changes may be partially attributed to the increased ligand rigidity upon coordination. It should be noted, however, that the conformational change of the ligand is not the only factor governing the change in the entropy of complexation. For example, the complexation reaction involves a change in the solvation of the cation and of the ligand. The relative enthalpy and entropy changes can be better understood if the ligand solvation is taken into consideration.

As seen from Table-3, both of these thermodynamic parameters ( $\Delta H^\circ_c$  and  $\Delta S^\circ_c$ ) change non-monotonically with the composition of the mixed solvents. Since there are many parameters which contribute to changes of enthalpy and entropy of complexation reactions, therefore, we should not expect to observe a monotonic behaviour between these thermodynamic parameters and the solvent composition of these binary solutions.



TABLE-3  
THERMODYNAMIC PARAMETERS FOR (DB24C8.Cs)<sup>+</sup> COMPLEX IN AN–MeOH,  
AN–EtOH, AN–DMF AND NM–MeOH BINARY MIXTURE

Medium	$-\Delta G_c^\circ \pm SD^a$ (kJ/mol)	$\Delta H_c^\circ \pm SD^a$ (kJ/mol)	$\Delta S_c^\circ \pm SD^a$ (J/mol k)
<b>AN–MeOH</b>			
93.7 % AN–6.3 % MeOH <sup>b</sup>	21.1 ± 0.2	-14.4 ± 2.2	22.4 ± 7.4
70.0 % AN–30.0 % MeOH	20.8 ± 0.2	-26.9 ± 2.5	-20.4 ± 8.2
43.8 % AN–56.2 % MeOH	20.0 ± 0.2	-18.9 ± 0.1	c
20.6 % AN–79.4 % MeOH	19.3 ± 0.2	-20.3 ± 1.0	c
Pure MeOH	20.5 ± 0.3	-40.70 ± 6.1	-67.6 ± 20.4
<b>AN–EtOH</b>			
95.5 % AN–4.5 % EtOH <sup>b</sup>	21.24 ± 0.2	-19.1 ± 0.8	c
77.0 % AN–20.3 % EtOH	20.84 ± 0.2	-24.8 ± 1.3	-13.3 ± 4.20
52.8 % AN–47.2 % EtOH	20.82 ± 0.3	-13.5 ± 4.1	c
27.2 % AN–73.8 % EtOH	22.10 ± 0.3	-23.1 ± 2.8	c
Pure EtOH	23.60 ± 0.5	-24.5 ± 2.2	c
<b>AN–DMF</b>			
93.0 % AN–7.0 % DMF <sup>b</sup>	19.4 ± 0.3	-18.9 ± 1.5	c
81.6 % AN–18.4 % DMF	19.4 ± 0.3	c	c
59.6 % AN–40.4 % DMF	16.9 ± 0.4	c	c
33.0 % AN–67.0 % DMF	15.5 ± 0.4	c	c
Pure DMF	15.8 ± 0.9	c	c
<b>NM–MeOH</b>			
93.4 % NM–6.6 % MeOH <sup>b</sup>	21.8 ± 0.4	-16.1 ± 2.3	19.0 ± 7.5
69.1 % NM–30.9 % MeOH	21.1 ± 0.2	-21.6 ± 1.2	c
43.7 % NM–57.3 % MeOH	20.5 ± 0.2	-24.7 ± 1.4	-13.9 ± 4.5
20.0 % NM–80.0 % MeOH	20.7 ± 0.3	-25.5 ± 1.9	-16.2 ± 3.9
Pure MeOH	20.5 ± 0.3	-40.7 ± 6.1	-67.6 ± 20.4

<sup>a</sup>SD = Standard deviation; <sup>b</sup>Composition of binary mixtures is expressed in mol % for each solvent system; <sup>c</sup>With high uncertainty.

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