

A conductometric study of complexation reaction between dibenzo-24-crown-8 with yttrium cation in some binary mixed non-aqueous solvents

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Received: 25 August 2008 / Accepted: 7 December 2008 / Published online: 14 January 2009
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Abstract The complexation reaction of macrocyclic ligand, dibenzo-24-crown-8 (DB24C8) with Y^{+3} cation was studied in some binary mixtures of methanol (MeOH), ethanol (EtOH), acetonitrile (AN) and tetrahydrofuran (THF) with dimethylformamide (DMF) at different temperatures using the conductometric method. The conductance data show that in all solvent systems, the stoichiometry of the complex formed between DB24C8 and Y^{+3} cation is 1:1 (ML). The stability order of $(DB24C8.Y)^{+3}$ complex in pure non-aqueous solvents was found to be: AN > EtOH > MeOH > DMF. A non-linear behaviour was observed for changes of $\log K_f$ of $(DB24C8.Y)^{+3}$ complex versus the composition of the binary mixed solvents, which was explained in terms of solvent–solvent interactions and also the heteroselective solvation of the species involved in the complexation reaction. The obtained results show that the stability of $(DB24C8.Y)^{+3}$ complex is sensitive to the mixed solvents composition. The values of thermodynamic parameters (ΔH°_c and ΔS°_c) for formation of $(DB24C8.Y)^{+3}$ complex were obtained from temperature dependence of the stability constant using the van't Hoff plots. The results show that in most cases, the $(DB24C8.Y)^{+3}$ complex is enthalpy destabilized but entropy stabilized and the values and also the sign of thermodynamic parameters are influenced by the nature and composition of the mixed solvents.

Keywords Dibenzo-24-crown-8 · Y^{+3} ·
Mixed non-aqueous solvents · Stability constant ·
Conductometry

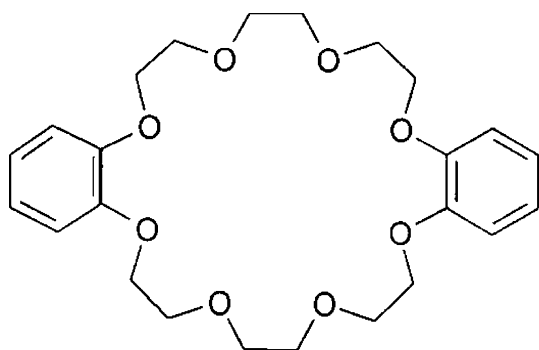
Introduction

The stability and selectivity of crown ether complexes with metal ions depend on several molecular factors. These include the cavity size of the ligand, the character of the heteroatoms in the polyether ring, the spatial distribution of ring binding sites, the charge density and polarizability of the cation and the cation diameter [1–3]. One of the major factors is also the type of solvent used in complexation reactions. The influence of the solvent on the complexation of cations by macrocyclic ligands is not restricted to the solvation of the cation, but the interaction between the ligand and solvent molecules and the solvation of the resulting complex may also play an important role in complexation reactions [4, 5]. As a result, the stability and selectivity of complexes and the thermodynamics of complexation processes can be greatly altered by changing the solvent properties [6].

In order to achieve appropriate solvent properties, we often use mixtures of two solvents. The physicochemical properties of mixed solvents are interesting both from a theoretical and practical point of view, because many chemical and electrochemical reactions might be carried out advantageously in these media. Usually mixed solvents do not behave as expected from statistical considerations, the solvating ability of solvents in mixtures can be different from those of neat media [7]. The deviations from ideal behaviour are indicative of the extent of preferential solvation and the existence of specific solvent–solute and solvent–solvent interactions [8, 9].

Although the complexation reaction of macrocyclic polyethers with metal cations has been extensively studied during the past two decades, most of these studies have been restricted to neat solvents or partly in mixtures of water with some organic solvents [10–12] and little

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Scheme 1 Dibenzo-24-crown-8

attention has been paid to the study of such complexations in mixed non-aqueous solvents [13–16]. Much more attention has been paid to the complexation of alkali and alkaline earth metal ions by macrocyclic ligands [17–19] and little attention has been paid to heavy metal ion complexes, particularly in mixed non-aqueous solvents [20].

A large number of physicochemical techniques such as potentiometry [21], calorimetry [22], conductometry [23–25], NMR spectrometry [26], spectrophotometry [27] and polarography [28, 29] have been used for study of complexation reactions between crown ethers with different metal cations in solutions.

In this paper, we report the results of a conductance study of the thermodynamics of Y^{+3} cation complexation with DB24C8 (Scheme 1), in methanol–dimethylformamide (MeOH–DMF), ethanol–dimethylformamide (EtOH–DMF), acetonitrile–dimethylformamide (AN–DMF) and tetrahydrofuran–dimethylformamide (THF–DMF) binary mixtures at different temperatures.

Experimental

DB24C8 (Fluka) and $Y(NO_3)_3 \cdot 6H_2O$ (Fluka) were used without further purification. The solvents: methanol, ethanol, acetonitrile, tetrahydrofuran 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 (1.0×10^{-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 (5.0×10^{-3} 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 ± 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 cm^{-1} was used throughout the studies.

Results

The changes of molar conductivity (Λ_m) versus the ligand to the cation molar ratio, ($[L]_t/[M]_t$), for complexation of DB24C8 with Y^{+3} cation were measured in pure MeOH, EtOH, AN, THF and DMF and also in MeOH–DMF, EtOH–DMF, AN–DMF and THF–DMF 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 as a function of Ligand/Metal cation mole ratios in pure EtOH and THF–DMF (mol%THF = 23.9) binary mixture are shown in Figs. 1 and 2, respectively.

The stability constant of $(DB24C8.Y)^{+3}$ complex in different solvent mixtures at various temperatures was obtained from variation of molar conductance as a function of Ligand/Metal cation mole ratios using a GENPLOT computer program [30]. The details of calculation of the stability constants of complexes by the conductometric

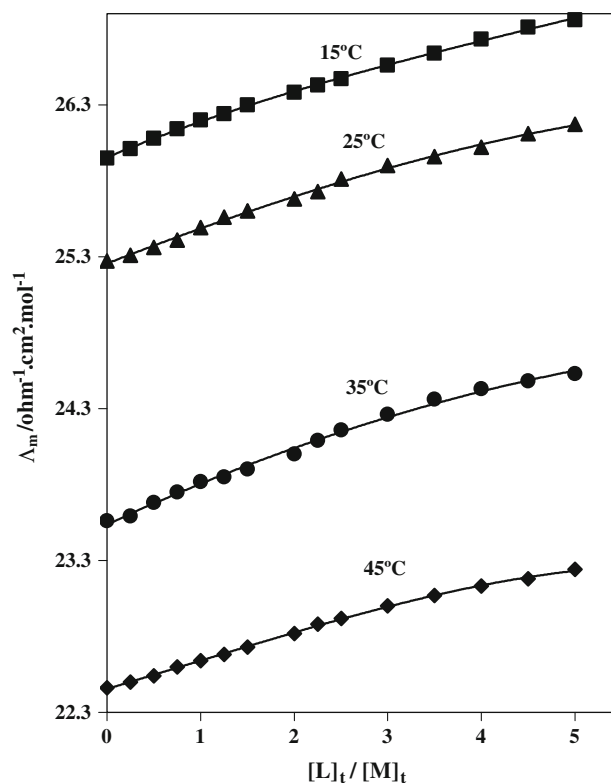


Fig. 1 Molar conductance-mole ratio plots for $(DB24C8.Y)^{+3}$ complex in pure EtOH at different temperatures

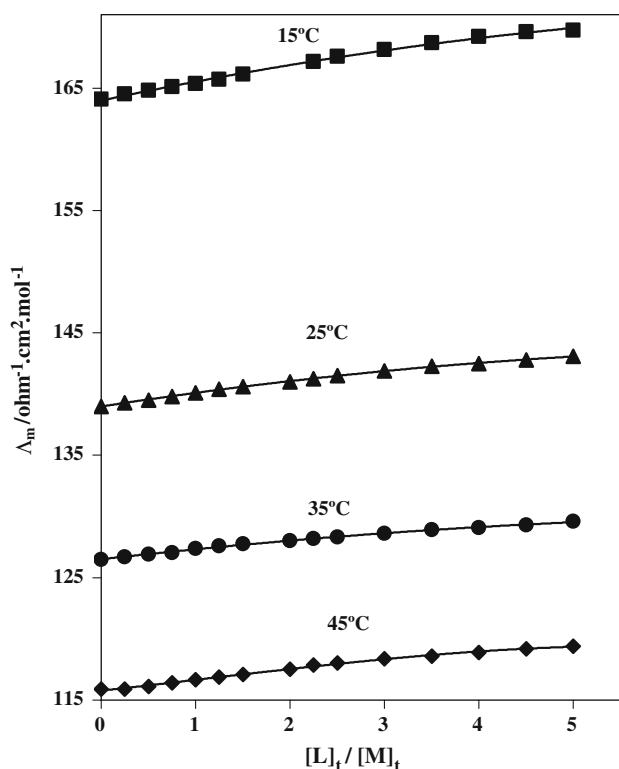


Fig. 2 Molar conductance-mole ratio plots for $(\text{DB24C8.Y})^{+3}$ complex in THF-DMF binary system (mole% THF = 23.9) at different temperatures

method have been described elsewhere [31]. The values of the stability constant ($\log K_f$) for the $(\text{DB24C8.Y})^{+3}$ complex in various solvent systems are listed in Table 1. Assuming that the activity coefficients of cation and complex have the same values, K_f is a thermodynamic equilibrium constant on the molar concentration scale, related to the Gibbs standard free energy of complexation reaction, ΔG°_c . The van't Hoff plots of $\ln K_f$ versus $1/T$ in all cases were linear and a typical example of these plots is shown in Fig. 3. The changes in the standard enthalpy (ΔH°_c) for complexation of DB24C8 with Y^{+3} cation were obtained from the slope of the van't Hoff plots assuming that ΔC_p is equal to zero over the entire temperature range investigated. The changes in standard entropy (ΔS°_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 mole fraction of DMF for $(\text{DB24C8.Y})^{+3}$ complex in MeOH-DMF binary systems at different temperatures is shown in Fig. 4.

Discussion

As is seen from Figs. 1 and 2, addition of DB24C8 to a solution of yttrium(III) cation in pure EtOH and THF-DMF

(mol% THF = 23.9) binary mixture at different temperatures shows a gradual increase in molar conductivity with an increase in the ligand concentration. This behaviour indicates that the $(\text{DB24C8.Y})^{+3}$ complex is more mobile than free solvated Y^{+3} cation. Similar behaviour was observed in all other solvent systems. The slope of the corresponding molar conductivity versus ligand/cation mole ratio plots changes at the point where the ligand to cation mole ratio is about one, which is an evidence for formation of a 1:1 [M:L] complex in solutions.

As is evident in Table 1, the stability constant of $(\text{DB24C8.Y})^{+3}$ complex increases with increasing the temperature in most of the solvent systems, which is an evidence for an endothermic complexation reaction between DB24C8 with Y^{+3} cation in solutions, but in the case of AN-DMF binary mixtures, the stability constant of this complex decreases with increasing the temperature, therefore, the complexation process between DB24C8 with Y^{+3} cation is exothermic in these binary solutions.

Comparison of the data given in Table 1 reveals that, the stability of $(\text{DB24C8.Y})^{+3}$ complex in various pure non-aqueous solvents decreases in the order: AN > EtOH > MeOH > DMF, which is consistent with the inverse order of their solvating abilities as expressed by the Gutmann donor number. In a solvent with a high solvating ability (high donor number), such as DMF (DN = 26.6), the complex formation tends to be weak, since the solvent solvates the cation strongly and competes with the ligand for the cation, but in solvents with lower donicity such as acetonitrile (DN = 14.1), ethanol (DN = 19.0), and methanol (DN = 20.0), the relatively poorer solvating ability of these solvents leads to an increase in the stability constant, therefore, there is actually an inverse relationship between the stability of the complex and the solvating ability of these organic solvents.

The stability of $(\text{DB24C8.Y})^{+3}$ complex in binary mixed solutions varies in the order: AN-DMF > EtOH-DMF > MeOH-DMF which can be attributed to the inherent solvating ability of the pure solvents which form the mixture. Since the donor ability of acetonitrile molecules is lower than ethanol and methanol molecules, therefore, the stability constant of the complex is higher in AN-DMF binary solutions compared to EtOH-DMF and MeOH-DMF binary solutions. It has been shown that the solvating ability of a solvent, as expressed by the Gutmann donicity scale [32], plays a fundamental role in complexation reactions [33].

As is seen from Fig. 4, the changes of the stability constant ($\log K_f$) of $(\text{DB24C8.Y})^{+3}$ complex versus the composition of AN-DMF binary system at various temperatures are not linear. Somewhat similar behaviour was observed in other binary solutions. This behaviour is probably due some kinds of solvent-solvent interactions

Table 1 Log K_f values of (DB24C8.Y)⁺³ complex in MeOH–DMF, EtOH–DMF, AN–DMF and THF–DMF binary mixtures at different temperatures

Medium	Log $K_f \pm SD^a$			
	15 °C	25 °C	35 °C	45 °C
<i>MeOH–DMF</i>				
Pure MeOH	2.82 ± 0.16	2.85 ± 0.06	2.91 ± 0.05	2.95 ± 0.06
85.0% MeOH–15.0% DMF ^b	c	c	c	c
65.4% MeOH–34.6% DMF	2.70 ± 0.08	2.79 ± 0.07	2.84 ± 0.08	2.90 ± 0.07
38.7% MeOH–61.3% DMF	2.78 ± 0.07	2.84 ± 0.05	2.90 ± 0.10	2.92 ± 0.11
Pure DMF	2.59 ± 0.06	2.79 ± 0.11	2.86 ± 0.06	2.90 ± 0.09
<i>EtOH–DMF</i>				
Pure EtOH	2.89 ± 0.05	2.95 ± 0.09	2.99 ± 0.10	2.95 ± 0.07
79.8% EtOH–20.2% DMF ^b	2.69 ± 0.10	2.73 ± 0.08	2.92 ± 0.11	c
56.8% EtOH–43.2% DMF	2.73 ± 0.06	2.83 ± 0.09	2.91 ± 0.06	c
30.5% EtOH–69.5% DMF	2.89 ± 0.07	2.92 ± 0.08	2.95 ± 0.05	2.99 ± 0.06
Pure DMF	2.59 ± 0.06	2.79 ± 0.11	2.86 ± 0.06	2.90 ± 0.09
<i>AN–DMF</i>				
Pure AN	3.07 ± 0.10	c	c	3.10 ± 0.10
81.6% AN–18.4% DMF ^b	2.95 ± 0.05	2.85 ± 0.11	2.75 ± 0.06	c
59.6% AN–40.4% DMF	2.93 ± 0.06	2.90 ± 0.11	2.87 ± 0.08	2.85 ± 0.07
33.0% AN–67.0% DMF	2.90 ± 0.17	2.79 ± 0.08	c	2.67 ± 0.08
Pure DMF	2.59 ± 0.06	2.79 ± 0.11	2.86 ± 0.06	2.90 ± 0.09
<i>THF–DMF</i>				
Pure THF	d	d	d	2.95 ± 0.07
73.9% THF–26.1% DMF ^b	d	d	d	d
48.5% THF–51.5% DMF	3.08 ± 0.19	c	c	c
23.9% THF–76.1% DMF	2.95 ± 0.13	3.11 ± 0.04	3.11 ± 0.06	3.02 ± 0.11
Pure DMF	2.59 ± 0.06	2.79 ± 0.11	2.86 ± 0.06	2.90 ± 0.09

^a SD = standard deviation

^b Composition of binary mixtures is expressed in mol% for each solvent system

^c With high uncertainty

^d The data cannot be fitted in equations

between these organic solvents, and hence 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. In addition, the heteroselective solvation of these species in these mixed solvents may be another reason for this kind of behaviour. The interactions between some binary mixed solvents have been studied [34]. For example, mixing of dimethylformamide with acetonitrile induces the mutual destruction of dipolar structures of these dipolar aprotic liquids and releasing the free dipoles [35]. As a result, strong dipolar interaction between acetonitrile and dimethylformamide molecules is expected.

The experimental values of standard enthalpy (ΔH°) and standard entropy (ΔS°) which are given in Table 2, show that in most cases, the (DB24C8.Y)⁺³ complex is enthalpy destabilized but entropy stabilized, therefore, the entropy of the complexation reaction is the principal

driving force for formation of this complex in most solvent systems, but in the case of acetonitrile–dimethylformamide binary mixtures, the values of standard enthalpy for complexation process are negative. Therefore, the (DB24C8.Y)⁺³ complex is stabilized from both enthalpy and entropy viewpoint in AN–DMF binary solutions.

The obtained results in this study, show that the enthalpy and entropy values for complexation reaction between DB24C8 with Y⁺³ cation vary with the nature and composition of the mixed solvents, but they do not vary monotonically with the solvent composition (see Table 2). This is due to variations in the extent of the contribution of such important parameters as solvation–desolvation of the species involved in the complexation reaction (i.e., Y⁺³ 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

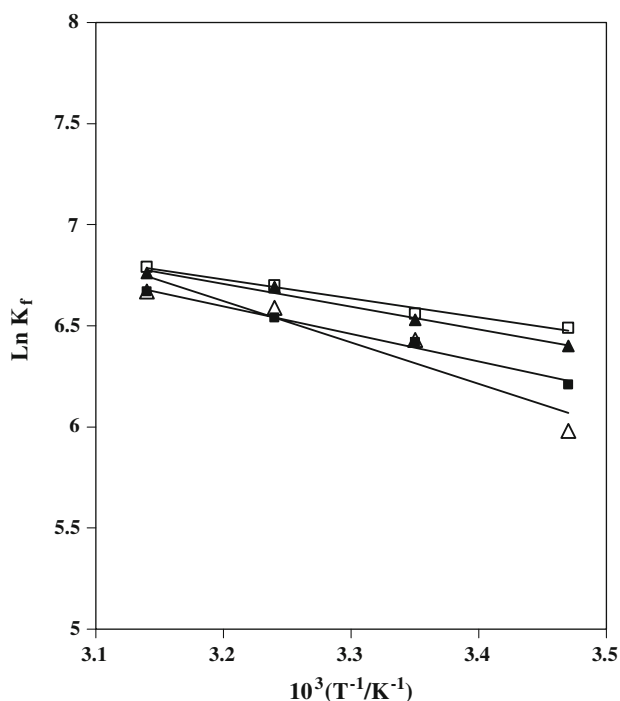


Fig. 3 van't Hoff plots for (DB24C8.Y)⁺³ complex in MeOH–DMF binary systems: (mol%MeOH: □ 100, ■ 65.4, ▲ 38.7, △ 0.0)

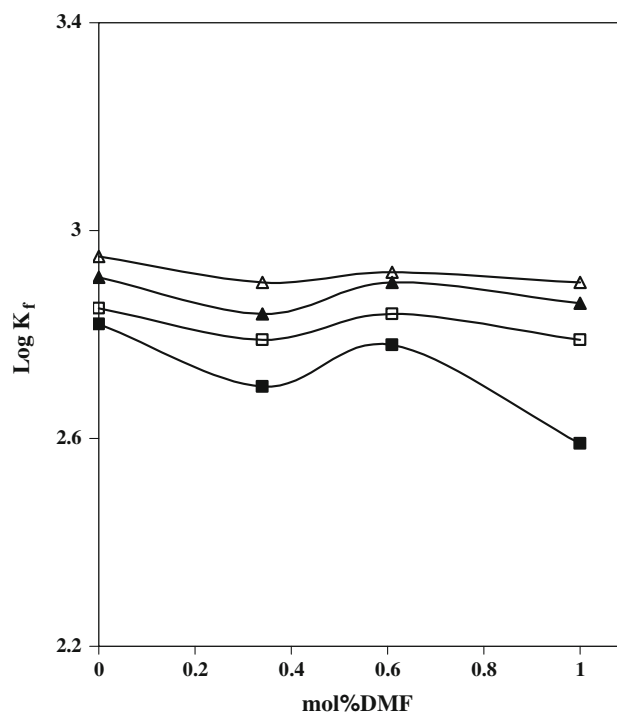


Fig. 4 Changes of the stability constant ($\log K_f$) of (DB24C8.Y)⁺³ complex with the composition of MeOH–DMF binary systems at different temperatures: (■ 15 °C, □ 25 °C, ▲ 35 °C, △ 45 °C)

Table 2 Thermodynamic parameters for (DB24C8.Y)⁺³ complex in MeOH–DMF, EtOH–DMF, AN–DMF and THF–DMF binary mixtures

Medium	$-\Delta G$ °C \pm SD ^a kJ/mol	ΔH °C \pm SD ^a kJ/mol	ΔS °C \pm SD ^a J/mol k
<i>MeOH–DMF</i>			
Pure MeOH	16.26 \pm 0.39	7.83 \pm 0.79	80.79 \pm 2.39
65.4% MeOH–34.6% DMF ^b	15.91 \pm 0.45	11.37 \pm 0.82	91.49 \pm 2.29
38.7% MeOH–61.3% DMF	16.18 \pm 0.34	7.60 \pm 2.50	79.75 \pm 8.30
Pure DMF	15.93 \pm 0.65	17.06 \pm 3.85	110.64 \pm 12.72
<i>EtOH–DMF</i>			
Pure EtOH	16.85 \pm 0.55	c	69.15 \pm 8.59
79.8% EtOH–20.2% DMF ^b	15.56 \pm 0.51	18.96 \pm 7.78	c
56.8% EtOH–43.2% DMF	16.13 \pm 0.57	15.19 \pm 0.44	105.04 \pm 1.21
30.5% EtOH–69.5% DMF	16.65 \pm 0.51	5.80 \pm 0.20	75.295 \pm 1.57
Pure DMF	15.93 \pm 0.65	17.06 \pm 3.85	110.64 \pm 12.72
<i>AN–DMF</i>			
81.6% AN–18.4% DMF ^b	16.26 \pm 0.64	−16.98 \pm 0.21	c
59.6% AN–40.4% DMF	16.55 \pm 0.68	−4.842 \pm 0.14	39.26 \pm 2.23
33.0% AN–67.0% DMF	15.93 \pm 0.51	−12.33 \pm 1.65	17.02 \pm 5.26
Pure DMF	15.93 \pm 0.65	17.06 \pm 3.85	110.64 \pm 12.72
<i>THF–DMF</i>			
23.9% THF–76.1% DMF ^b	17.77 \pm 0.26	c	c
Pure DMF	15.93 \pm 0.65	17.06 \pm 3.85	110.64 \pm 12.72

^a SD = standard deviation

^b Composition of binary mixtures is expressed in mol% for each solvent system

^c With high uncertainty

and the solvent composition of binary mixtures. Somewhat similar thermodynamic behaviour has been observed for complexation of DB24C8 with alkaline earth metal cations in AN–DMF binary mixtures [36].

Acknowledgements We gratefully acknowledge the support of this work by Islamic Azad University, Mashhad Branch, Iran.

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