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Solvent Influence upon Complex Formation between Dibenzo-18-crown-6 with the Y^{3+} Metal Cation in Pure and Binary Mixed Organic Solvents

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ABSTRACT: The complexation reaction between the Y^{3+} cation with the macrocyclic ligand dibenzo-18-crown-6 (DB18C6) was studied in acetonitrile−dimethylformamide (AN-DMF), acetonitrile−ethanol (AN-EtOH), acetonitrile−propanol (AN-PrOH), and dimethylformamide−methanol (DMF-MeOH) binary mixtures at different temperatures using a conductometric method. In all cases, DB18C6 forms a 1:1 complex with the Y^{3+} cation. The stability order of $(DB18C6.Y)^{3+}$ complex changes with the composition of the mixed solvents. For example, the stability constant of the complex in the binary mixed solutions with 75 % AN at 25 °C varies in order: AN-EtOH > AN-PrOH ∼ AN-DMF, but in the case of 50 % AN was found to be: AN-DMF > AN-PrOH ∼ AN-EtOH. A nonlinear behavior was observed between the log K_f of the complex versus the composition of the mixed solvents, which may be related to solvent−solvent interactions which result in changing the solvation of the metal cation, ligand, and even the resulting complex in the binary mixed solvents. The values of the standard thermodynamic parameters ($\Delta S°_c$, $\Delta H°_c$) for formation of the $(DB18C6.Y)^{3+}$ complex were obtained from the temperature dependence of the formation constant of the complex using van't Hoff plots. The obtained results show that the complexation reaction between DB18C6 with this metal cation in most cases is entropy-destabilized, but from the enthalpy viewpoint, depending on the nature of the medium, the complexation process is enthalpy-stabilized or -destabilized.

INTRODUCTION

Thermodynamic studies on the complexation of crown ethers with metal cations have been performed to elucidate the nature of the cation-binding behavior from the thermodynamic point of view and also to gain insight into the factors governing cation−ligand complexation phenomena.[1−5] The ability of the solvent molecules to compete with the donor atoms of the ligand toward the cation is one of critical factors that can thermodynamically influence the complexation process.[6]

To achieve appropriate solvent properties, mixtures of two solvents are often used. The physiochemical properties of mixed solvents are interesting both from theoretical and practical points 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 their mixtures can be different from those of neat media.[7] The deviations from ideal behavior are indicative of the extent of preferential solvation and the existence of specific solvent−solute and solvent−solvent interactions.[8,9]

We are especially interested in the thermodynamics of complexation and selectivity profiles of crown ethers toward the various metal cations.[10,11] Little attention has been paid to rare earth complexation; hence, information about the coordination behavior of crown ethers toward these metal cations is relatively scarce. Furtheremore, such studies on cation−crown ether complexation have been carried out in pure solvents, and information in mixed organic solvents is very sparse.

In this paper, we studied the complexation process between DB18C6 (Figure 1) and the Y^{3+} cation in acetonitrile−dimethylformamide (AN-DMF), acetonitrile−ethanol (AN-EtOH), acetonitrile−propanol (AN-PrOH), and dimethylformamide−methanol (DMF-MeOH) binary mixtures at different temperatures using the conductometric method.

EXPERIMENTAL SECTION

Dibenzo-18-crown-6 (DB18C6) (Merck) and yttrium nitrate ($Y(NO_3)_3 \cdot 6H_2O$) (RIEDEL) were used without further purification. The solvents: acetonitrile, dimethylformamide, methanol, ethanol, and propanol, 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 ($1 \cdot 10^{-4}$ M) was placed in a titration cell, and the conductance of the solution was measured. Then a step-by-step increase in the crown ether concentration was performed by a rapid transfer from a crown ether solution in the same solvent ($2 \cdot 10^{-3}$ M) to the titration cell, using a microburette, and the conductance of the resulting 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 water bath (Julabo model F12) thermostatted at 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 0.84 cm^{-1} was used throughout the studies.

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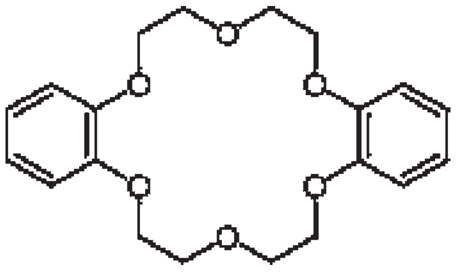

Figure 1. Structure of dibenzo-18-crown-6.

Table 1. Log K_f Values of the $(DB18C6.Y)^{3+}$ Complex in Binary Mixed Nonaqueous Solvents at Different Temperatures

	log K_f ± SD[a]			
medium	15 °C	25 °C	35 °C	45 °C
		AN-DMF		
pure AN	2.8 ± 0.1	2.5 ± 0.3	2.8 ± 0.1	2.5 ± 0.3
75 % AN-25 % DMF	2.7 ± 0.1	2.5 ± 0. 2	2.7 ± 0.1	2.8 ± 0.1
50 % AN-50 % DMF	2.5 ± 0.1	2.8 ± 0.1	2.7 ± 0.1	2.7 ± 0.1
25 % AN-75 % DMF	2.4 ± 0.2	2.5 ± 0.1	2.7 ± 0.1	2.8 ± 0.1
pure DMF	2.5 ± 0.2	2.5 ± 0.2	2.7 ± 0.1	2.6 ± 0.2
		AN-EtOH		
pure AN	2.8 ± 0.1	2.5 ± 0.3	2.8 ± 0.1	2.5 ± 0.3
75 % AN-25 % EtOH	3.0 ± 0.1	2.7 ± 0.2	2.7 ± 0.2	3.2 ± 0.1
50 % AN-50 % EtOH	2.8 ± 0.1	2.6 ± 0.2	2.8 ± 0.1	2.5 ± 0.2
25 % AN-75 % EtOH	3.2 ± 0.1	2.6 ± 0.2	2.5 ± 0.2	2.5 ± 0.2
10 % AN-90 % EtOH	3.0 ± 0.1	2.5 ± 0.2	2.6 ± 0.2	2.6 ± 0.2
pure EtOH	[b]	[b]	[b]	[b]
		AN-PrOH		
pure AN	2.8 ± 0.1	2.5 ± 0.3	2.7 ± 0.1	2.5 ± 0.3
75 % AN-25 % PrOH	2.8 ± 0.1	2.5 ± 0.2	2.8 ± 0.1	2.5 ± 0.2
50 % AN-50 % PrOH	2.6 ± 0.2	2.6 ± 0.2	2.5 ± 0.2	2.8 ± 0.2
25 % AN-75 % PrOH	2.5 ± 0.2	2.5 ± 0.2	2.7 ± 0.2	2.5 ± 0.2
20 % AN-90 % PrOH	2.8 ± 0.1	2.7 ± 0.1	2.5 ± 0.2	2.6 ± 0.2
pure PrOH	[b]	[b]	[b]	[b]
		DMF-MeOH		
pure DMF	2.5 ± 0.2	2.5 ± 0.2	2.7 ± 0.1	2.6 ± 0.2
75 % DMF-25 % MeOH	2.5 ± 0.2	2.7 ± 0.1	2.5 ± 0.2	2.5 ± 0.2
50 % DMF-50 % MeOH	2.7 ± 0.2	2.5 ± 0.2	2.5 ± 0.2	2.5 ± 0.2
25 % DMF-75 % MeOH	2.7 ± 0.1	2.9 ± 0.1	2.7 ± 0.2	2.8 ± 0.2
10 % DMF-90 % MeOH	2.5 ± 0.2	2.8 ± 0.1	3.3 ± 0.2	2.7 ± 0.2
pure MeOH	[b]	[b]	[b]	[b]

[a] SD = standard deviation. [b] The ligand is not dissolved.

DATA ANALYSIS PROGRAM

The 1:1 complexation of a metal cation, M^{n+}, with a crown ether (L) is represented by the following equilibrium:

$$M^{n+} + L \rightleftarrows ML^{n+} \qquad (1)$$

The corresponding equilibrium constant, K_f, is given by:

$$K_f = [ML^{n+}]f_{ML}{}^{n+}/[M^{n+}]f_{M}{}^{n+} \cdot [L]f_L \qquad (2)$$

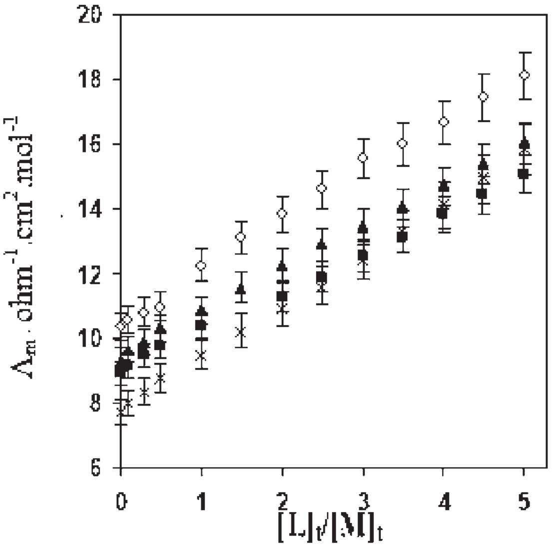

Figure 2. Molar conductance—mole ratio plots for the $(DB18C6.Y)^{3+}$ complex in pure AN at different temperatures (◇, 15 °C; ■, 25 °C; ▲, 35 °C; ×, 45 °C).

where $[ML^{n+}]$, $[M^{n+}]$, and [L] represent the equilibrium molar concentration of the complex, free cation, and free ligand, respectively, and f represents the activity coefficient of the species indicated.

Under the highly dilute conditions used, in this investigation, the activity coefficient of the uncharged ligand, f_L can be reasonably assumed as unity.[12,13] Using the Debye–Huckel limiting law,[14] we can neglect the $f_M{}^+$ and $f_{ML}{}^{n+}$ values in eq 2. Thus the complex formation constant in terms of the molar conductance can be expressed as:

$$\begin{aligned} K_f &= [ML^{n+}]/[M^{n+}][L] \\ &= (\Lambda_M - \Lambda_{obs})/(\Lambda_{obs} - \Lambda_{ML}) \end{aligned} \qquad (3)$$

where

$$C_L = C_M(\Lambda_M - \Lambda_{obs})/(\Lambda_M - \Lambda_{ML}) \qquad (4)$$

Here Λ_M is the molar conductance of the metal ion before addition of the ligand, Λ_{ML} is the molar conductance of the complexed ion, Λ_{obs} is the molar conductance of the solution during the titration, C_L is the analytical concentration of the L added, and C_M is the analytical concentration of the metal ion. The complex formation constant, K_f, and the molar conductanc of the complex, Λ_{ML}, were obtained by computer fitting of eqs 3 and 4 to the molar conductance as a function of the ligand/metal cation mole ratio data, using a nonlinear least-squares program GENPLOT.[15] All calculated stability constants are summarized in Table 1.

The details of the calculation of the stability constants of the metal ion complexes by the conductometric method have been described elsewhere.[16]

RESULTS AND DISCUSSION

The complex formation between DB18C6 and the Y^{3+} cation in AN-DMF, AN-EtOH, AN-PrOH, and DMF-MeOH binary mixtures was investigated by molar conductance changes upon addition of the ligand to the Y^{3+} cation solution at (15, 25, 35, and 45) °C. Some of the resulting molar conductance (Λ_m) versus

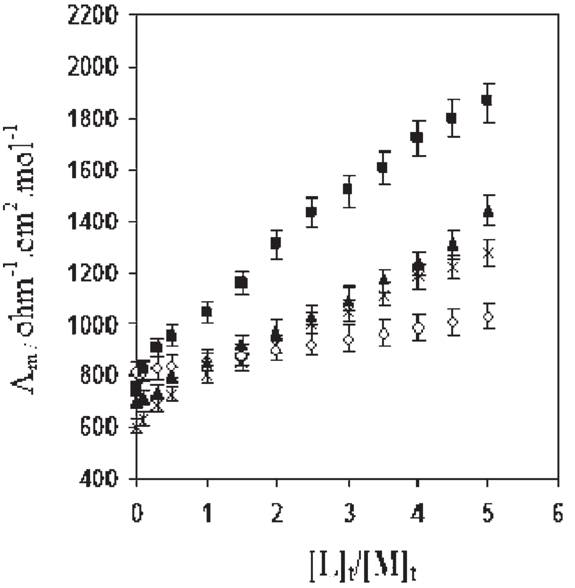

Figure 3. Molar conductance—mole ratio plots for the $(DB18C6.Y)^{3+}$ complex in AN-DMF binary solutions (%AN = 75) at different temperatures (◇, 15 °C; ■, 25 °C; ▲, 35 °C; ×, 45 °C).

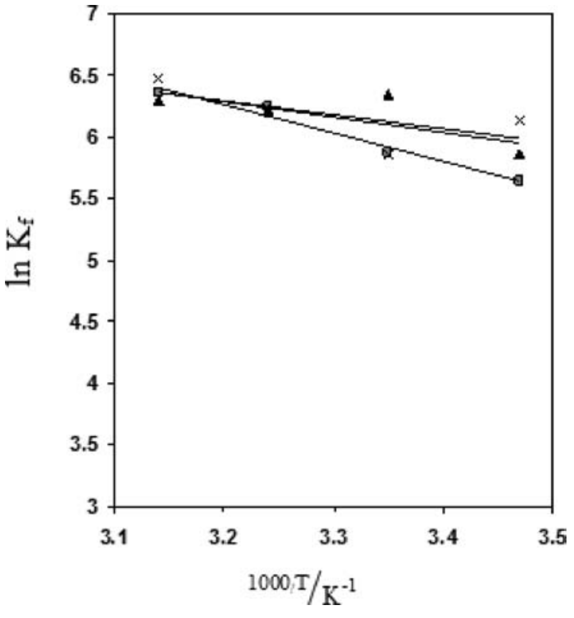

Figure 4. van't Hoff plots for the $(DB18C6.Y)^{3+}$ complex in AN-DMF binary systems (% AN: ■ = 50.0, ▲ = 76.0, × = 100).

macrocycle to Y^{3+} molar ratio $([L]_t/[M]^t)$ plots are shown in Figures 2 and 3. As is evident from these figures, the addition of DB18C6 to a solution of the Y^{3+} cation in pure AN and in AN-DMF (% AN = 75) binary mixture at different temperatures results in an increase in molar conductivity with an increase in the ligand concentration which indicates that the $(DB18C6.Y)^{3+}$ complex is more mobile than the free solvated Y^{3+} cation. A similar behavior was observed in all other binary mixed nonaqueous solvents. 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 1, which is evidence for the formation of a relatively stable 1:1 complex.

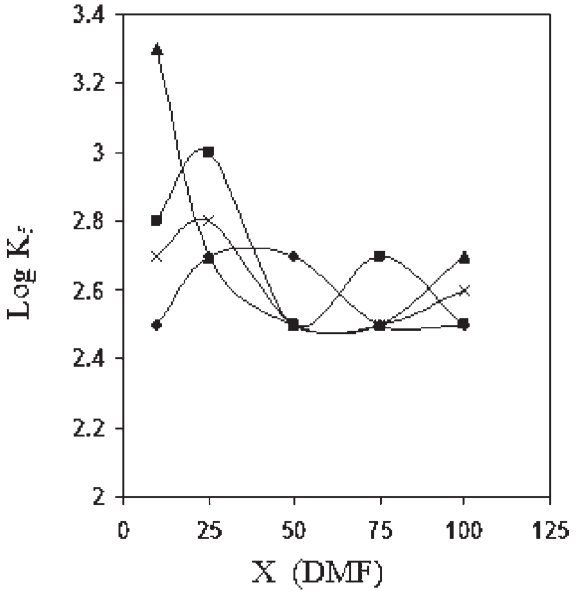

Figure 5. Changes of stability constant (log K_f) of the $(DB18C6.Y)^{3+}$ complex with the mole fraction of DMF in AN-DMF binary solusion at different temperatures (◇ = 15 °C, ■ = 25 °C, ▲ = 35 °C, × = 45 °C).

The log K_f data in Table 1 show that the stability constant of $(DB18C6.Y)^{3+}$ complex is larger in acetonitrile than dimethylformamide. The ligand is not dissolved in pure MeOH, EtOH, and PrOH. The solvation of the ligand and the metal cation is influenced by the donor ability and dielectric constant of the solvent. It is known that the donor ability and dielectric constant of the solvent play an important role in complexation reactions.[17,18] 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 metal cation, but in solvents with lower donicity such as acetonitrile (DN = 14.1), the relatively poorer solvating ability of this solvent 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 constant of the $(DB18C6.Y)^{3+}$ complex in the binary mixed solvent solutions (% AN = 75) at 25 °C varies in the order: AN-EtOH > AN-PrOH ~ AN-DMF, but in the case of 50 % AN at the same temperature it changes to: AN-DMF > AN-PrOH ~ AN-EtOH. The results obtained in this study reveal that the stability constant of cation—macrocyclic complexes may change with the composition of the binary mixed solvent solutions. The changes of log K_f of $(DB18C6.Y)^{3+}$ complex versus the mole fraction of DMF in the DMF-MeOH binary system at different temperatures are shown in Figure 4. As shown in this figure, the change of the stability constant (log K_f) of the $(DB18C6.Y)^{3+}$ complex with the composition of DMF-MeOH binary solutions is not linear. Similar behavior was also observed in other binary solutions. This behavior may be due to preferential solvation of the cation, ligand, the resulting complex, and even the counter ion in the binary mixed solvents. The interactions between the solvent molecules may also be effective in this non-monotic behavior. In addition, the heteroselective 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 the complexation process.[19]

Table 2. Thermodynamic Parameters for the $(\mathrm{DB18C6.Y})^{3+}$ Complex in Binary Mixed Solvents

	$-\Delta G^\circ_{c} \pm \mathrm{SD}^{a}$	$\Delta H^\circ_{c} \pm \mathrm{SD}^{a}$	$\Delta S^\circ_{c} \pm \mathrm{SD}^{a}$
medium	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$
	AN-DMF		
pure AN	14 ± 1	^{b}	^{b}
75 % AN-25 % DMF	14 ± 1	^{b}	-75 ± 14
50 % AN-50 % DMF	15.3 ± 0.8	10 ± 3	-86 ± 12
25 % AN-75 % DMF	14.6 ± 0.8	11 ± 3	-84 ± 13
pure DMF	14 ± 1	1.9 ± 0.6	-68 ± 24
	AN-EtOH		
pure AN	14 ± 1.50	^{b}	^{b}
75 % AN-25 % EtOH	15.7 ± 0.9	-30 ± 13	^{b}
50 % AN-50 % EtOH	14.5 ± 0.9	^{b}	^{b}
25 % AN-75 % EtOH	15 ± 1	^{b}	^{b}
10 % AN-90 % EtOH	14 ± 1	-27 ± 9	^{b}
pure EtOH		^{c}	^{c}
	AN-PrOH		
pure AN	14 ± 1	^{b}	^{b}
75 % AN-25 % PrOH	14.47 ± 1	^{b}	^{b}
50 % AN-50 % PrOH	14 ± 1	^{b}	-85 ± 25
25 % AN-75 % PrOH	14 ± 1	^{b}	^{b}
20 % AN-90 % PrOH	15.5 ± 0.8	-14 ± 5	^{b}
pure PrOH	^{c}	^{c}	^{c}
	DMF-MeOH		
pure DMF	14 ± 1	^{b}	^{b}
75 % DMF-25 % MeOH	15.4 ± 0.8	4.2 ± 0.1	^{b}
50 % DMF-50 % MeOH	14 ± 1	^{c}	^{b}
25 % DMF-75 % MeOH	16.8 ± 0.6	-6.1 ± 0.1	^{b}
10 % DMF-90 % MeOH	16.0 ± 0.4	-2 ± 1	65 ± 24
pure MeOH	^{c}	^{c}	^{c}

[a] SD = standard deviation. [b] With high uncertainty. [c] The ligand is not dissolved.

Assuming that the activity coefficients of the cation and the complex have the same values, K_f, is a thermodynamic equilibrium constant on the molar concentration scale, related to the Gibbs energy of the complexation reaction, ΔG°_c. The van't Hoff plots of $\ln K_f$ versus $1/T$ in all cases were linear. The changes in the standard enthalpy (ΔH°_c) for the complexation of DB18C6 with the 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 $(\Delta G^\circ_{c,298.15} = \Delta H^\circ_c - 298.15\Delta S^\circ_c)$. A typical example of these plots for the AN-DMF binary system is shown in Figure 5. It is evident from this figure that the slope of the plots is negative; therefore, the ΔH°_c value is positive which is evidence for an endothermic reaction between DB18C6 and the Y^{3+} cation in these solvent systems. The experimental values of the standard enthalpy (ΔH°_c) and standard entropy (ΔS°_c) are given in Table 2 and show that in most cases, the $(\mathrm{DB18C6.Y})^{3+}$ complex is enthalpy-stabilized, but entropy-destabilized. Therefore, the enthalpy of the complexation reaction is the principal driving force for formation of the $(\mathrm{DB18C6.Y})^{3+}$ complex in solutions.

As expected, the values of ΔH°_c and ΔS°_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. As is evident from Table 2, the standard thermodynamic parameters $(\Delta H^\circ_c$ and $\Delta S^\circ_c)$ change nonmonotonically with the composition of the mixed solvents. Since there are many parameters which contribute to changes of enthalpy and entropy of the complextion reaction, we should not expect to observe a monotonic behavior between these thermodynamic quantities and the solvent composition of these binary solutions.

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