A Conductometric Study of Complexation Reactions Between Dibenzo-18-Crown-6 (DB18C6) with Cu^{2+}, Zn^{2+}, Tl^+ and Cd^{2+} Metal Cations in Dimethylsulfoxide–Ethylacetate Binary Mixtures

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Abstract

The complex formation between Cu^{2+}, Zn^{2+}, Tl^+ and Cd^{2+} metal cations with macrocyclic ligand, dibenzo-18-crown-6 (DB18C6) was studied in dimethylsulfoxide (DMSO)–ethylacetate (EtOAc) binary systems at different temperatures using conductometric method. In all cases, DB18C6 forms 1:1 complexes with these metal cations. The stability constants of the complexes were obtained from fitting of molar conductivity curves using a computer program, Genplot. The non-linear behaviour which was observed for variations of log K_f of the complexes *versus* the composition of the mixed solvent was discussed in terms of changing the chemical and physical properties of the constituent solvents when they mix with one another and, therefore, changing the solvation capacities of the metal cations, crown ether molecules and even the resulting complexes with changing the mixed solvent composition. The results show that the selectivity order of DB18C6 for the metal cations in pure ethylacetate and pure dimethylsulfoxide is: $Tl^+ > Cu^{2+} > Zn^{2+} > Cd^{2+}$ but the selectivity order is changed with the composition of the mixed solvents. The values of enthalpy changes ($\Delta H°_C$) for complexation reactions were obtained from the slope of the van't Hoff plots and the changes in standard enthalpy ($\Delta S°_C$) were calculated from the relationship: $\Delta G°_{C,298.15} = \Delta H°_C - 298.15\,\Delta S°_C$. The obtained results show that in most cases, the complexes are enthalpy stabilized, but entropy destabilized and the values of $\Delta H°_C$ and $\Delta S°_C$ depend strongly on the nature of the medium.

Introduction

Crown ethers are important class of both inherent and practical interest, since they were initially described by Pedersen in 1967 [1, 2], they have been heavily studied in solutions [3–5] and more recently they have also been examined in the gas phase [6].

Among the earliest- recognized remarkable properties of these macrocyclic ligands is their ability to selectivity bind metal cations in solutions. The crown compounds are of practical interest for a number of reasons, they have found applications in such diverse areas as selective transport of metal cations [7], separation of metal cations [8], phase transfer catalysis [9] and stabilization of protonation sites in the electrospary ionization mass spectrometry of peptides [10, 11]. Crown ethers are often cited as one of the key components in some of the most promising means of isolating radioactive components of nuclear waste [12, 13].

Dibenzo-18-Crown-6 was one of the first crown ethers described by Pedersen [1]. Its aromatic substituents make it less soluble in a aqueous media, but increase its solubility in non- polar solvents. Because of the vital role of heavy metal cations in biological systems and also in industrial, the study of the complexes of these heavy metal cations with crown compounds is important.

In order to achieve appropriate solvent properties, we often use mixtures of two or more solvents (mixed solvents), although mixtures of water and organic solvents are most frequently used, mixtures of two organic solvents are also used in many applications such as separations, electrochemistry and organic synthesis. Since the data about complexation process of crown ethers in mixed non-aqueous solvents, especially in dipolar aprotic solvents is very sparse, therefore, we used DMSO and EtOAc for this investigation. In addition, the ligand and the metal salts are soluble in these solvent systems. Mixed solvents play important roles in modern electrochemical technologies [14, 15].

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Many of the methods for measuring the stability constants of crown ether complexes in mixed solvents include potentiometric [16], calorimetric [17], NMR spectrometry [18], competitive potentiometry and polarography [19–21] and condutometry [22, 23].

In the present paper, we report a conductometric study of complexation of Cu^{2+}, Zn^{2+}, Tl^+ and Cd^{2+} cations by DB18C6 in dimethylsulfoxide–ethylacetate binary systems at different temperatures.

Material and experimental procedures

DB18C6 (Fluka), cupper nitrate, zinc nitrate, thalium nitrate and cadmium nitrate (all from Merck) were used without further purification. Dimethylsulfoxide and ethylacetate (both from Merck) were used with the highest purity.

The experimental procedure to obtain the formation constants of complexes is as follows: a solution of metal salt (5×10^{-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 crown ether (5×10^{-3} M) to the titration cell using a microburette and the conductance of the solution in the cell was measured after each transfer at the desired temperature.
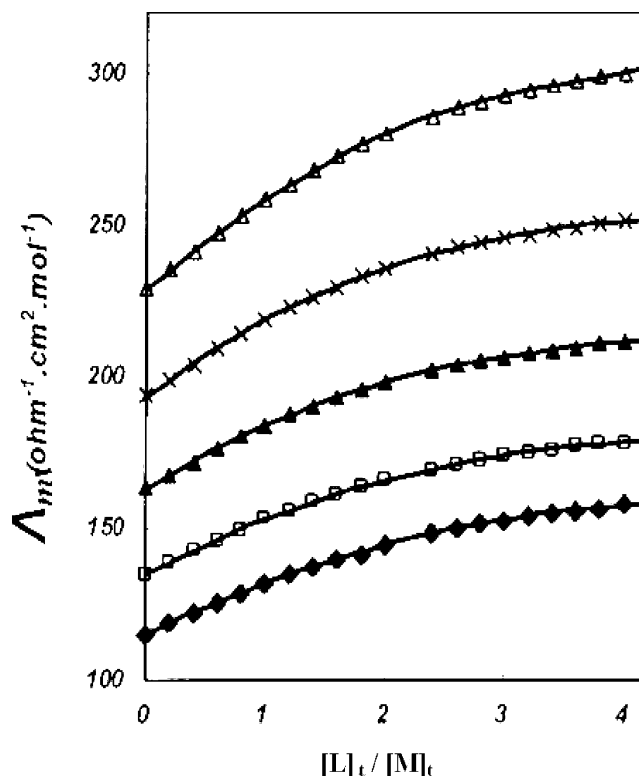

Figure 1. Molar conductance- mole ratio plots for (DB18C6–Cu^{2+}) complex in pure DMSO at 15 °C (◆), 25 °C (□), 35 °C (▲), 45 °C (×) and 55 °C (Δ).

Table 1. Log K_f values of (DB18C6–Cu^{2+}), (DB18C6–Cd^{2+}), (DB18C6–Tl^+) and (DB18C6–Zn^{2+}) complexes in DMSO–EtOAc binary mixtures at different temperatures

Medium	log K_f ± SD[a]				
	15 °C	25 °C	35 °C	45 °C	55 °C
(DB18C6–Cu^{2+})					
Pure DMSO	2.93 ± 0.03	3.00 ± 0.03	3.06 ± 0.02	3.08 ± 0.03	3.03 ± 0.03
25%EtOAc–75%DMSO[b]	2.67 ± 0.02	2.78 ± 0.02	2.85 ± 0.02	2.86 ± 0.02	2.92 ± 0.02
50%EtOAc–50%DMSO	2.63 ± 0.02	2.66 ± 0.02	2.57 ± 0.02	2.45 ± 0.03	2.57 ± 0.03
75%EtOAc–25%DMSO	2.68 ± 0.02	2.83 ± 0.03	2.85 ± 0.02	2.84 ± 0.01	2.85 ± 0.02
Pure EtOAc	3.6 ± 0.1	3.3 ± 0.1	3.3 ± 0.2	3.6 ± 0.2	3.6 ± 0.2
(DB18C6–Cd^{2+})					
Pure DMSO	2.99 ± 0.02	2.92 ± 0.01	2.92 ± 0.01	2.93 ± 0.01	2.95 ± 0.01
25%EtOAc–75%DMSO[b]	2.86 ± 0.03	2.90 ± 0.02	2.88 ± 0.02	2.87 ± 0.02	2.71 ± 0.03
50%EtOAc–50%DMSO	2.82 ± 0.03	3.07 ± 0.02	3.00 ± 0.02	2.91 ± 0.02	2.73 ± 0.02
75%EtOAc–25%DMSO	2.75 ± 0.01	2.72 ± 0.03	2.75 ± 0.03	2.63 ± 0.02	2.58 ± 0.02
Pure EtOAc	3.2 ± 0.1	2.8 ± 0.1	3.0 ± 0.1	3.0 ± 0.1	2.77 ± 0.09
(DB18C6–Tl^+)					
Pure DMSO	3.17 ± 0.02	3.17 ± 0.01	3.21 ± 0.02	3.11 ± 0.02	3.05 ± 0.02
25%EtOAc–75%DMSO[b]	3.15 ± 0.03	3.34 ± 0.05	3.11 ± 0.02	3.10 ± 0.04	2.97 ± 0.02
50%EtOAc–50%DMSO	3.12 ± 0.02	3.19 ± 0.03	2.81 ± 0.02	2.71 ± 0.02	2.78 ± 0.01
75%EtOAc–25%DMSO	2.51 ± 0.03	2.57 ± 0.03	2.58 ± 0.03	2.56 ± 0.03	2.55 ± 0.02
Pure EtOAc	3.7 ± 0.2	3.5 ± 0.1	3.5 ± 0.1	3.5 ± 0.1	3.2 ± 0.2
(DB18C6–Zn^{2+})					
Pure DMSO	3.24 ± 0.02	2.94 ± 0.04	3.00 ± 0.01	3.03 ± 0.04	3.10 ± 0.03
25%EtOAc–75%DMSO[b]	3.09 ± 0.01	3.11 ± 0.01	3.17 ± 0.01	3.24 ± 0.01	3.24 ± 0.01
50%EtOAc–50%DMSO	2.96 ± 0.02	3.04 ± 0.01	3.03 ± 0.01	2.87 ± 0.01	2.87 ± 0.01
75%EtOAc–25%DMSO	2.90 ± 0.01	2.77 ± 0.01	2.85 ± 0.01	2.80 ± 0.01	2.58 ± 0.01
Pure EtOAc	3.2 ± 0.1	3.2 ± 0.1	2.9 ± 0.1	2.84 ± 0.08	2.83 ± 0.09

[a]SD = Standard deviation.
[b]The composition of the mixed solvents is expressed in mol% of each solvent.

Table 2. Thermodynamic parameters for (DB18C6–Cu^{2+}), (DB18C6–Cd^{2+}), (DB18C6–Tl^{+}) and (DB18C6–Zn^{2+}) complexes in DMSO-EtOAc binary mixtures at 25 °C

Medium	Log K_f ± SD[a] (25 °C)	$\Delta G°_C$ ± SD[a] kJ mol^{-1}	$\Delta H°_C$ ± SD[a] kJ mol^{-1}	$\Delta S°_C$ ± SD[a] J mol^{-1} K^{-1}
(DB18C6–Cu^{2+})				
Pure DMSO	3.00 ± 0.03	17.13 ± 0.07	8.8 ± 0.05	87 ± 2
25%EtOAc–75%DMSO[b]	2.78 ± 0.02	15.85 ± 0.08	10.4 ± 0.2	88.0 ± 0.6
50%EtOAc–50%DMSO	2.66 ± 0.02	15.2 ± 0.1	−6.2 ± 0.5	30 ± 2
75%EtOAc–25%DMSO	2.83 ± 0.03	16.1 ± 0.1	6.8 ± 0.4	76 ± 1
Pure EtOAc	3.3 ± 0.1	18.9 ± 0.1	−2.19 ± 0.06	61.6 ± 0.2
(DB18C6–Cd^{2+})				
Pure DMSO	2.92 ± 0.01	16.68 ± 0.03	1.7 ± 0.1	61.6 ± 0.3
25%EtOAc–75%DMSO[b]	2.90 ± 0.02	16.55 ± 0.06	−10.4 ± 0.5	21 ± 2
50%EtOAc–50%DMSO	3.07 ± 0.02	17.52 ± 0.04	−20 ± 1	−8 ± 3
75%EtOAc–25%DMSO	2.72 ± 0.02	15.52 ± 0.09	−7.66 ± 0.07	26.4 ± 0.2
Pure EtOAc	2.8 ± 0.1	16.1 ± 0.4	−2.0.1 ± 0.5	−13 ± 1
(DB18C6–Tl^{+})				
Pure DMSO	3.17 ± 0.01	18.07 ± 0.02	−5.1 ± 0.3	44 ± 1
25%EtOAc–75%DMSO[b]	3.34 ± 0.05	19.02 ± 0.06	−20 ± 1	−5 ± 3
50%EtOAc–50%DMSO	3.19 ± 0.03	18.17 ± 0.05	−21 ± 1	−10 ± 3
75%EtOAc–25%DMSO	2.52 ± 0.03	14.4 ± 0.2	1.9 ± 0.2	54.7 ± 0.6
Pure EtOAc	3.4 ± 0.2	19.6 ± 0.2	−2.1.1 ± 0.2	−5.4 ± 0.3
(DB18C6–Zn^{2+})				
Pure DMSO	2.94 ± 0.04	16.8 ± 0.1	9.5 ± 0.6	88 ± 2
25%EtOAc–75%DMSO[b]	3.11 ± 0.05	17.72 ± 0.02	7.7 ± 0.2	85.3 ± 0.7
50%EtOAc–50%DMSO	3.04 ± 0.03	17.32 ± 0.02	−12.1 ± 0.7	18 ± 2
75%EtOAc–25%DMSO	2.72 ± 0.01	15.82 ± 0.04	−3.2 ± 0.2	42.3 ± 0.7
Pure EtOAc	3.2 ± 0.1	18.3 ± 0.2	−2.1.3 ± 0.5	−10 ± 2

[a]SD = Standard deviation.
[b]The composition of the mixed solvents is expressed in mol% of each solvent.

The conductance measurements were performed on a digital AMEL conductivity apparatus, model 60, in a water-bath thermostated at a constant temperature maintained within ± 0.03 °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 0.74 cm^{-1} was used throughout the studies.
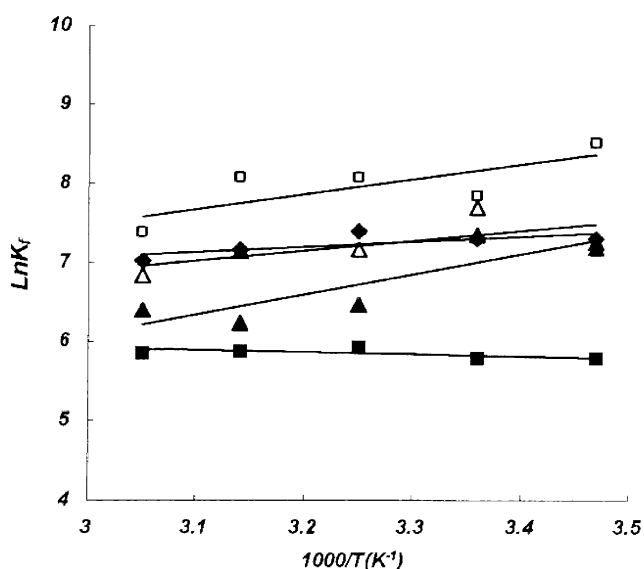

Figure 2. Van't Hoff plots for (DB18C6–Tl^{+}) complex in DMSO–EtOAc binary systems: pure DMSO (■), mol% EtOAc = 25 (▲), mol% EtOAc = 50 (△), mol% EtOAc = 75 (♦) and pure EtOAc (□).
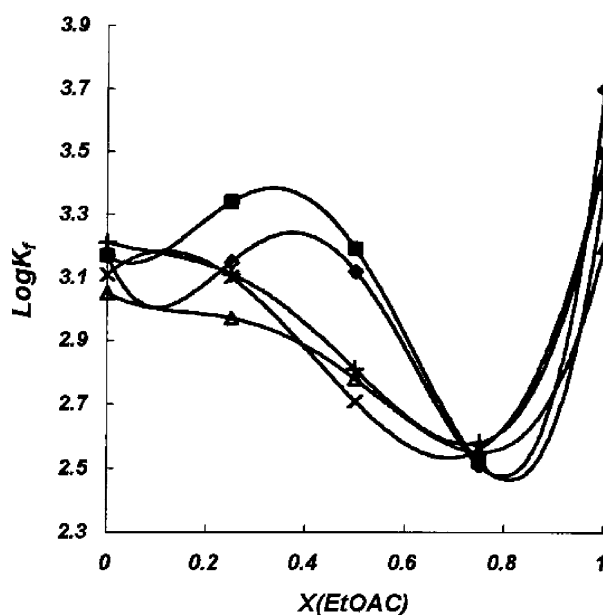

Figure 3. Variation of stability constant (log K_f) of (DB18C6–Tl^{+}) complex with the composition of the DMSO–EtOAc binary systems at different temperatures: 15 °C (◇), 25 °C (■), 35 °C (+), 45 °C (×) and 55 °C (△).

Results and discussion

The variation of molar conductivity (Λ_m) with $[L]_t/[M]_t$ for complexation of DB18C6 with Cu^{2+}, Zn^{2+}, Tl^+ and Cd^{2+} cations in DMSO-EtOAc binary systems were studied at different temperatures. $[L]_t$ is the total concentration of DB18C6 and $[M]_t$ is the total concentration of each metal cation in solution. As an example, the variation of Λ_m *versus* $[L]_t/[M]_t$ for DB18C6-Cu^{2+} in neat DMSO is shown in Figure 1. It is obvious, from this figure, addition of DB18C6 to cupper ion solution at different temperatures results in an increase in molar conductivity. This indicates that (DB18C6–Cu^{2+}) complex is more mobile than free solvated Cu^{2+} cation. Similar behaviour was observed for Zn^{2+}, Tl^+ and Cd^{2+} cations in various solvent systems.

The stability constants of DB18C6 crown ether complexes at each temperature were calculated from variation of molar conductance as a function of $[L]_t/[M]_t$ molar ratio using a Genplot computer program [24]. The details of calculation of the stability constants of complexes by conductometric method have been described in reference [25]. The stability constants (log K_f) for DB18C6–M^{n+} (M^{n+} = Cu^{2+}, Zn^{2+}, Tl^+ and Cd^{2+}) complexes in various solvent system at various temperatures are listed in Table 1.

The variation of log K_f *versus* the mole fraction of EtOAc for DB18C6–Tl^+ complex in DMSO–EtOAc binary system at different temperatures is shown in Figure 2. The non-linear behaviour which is observed for the stability constants (log K_f) of DB18C6–Tl^+ complex with the composition of DMSO–EtOAc binary systems (Figure 2), may be due to strong interactions between the constituent solvents which result in some of the chemical and physical properties of each of solvent such as acidity, basicity, polarity, relative permitivity [26] and even the structure of the solvent molecules

change when they mix with one another and, therefore, changing their solvating ability towards the metal cations, ligand and the resulting complexes. A non-monotonic behaviour was also observed for the other metal-ion complexes in these binary solutions.

The variation of stability constant (log K_f) of DB18C6–M^{n+} (M^{n+} = Cu^{2+}, Zn^{2+}, Tl^+ and Cd^{2+}) complexes as function of cationic radii in DMSO–EtOAc binary systems is shown in Figures 3 and 4.

As is evident in Figure 3, the order of selectivity of the metal-ion complexes in neat DMSO and neat EtOAc at 25 °C is: (DB18C6–Tl^+) > (DB18C6–Cu^{2+}) > (DB18C6–Zn^{2+}) > (DB18C6–Cd^{2+}).

The Tl^+ ion forms the most stable complex with DB18C6 since its ionic size (ionic radius = 1.45 Å) is very close to the size of the DB18C6 cavity (2.6–3.2 Å) [27]. As is seen from Table 1, in most cases, the stabilities of these complexes in pure ethylacetate are bigger than in pure dimethylsulfoxide. In DMSO with a high Gutman Donor Number (DN = 29.8), the solvation of the metal cations must be stronger than EtOAc (DN = 17.1) with lower solvating ability. DMSO has a negative charged oxygen and preferentially solvates the metal cations [28].

Comparison of Figures 3 and 4 show that the selectivity order of these metal-ion complexes at 25 °C changes with the composition of DMSO–EtOAc binary systems. It is interesting to note that the selectivity order of the complexes in mixtures of DMSO–EtOAc with 25 and 50 mol% EtOAc is: (DB18C6–Tl^+) > (DB18C6–Zn^{2+}) > (DB18C6–Cd^{2+}) > (DB18C6–Cu^{2+}), but in the case of 75 mol% of EtOAc, the selectivity sequence is: (DB18C6–Cu^{2+}) > (DB18C6–Zn^{2+}) > (DB18C6–Cd^{2+}) > (DB18C6–Tl^+). The results obtained in this study show that the selection of solvents as mixture components and their concentration may create possibilities to change the properties of the solvent system in a desired direction.
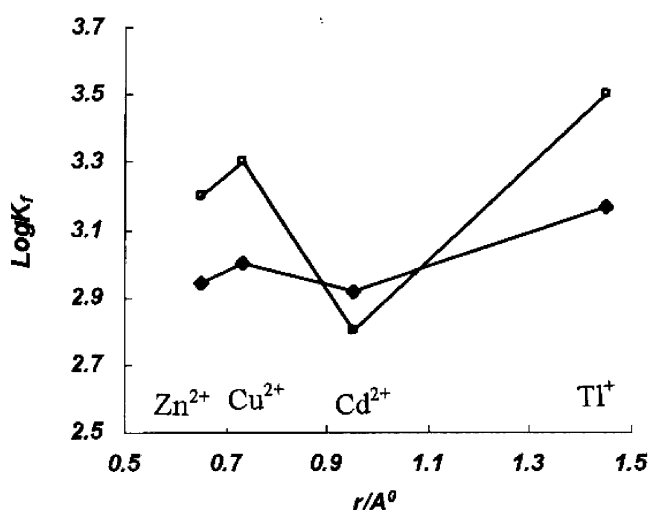

Figure 4. Variation of log K_f for (DB18C6–Cu^{2+}), (DB18C6–Zn^{2+}), (DB18C6–Cd^{2+}) and (DB18C6–Tl^+) complexes *versus* cationic radii in various solvent systems at 25 °C: pure DMSO (♦) and pure EtOAc (□).

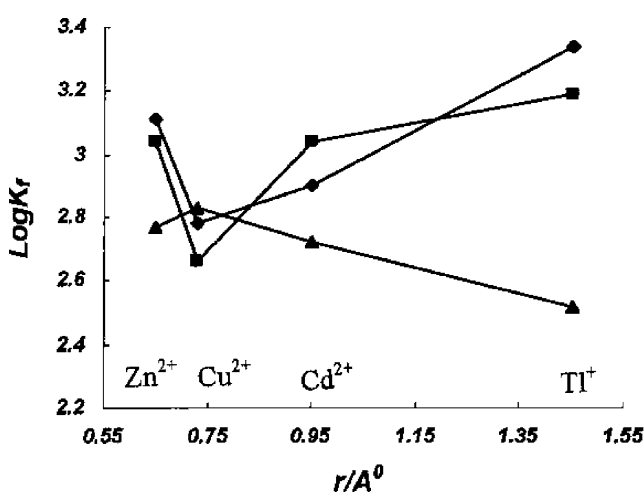*Figure 5.* Variation of log K_f for (DB18C6–Cu^{2+}), (DB18C6–Zn^{2+}), (DB18C6–Cd^{2+}) and (DB18C6–Tl^+) complexes *versus* cationic radii in various solvent systems at 25 °C: mol% EtOAc = 25 (♦), mol% EtOAc = 50 (■) and mol% EtOAc = 75 (▲).

The changes in the standard enthalpy (ΔH°_C) for complexation reactions 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 and the values of ΔS°_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. A typical example of the van' t Hoff plots is shown in Figure 5.

The data which are summarized in Table 2, show that in most cases, the complexation reactions between DB18C6 and the studied heavy metal cations in DMSO–EtOAc binary solutions are enthalpy stabilized but entropy destabilized. As seen from Figures 6 and 7, both of these thermodynamic parameters (ΔH°_C and ΔS°_C) change non-monotonically with the composition of the mixed solvents. This anomalous behaviour may be related to changes occurring in the structure of the solvent mixtures due to dipole–dipole interactions between these two dipolar aprotic solvents and, therefore, changing the structure of the solvent system which results in the change the solvation number of the dissolved species in solutions. A non-monotonic behaviour has also been observed for thermodynamic functions of $(15C5\text{-Li})^+$ complex formation in some of the binary mixed solvents [29].

Conclusion

The selectivity of crown ethers has often been explained in terms of the size-fit concept that a crown ether forms a most stable complex with the cation which has the best fit condition for the crown ether cavity. On the other hand, the results obtained in our studies suggest that the selectivity of crown ethers for the metal cations in solutions also undergoes solvent effect.

The results of this work show that the sequence of stability of complexes of DB18C6 with the studied heavy
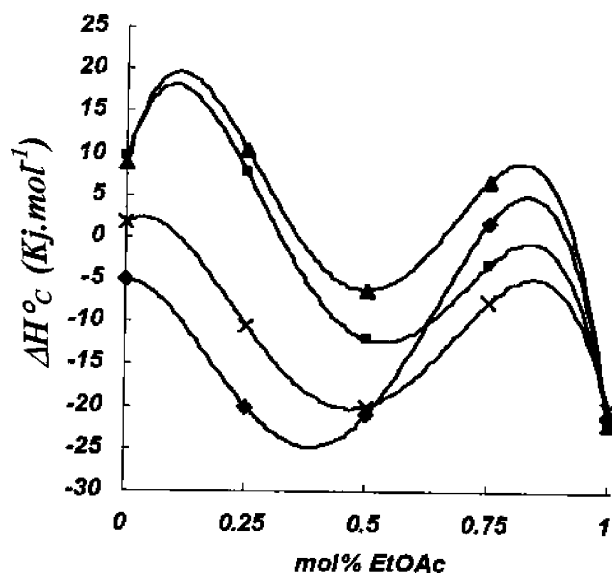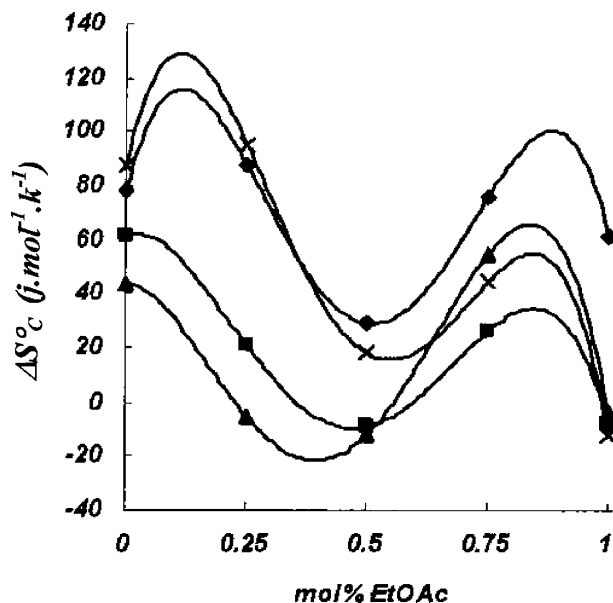

Figure 7. Changes of ΔS°_C with the composition of the DMSO–EtOAc binary systems at 25 °C: (DB18C6–Tl$^+$) (▲), (DB18C6–Cd^{2+}) (■), (DB18C6–Zn^{2+}) (×) and (DB18C6–Cu^{2+}) (♦).

metal cations changes with the composition of the mixed solvent. These results indicate the possibility of changes in stabilities and, therefore, changes of selectivities of the ligands which may be obtained in certain composition of the mixed solvent systems.

In this mixed solvent, DMSO–EtOAc, the enthalpy effect is a decisive factor in the complexation process of DB18C6 with Cu^{2+}, Zn^{2+}, Tl$^+$ and Cd^{2+} metal cations and it seems that the changes of thermodynamic parameters (ΔH°_C and ΔS°_C) for complexation processes in this binary mixed solvent are affected by the solvation capacity of the metal cations and the ligand which depends on the structural and energetic properties of the mixture.

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Figure 6. Changes of ΔH°_C with the composition of the DMSO–EtOAc binary systems at 25 °C: (DB18C6–Tl$^+$)(♦), (DB18C6–Cd^{2+}) (×), (DB18C6–Zn^{2+}) (■) and (DB18C6–Cu^{2+}) (▲).

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