

# A thermodynamic study of complexation of 18-crown-6 with $\text{Zn}^{2+}$ , $\text{Tl}^+$ , $\text{Hg}^{2+}$ and $\text{UO}_2^{2+}$ cations in acetonitrile-dimethylformamide binary media and study the effect of anion on the stability constant of (18C6- $\text{Na}^+$ ) complex in methanol solutions

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**Abstract** The equilibrium constants and thermodynamic parameters for complex formation of 18-crown-6(18C6) with  $\text{Zn}^{2+}$ ,  $\text{Tl}^+$ ,  $\text{Hg}^{2+}$  and  $\text{UO}_2^{2+}$  cations have been determined by conductivity measurements in acetonitrile(AN)-dimethylformamide(DMF) binary solutions. 18-crown-6 forms 1:1 complexes [M:L] with  $\text{Zn}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{UO}_2^{2+}$  cations, but in the case of  $\text{Tl}^+$  cation, a 1:2 [M:L<sub>2</sub>] complex is formed in most binary solutions. The thermodynamic parameters ( $\Delta H_c^\circ$  and  $\Delta S_c^\circ$ ) which were obtained from temperature dependence of the equilibrium constants show that in most cases, the complexes are enthalpy destabilized but entropy stabilized and a non-monotonic behaviour is observed for variations of standard enthalpy and entropy changes versus the composition of AN/DMF binary mixed solvents. The obtained results show that the order of selectivity of 18C6 ligand for these cations changes with the composition of the mixed solvent. A non-linear relationship was observed between the stability constants ( $\log K_f$ ) of these complexes with the composition of AN/DMF binary solutions. The influence of the  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$  anions on the stability constant of (18C6- $\text{Na}^+$ ) complex in methanol (MeOH) solutions was also studied by potentiometry method. The results show that the stability of (18C6- $\text{Na}^+$ ) complex in the presence of the anions increases in order:  $\text{ClO}_4^- > \text{NO}_3^- > \text{Cl}^-$ .

**Keywords** 18-crown-6 ·  $\text{Zn}^{2+}$  ·  $\text{Tl}^+$  ·  
 $\text{Hg}^{2+}$  and  $\text{UO}_2^{2+}$  cations ·  
Acetonitrile-dimethylformamide binary media ·  
Conductometry · Potentiometry

## Introduction

It is well known that crown ethers interact with various metal cations to form stable stoichiometric complexes [1]. The stability of crown ether complexes in solutions is mainly affected by the solvent medium, the relative size of the cation and the crown ether cavity and the co-anion with the cationic species [2, 3].

Different physicochemical techniques such as UV spectrophotometry [4], CD measurements [5], potentiometry [6], polarography [7] and conductometry [8, 9] have been used to study the complex formation between crown ethers and various cations in solutions. Studies of crown ethers complexation in different solvents show that the thermodynamic and kinetic parameters are affected by the nature and the composition of the solvent system [10, 11].

The effect of mixed solvent properties on the formation of crown ether-metal cation complexes is of interest due to, among other things, the fact that the solvation capacities of crown ether molecules and cations change with changing the mixed solvent composition on the other hand, the species are solvated competitively by the constituent solvents. The effects of the mixed solvent properties on the formation of the crown ether complexes have been studied to a very limited extent.

The widespread use of non-aqueous solvents, especially dipolar aprotic solvents in various fields of pure and applied chemistry has contributed greatly to advances in chemical sciences technologies [12].

Using non-aqueous solutions play an important role in exploring new chemical possibilities as well as in providing the methods to evaluate static solvent effects on various chemical processes. In order to obtain desirable solvent properties, we can use mixed solvents.

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In this work, we studied the complex formation between 18-crown-6(18C6) with  $Zn^{2+}$ ,  $Tl^+$ ,  $Hg^{2+}$  and  $UO_2^{2+}$  cations in acetonitrile(AN)-dimethylformamide(DMF) binary systems using conductometric method and the influence of the  $ClO_4^-$ ,  $NO_3^-$  and  $Cl^-$  anions on the stability constant ( $\log K_f$ ) of (18C6- $Na^+$ ) complex in methanol solutions was investigated by potentiometry.

## Experimental

### Materials

18-crown-6 (Aldrich) was recrystallized from acetonitrile and dried at room temperature under vacuum for 72 h. Thallium (I) nitrate (Prolabo), mercury (II) chloride, zinc (II) nitrate ( $Zn(NO_3)_2 \cdot 6H_2O$ ), sodium perchlorate (all from Riedel), sodium chloride (Aldrich) and uranyl nitrate ( $UO_2(NO_3)_2 \cdot 6H_2O$ ) (Riedel) were used without further purification. Acetonitrile (Merck), dimethylformamide (BDH) and methanol (Merck) were used as solvents.

### Apparatus and procedure

The conductance measurements were performed on an AMEL model 60 conductometer in a water-bath thermostated with a constant temperature maintained within  $\pm 0.03$  °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  $0.79 \text{ cm}^{-1}$  was used throughout the studies.

The experimental procedure to obtain the formation constants of complexes is as follow: a solution of metal cation salt ( $2 \times 10^{-4}$  M) was placed in a titration cell, then a step-by-step increase in the crown ether solution prepared in the same solvent ( $3 \times 10^{-2}$  M) was performed to the titration cell using a microburette and the conductance of the solution in the cell was measured after each transfer at desired temperature.

The activity of  $Na^+$  cation was measured by potentiometry using a sodium-ion selective electrode (ORION96-11). All potentiometric measurements were conducted at  $29 \pm 1$  °C. The emf was determined with a Metrohm 632 model potentiometer. The electrode system was calibrated by a standard solution of  $Na^+$  ion.

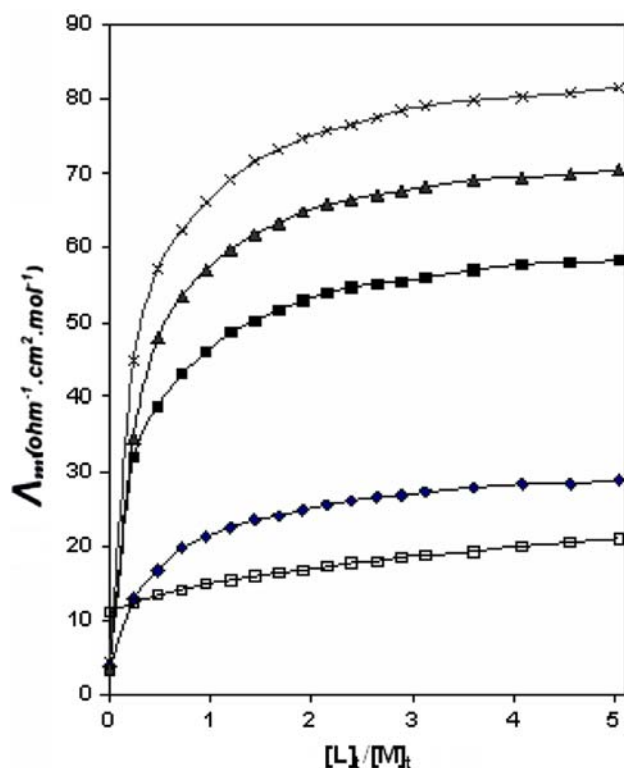
Each run was started by measuring the emf of the sodium salt solution ( $2 \times 10^{-3}$  M) and then, 18-crown-6 ligand ( $6 \times 10^{-3}$  M) was added by two different procedures: i.e. titration and weight-addition methods.

## Results

The changes of molar conductivity ( $\Lambda_m$ ) versus the ligand to cation mole ratio for the complexation of 18-crown-6 with  $Zn^{2+}$ ,  $Tl^+$ ,  $Hg^{2+}$  and  $UO_2^{2+}$  cations in acetonitrile-dimethylformamide (AN-DMF) binary systems were studied at different temperatures.

Three typical examples of molar conductance-mole ratio plots are shown in Figs. 1, 2, 3. The stability constants ( $\log K_f$ ) for 18C6 -  $M^{n+}$  ( $M^{n+}$ :  $Zn^{2+}$ ,  $Tl^+$ ,  $Hg^{2+}$  and  $UO_2^{2+}$ ) complexes in various solvent systems are listed in Table 1. Plots of  $\log K_f$  versus  $1/T$  in all cases were linear. The changes in standard enthalpy ( $\Delta H^\circ_c$ ) for the complexation reactions were determined in the usual manner from the slopes of the van't Hoff plots, and the changes in standard entropy ( $\Delta S^\circ_c$ ) were calculated from the relationship  $\Delta G^\circ_{c,298.15} = \Delta H^\circ_{c,298.15} - 298.15 \Delta S^\circ_c$ . The results are summarized in Table 2. A non-linear behaviour is observed for the stability constants ( $\log K_f$ ) of these complexes with the composition of AN-DMF binary system. For example, the variations of stability constant of (18C6- $Hg^{2+}$ ) complex with the composition of AN-DMF binary system at different temperatures are shown in Fig. 4.

The results obtained for investigation of the effect of anion on the stability of (18-crown-6 ·  $Na^+$ ) complex in

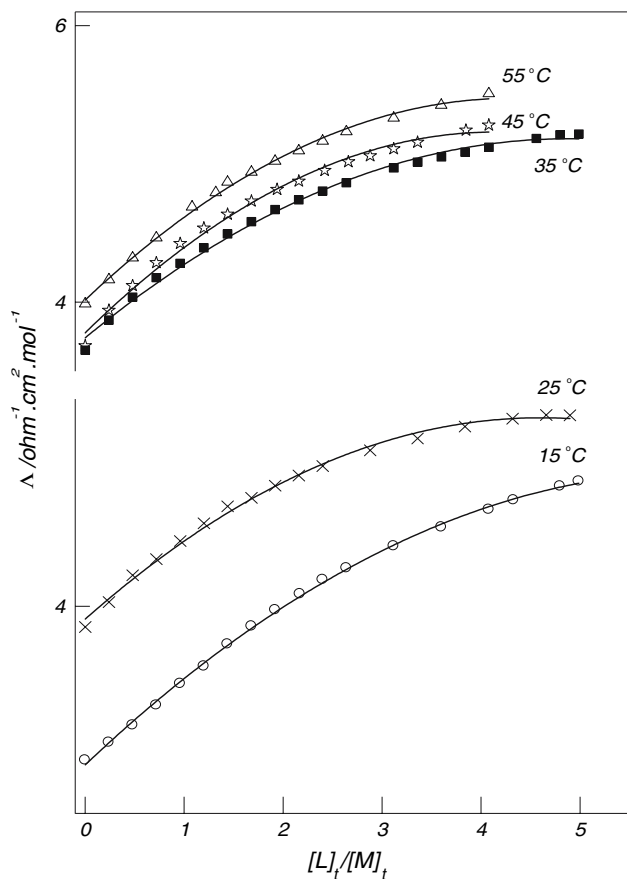


**Fig. 1** Molar conductance-mole ratio plots for (18C6 -  $UO_2^{2+}$ ) complex in pure AN at 15 °C (□), 25 °C (◆), 35 °C (■), 45 °C (▲) and 55 °C (×)

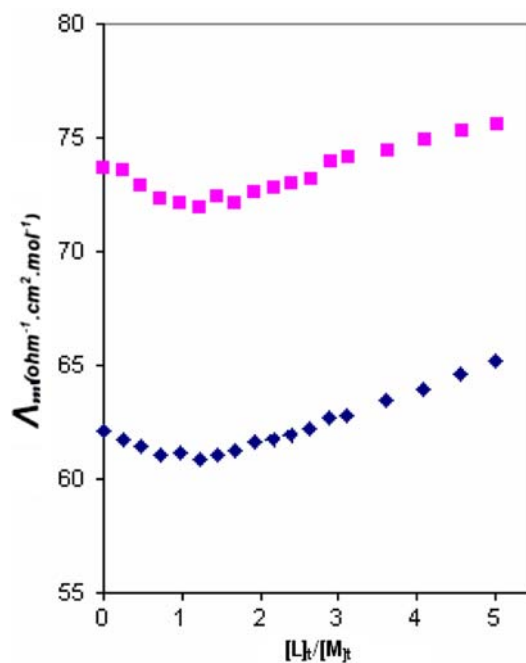
methanol solutions are given in Table 3. LogK<sub>f</sub> values of this complex in the presence of ClO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> anions were determined by Frensdroff equation [13]. The calibration plots (emf versus logc) were linear from 10<sup>-2</sup> to 5 × 10<sup>-5</sup> M (Fig. 5).

### Discussion

Addition of 18C6 ligand to solutions of Zn<sup>2+</sup>, Hg<sup>2+</sup> and UO<sub>2</sub><sup>2+</sup> cations in AN-DMF binary mixtures at different temperatures shows that the molar conductivity (Λ<sub>m</sub>) values increase with increasing [18C6]<sub>t</sub>/[M<sup>2+</sup>]<sub>t</sub> mole ratio which indicates that the (18C6-M<sup>2+</sup>) complexes in these binary systems have higher mobility than free solvated Zn<sup>2+</sup>, Hg<sup>2+</sup> and UO<sub>2</sub><sup>2+</sup> cations. The slope of the corresponding mole ratio plots changes at the point where the ligand to cation mole ratio is about 1 which is an evidence for formation of relatively stable 1:1 complexes between 18C6 ligand and Zn<sup>2+</sup>, Hg<sup>2+</sup> and UO<sub>2</sub><sup>2+</sup> cations.

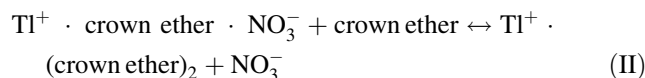
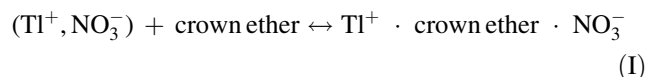


**Fig. 2** Molar conductance-mole ratio plots for (18C6-Hg<sup>2+</sup>) complex in pure AN at 15 °C (○), 25 °C (×), 35 °C (■), 45 °C (\*) and 55 °C (Δ)



**Fig. 3** Molar conductance-mole ratio plots for (18C6-Tl<sup>+</sup>) complex in AN-DMF binary system (mol% AN = 50) at 15 °C (◆) and 25 °C (■)

As is obvious from Fig. 3, addition of 18C6 to thallium ion in AN-DMF binary mixture at different temperatures causes the molar conductivity to decrease until the mole ratio reaches 1:1 and then to increase. Such behaviour may be described according to the following equilibria:



It is known that crown ethers are strongly ion-pair separators [14]. It is believed that 18C6 occupies only equatorial coordination sites of this metal ion and its axial sites are exposed to anion and solvent molecules. It seems, therefore, that addition of 18C6 ligand to Tl<sup>+</sup> ion in these solvent systems results in formation of stable 1:1 complex which is present as ion-pair (I). Further addition of the ligand to ion-pair complexes causes formation of 1:2 (ML<sub>2</sub><sup>+</sup>) complex between 18C6 with Tl<sup>+</sup> ion with a sandwich structure which decreases the space for diffusion and interaction of NO<sub>3</sub><sup>-</sup> for with Tl<sup>+</sup> ion which results in dissociation of the ion-pair (II) and, therefore, the molar conductivity increases.

A different behaviour was observed for complexation of Tl<sup>+</sup> ion with the ligand in one of the binary solutions of AN-DMF (mol% AN = 75). Addition of 18C6 to Tl<sup>+</sup> ion in this solution results in an increase in molar conductivity,

**Table 1** Log  $K_f$  values of (18C6-Zn<sup>2+</sup>), (18C6-Tl<sup>+</sup>), (18C6-Hg<sup>2+</sup>) and (18C6 - UO<sub>2</sub><sup>2+</sup>) complexes in AN-DMF binary mixtures at different temperatures

Meduim	Log $K_f \pm SD^a$				
	15 °C	25 °C	35 °C	45 °C	55 °C
<i>(18C6-Zn<sup>2+</sup>)</i>					
Pure AN	d	d	d	d	d
75%AN-25%DMF <sup>b</sup>	2.55 ± 0.10	2.25 ± 0.04	3.05 ± 0.04	3.10 ± 0.03	2.83 ± 0.06
50%AN-50%DMF	2.27 ± 0.08	2.57 ± 0.08	2.83 ± 0.07	3.06 ± 0.04	3.02 ± 0.04
25%AN-75%DMF	2.22 ± 0.06	2.40 ± 0.04	2.23 ± 0.05	2.23 ± 0.04	2.57 ± 0.06
Pure DMF	2.25 ± 0.07	2.16 ± 0.07	2.13 ± 0.03	2.37 ± 0.04	2.54 ± 0.04
<i>(18C6-Tl<sup>+</sup>)</i>					
Pure AN	e	e	e	e	e
75%AN-25%DMF <sup>b</sup>	2.91 ± 0.03	3.02 ± 0.04	3.04 ± 0.03	3.44 ± 0.30	3.07 ± 0.07
50%AN-50%DMF	c	c	c	c	c
25%AN-75%DMF	c	c	c	c	c
Pure DMF	c	c	c	c	c
<i>(18C6-Hg<sup>2+</sup>)</i>					
Pure AN	2.66 ± 0.04	3.09 ± 0.02	3.06 ± 0.01	3.16 ± 0.03	3.04 ± 0.02
75%AN-25%DMF <sup>b</sup>	2.28 ± 0.03	2.21 ± 0.06	2.06 ± 0.09	2.1 ± 0.1	–
50%AN-50%DMF	2.36 ± 0.04	2.60 ± 0.03	2.61 ± 0.03	2.50 ± 0.04	2.64 ± 0.05
25%AN-75%DMF	1.93 ± 0.07	2.48 ± 0.02	2.34 ± 0.03	2.26 ± 0.05	2.32 ± 0.07
Pure DMF	2.71 ± 0.08	1.91 ± 0.06	2.07 ± 0.07	2.21 ± 0.03	2.69 ± 0.04
<i>(18C6 - UO<sub>2</sub><sup>2+</sup>)</i>					
Pure AN	4.03 ± 0.15	4.25 ± 0.40	4.56 ± 0.34	4.57 ± 0.40	2.87 ± 0.05
75%AN-25%DMF <sup>b</sup>	1.48 ± 0.16	1.75 ± 0.10	2.11 ± 0.04	1.75 ± 0.10	1.93 ± 0.03
50%AN-50%DMF	3.34 ± 0.05	1.29 ± 0.20	2.24 ± 0.10	2.11 ± 0.20	2.33 ± 0.03
25%AN-75%DMF	<1	<1	<1	<1	<1
Pure DMF	<1	<1	<1	<1	<1

<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 can not be fitted in equation

<sup>d</sup> The conductance increases with time

<sup>e</sup> The salt is not soluble

which may be explained on the basis of solvation sphere of the Tl<sup>+</sup> ion [15]. It seems that the Tl<sup>+</sup> ion is solvated to a higher extent with increasing the concentration of AN in AN-DMF binary solutions. The possible reason is that since the Tl<sup>+</sup> ion is a soft acid [16], it interacts with the nitrogen atom of the acetonitrile molecule as a soft base and, therefore, it prevents the ion-pair formation in this solvent system.

As is evident in Fig. 4, the changes of stability constant (log $K_f$ ) of (18C6-Hg<sup>2+</sup>) complex versus the composition of AN-DMF binary solution at various temperatures are not linear. Somewhat similar behaviour was observed for (18C6-Zn<sup>2+</sup>) and (18C6 - UO<sub>2</sub><sup>2+</sup>) complexes in this solvent system. This behaviour may be due to preferential solvation of the cations and possibly of the ligand by dimethylformamide molecules in acetonitrile-dimethyl-

formamide binary mixtures or it may be due to some kinds of solvent-solvent interactions between these two solvent molecules. The acetonitrile and dimethylformamide solvents both are dipolar *aprotic* liquids with large but nearly equal dipole moments [17]. Thus mixing of DMF with AN will induce the mutual destruction of dipolar structures of the component liquids and releasing free dipoles. As a result, strong dipolar interaction between AN and DMF molecules is expected. The observed negative values of excess adiabatic compressibility ( $\beta^E$ ) and excess intermolecular *free length* ( $L_f^E$ ) over the complete range of composition of AN-DMF binary mixtures support the above observation [18].

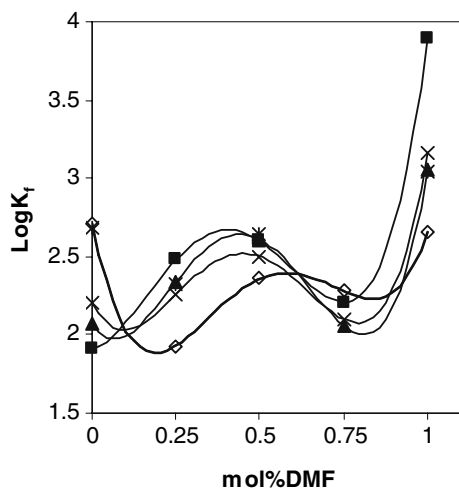
As is shown in Fig. 6, the selectivity order of the 18C6 ligand for the cations in a binary mixture of AN-DMF (mol% AN = 75) is: (18C6-Tl<sup>+</sup>) > (18C6-Zn<sup>2+</sup>) > 18C6-Hg<sup>2+</sup>)

**Table 2** Thermodynamic parameters for (18C6-Zn<sup>2+</sup>), (18C6-Tl<sup>+</sup>), (18C6-Hg<sup>2+</sup>) and (18C6 - UO<sub>2</sub><sup>2+</sup>) complexes in AN-DMF binary mixtures

Medium	LogK <sub>f</sub> ± SD <sup>a</sup> (25 °C)	-ΔG° <sub>c</sub> ± SD <sup>a</sup> Kcal mol <sup>-1</sup>	ΔH° <sub>c</sub> ± SD <sup>a</sup> Cal mol <sup>-1</sup>	ΔS° <sub>c</sub> ± SD <sup>a</sup> Cal mol <sup>-1</sup>
<i>(18C6-Zn<sup>2+</sup>)</i>				
75%AN-25%DMF <sup>b</sup>	2.25 ± 0.04	3.07 ± 0.07	10 ± 6	40 ± 2
50%AN-50%DMF	2.57 ± 0.08	3.5 ± 0.1	9 ± 1	48 ± 1
25%AN-75%DMF	2.40 ± 0.04	3.24 ± 0.06	4 ± 2	23 ± 6
Pure DMF	2.16 ± 0.07	2.95 ± 0.09	6 ± 2	30 ± 7
<i>(18C6-Tl<sup>+</sup>)</i>				
75%AN-25%DMF <sup>b</sup>	3.02 ± 0.04	4.13 ± 0.05	7 ± 2	37 ± 7
<i>(18C6-Hg<sup>2+</sup>)</i>				
Pure AN	3.09 ± 0.02	4.22 ± 0.02	6 ± 3	30 ± 10
75%AN-25%DMF <sup>b</sup>	2.21 ± 0.06	3.01 ± 0.08	-2 ± 1	-
50%AN-50%DMF	2.60 ± 0.03	3.55 ± 0.04	3 ± 1	22 ± 7
25%AN-75%DMF	2.48 ± 0.02	3.40 ± 0.30	4 ± 2	25 ± 7
Pure DMF	1.91 ± 0.06	2.61 ± 0.09	11 ± 3	50 ± 10
<i>(18C6 - UO<sub>2</sub><sup>2+</sup>)</i>				
Pure AN	4.25 ± 0.40	-6.20 ± 0.05	7.1 ± 3.4	43.8 ± 11.0
75%AN-25%DMF <sup>b</sup>	1.75 ± 0.10	-2.39 ± 0.02	3.9 ± 2.9	-
50%AN-50%DMF	1.29 ± 0.20	-1.76 ± 0.02	-12 ± 5.3	-

<sup>a</sup> SD: standard deviation

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



**Fig. 4** Changes of stability constant ( $\log K_f$ ) of (18C6-Hg<sup>2+</sup>) complex with the composition of AN-DMF binary system at different temperatures: 15 °C (◆), 25 °C (◇), 35 °C (▲), 45 °C (×) and 55 °C (■)

(18C6 - UO<sub>2</sub><sup>2+</sup>). The Tl<sup>+</sup> ion forms the most stable complex with 18C6 since its ionic size (2.9 Å) is very close to the size of the 18C6 cavity (2.6–3.2 Å), but in the cases of the other two AN-DMF binary solutions (mol% AN = 25 and 50), the selectivity sequence is: (18C6-Hg<sup>2+</sup>) > (18C6-Zn<sup>2+</sup>) > (18C6-Tl<sup>+</sup>). The results obtained in this study show that the selection of

solvents as mixture components and their concentration may change the selectivity of the macrocyclic ligands for the metal cations.

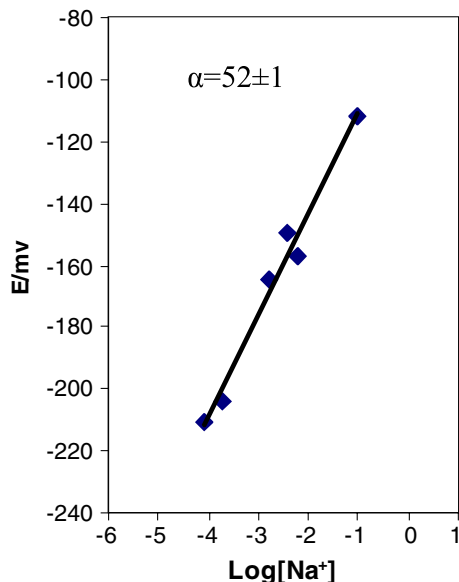
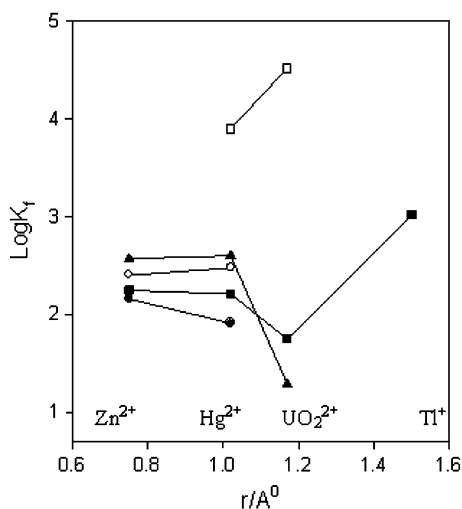
The results which are summarised in Table 2, show that in most cases, the complexation reactions between 18C6 and the studied metal cations in AN-DMF binary solutions are enthalpy destabilized but entropy stabilized. As is obvious from this Table, the thermodynamic quantities are quite sensitive to the nature and composition of the mixed solvent and a non-monotonic behaviour is observed for variations of standard enthalpy and entropy changes versus the composition of acetonitrile-dimethylformamide binary solutions. It seems that the thermodynamics of complexation reactions between 18-crown-6 and Zn<sup>2+</sup>, Tl<sup>+</sup>, Hg<sup>2+</sup> and UO<sub>2</sub><sup>2+</sup> cations is affected by the solvation capacity of the metal cations and the ligand which depends on the structural and energetic properties of the mixture solvent systems.

The summarized data in Table 3 which are obtained from potentiometric measurements show that the stability constant ( $\log K_f$ ) of (18C6-Na<sup>+</sup>) complex decreases in the presence of the studied anions in order: ClO<sub>4</sub><sup>-</sup> > NO<sub>3</sub><sup>-</sup> > Cl<sup>-</sup>.

In aqueous media, the low surface charge density for a large anion creates a loosely packed anion hydration sphere, but in an organic medium, the reverse trend is true and larger anions are better solvated than smaller anions in such media [19]. It seems that since the larger ClO<sub>4</sub><sup>-</sup> and

**Table 3** Effect of anion on log  $K_f$  values of (18C6-Na<sup>+</sup>) complex in methanol solutions

Anion	Log $K_f \pm$ SD <sup>a</sup>	
	Titration method	Weight addition method
ClO <sub>4</sub> <sup>-</sup>	4.60 ± 0.01	4 ± 0.3
NO <sub>3</sub> <sup>-</sup>	4.46 ± 0.01	4.31 ± 0.03
Cl <sup>-</sup>	4.25 ± 0.05	4.14 ± 0.05

<sup>a</sup> SD: standard deviation**Fig. 5** Calibration curve for Na<sup>+</sup> cation in methanol at 29 °C**Fig. 6** Changes of log $K_f$  for (18C6-Zn<sup>2+</sup>), (18C6-Tl<sup>+</sup>), (18C6-Hg<sup>2+</sup>) and (18C6 - UO<sub>2</sub><sup>2+</sup>) complexes versus cationic radii at 25 °C in various AN-DMF binary solutions: mol% AN = 0(●), mol% AN = 25(○), mol% AN = 50(▲), mol% AN = 75(■), and mol% AN = 100(□)

NO<sub>3</sub><sup>-</sup> anions are more strongly solvated than Cl<sup>-</sup> anion by methanol molecules, the competition of these anions with the ligand for the sodium ion is *weakened* compared to Cl<sup>-</sup> anion in methanol solutions.

## Conclusion

The results obtained in this work, indicate the possibility of changes in stabilities, selectivities and stoichiometry of complexes, which are formed between macrocyclic ligands and metal cations with the composition of the mixed solvent systems. 18C6 forms a 1:1 complex with Tl<sup>+</sup> cation in 75% mol of AN-DMF binary solution. But in the case of other compositions, a 1:2 complex is formed in solutions.

Solvent molecules can solvate the free ligand, the metal cation and also the anion, which accompanies the metal cation. In the complexation process, in addition of solvent molecules, the anion can also compete with the ligand for the metal cation. The large anions such as ClO<sub>4</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> are more solvated in methanol solutions than small Cl<sup>-</sup> anion, therefore, the stability constant of (18C6 · Na<sup>+</sup>) complex decreases in the presence of chloride ion.

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