

Conductance Studies on Complex Formation Between Aza-18-Crown-6 with Ag^+ , Hg^{2+} and Pb^{2+} Cations in DMSO– H_2O Binary Solutions

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Abstract

The complexation reactions between Ag^+ , Hg^{2+} and Pb^{2+} metal cations with aza-18-crown-6 (A18C6) were studied in dimethylsulfoxide (DMSO)–water (H_2O) binary mixtures at different temperatures using the conductometric method. The conductance data show that the stoichiometry of the complexes in most cases is 1:1(ML), but in some cases 1:2 (ML₂) complexes are formed in solutions. A non-linear behaviour was observed for the variation of $\log K_f$ of the complexes vs. the composition of the binary mixed solvents. Selectivity of A18C6 for Ag^+ , Hg^{2+} and Pb^{2+} cations is sensitive to the solvent composition and in some cases and in certain compositions of the mixed solvent systems, the selectivity order is changed. The values of thermodynamic parameters (ΔH_c° , ΔS_c°) for formation of A18C6– Ag^+ , A18C6– Hg^{2+} and A18C6– Pb^{2+} complexes in DMSO– H_2O binary systems were obtained from temperature dependence of stability constants and the results show that the thermodynamics of complexation reactions is affected by the nature and composition of the mixed solvents.

Introduction

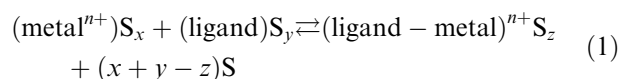
The discovery of the first crown ether in 1967 by Pedersen was a great revolution in chemistry of the macrocyclic compounds [1, 2]. It was accidentally discovered during synthesis of bisphenol from catechol and dichlorodiethylether [3]. The attention which was considerably drawn towards the new compound, was named by Pedersen as dibenzo-18-crown-6. It had considerable solubility in water in presence of sodium hydroxide. In fact, this observation gave him due recognition of his discovery of complexation of this ligand with sodium ion in solution [4]. The complexation reactions between crown ethers and various metal cations have been studied in various solvent systems [5–7], but the data available for complexation of metal cations in mixed binary solvents are sparse [8–14].

A variety of monocyclic composite donor crown compounds such as aza-crown ethers with oxygen and nitrogen atoms as electron donors have been synthesized and their capacity to form complexes with metal cations has been investigated [15]. However, little work has been reported so far for the structure of complexes, the thermodynamics or the kinetic of the complexation reactions of these macrocyclic ligands.

When 1 or 2 of the oxygen donors in 18-crown-6 and dibenzo-18-crown-6 are replaced with nitrogen atoms, the stability constants of the complexes of the resulting aza-crown ethers with alkali and alkaline earth metal ions are smaller than those of the corresponding crown ethers. In contrast, the complexation abilities with transition metal ions and also heavy metal ions which belong to a class of soft acids, increase markedly to nearly the same level as the corresponding acyclic amines. Therefore, aza-crown ethers are suitable complexing agents for transition and heavy metal ions [15].

The most important property of crown ethers is their selective complexing ability. They bound the metal cations in their cavity via ion-dipole interactions between the metal cations and negatively charged donor atoms of the polyether ring. Such selectivity depends upon the relative size of the cavity of crown ether to the diameter of the metal cation, the number and the nature of the donor atoms in the crown ether ring, the charge of metal cation and also the nature of the medium.

The complexation process between the ligand and metal cation is represented by the following general equation:



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in which, S is the solvent molecule, x , y , z are the solvation numbers of metal cation, ligand and the resulting complex, respectively. The formation of a complex in solution is, therefore, not only a competition for the metal ion between the ligand and the solvent molecules, but also a competition for the ligand between metal ion and the solvent molecules. Hence, the formation of the complex for a particular ion may be minimized, or even prevented, if the metal cation and the ligand are strongly solvated by the solvent molecules. In addition, selectivity for certain cations over others may be altered according to the nature of solvent.

The goal of the present investigation is to study the effect of nature of the cations and especially the solvent properties on the stability, selectivity and thermodynamic parameters of complexes of aza-18-crown-6 with Ag^+ , Hg^{2+} and Pb^{2+} cations in DMSO– H_2O binary mixtures using the conductometric technique.

Experimental

A18C6 (Fluka), lead nitrate (Merck), silver nitrate (Merck) and mercury chloride (Riedel) were used without further purification. Dimethylsulfoxide (Merck) with the highest purity and the triplet distilled water were used as solvents.

The experimental procedure to obtain the formation constants of complexes was 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, step-by-step additively the crown ether solution prepared in the same solvent (2.5×10^{-3} M) by a rapid transfer to the titration cell using a microburette. The conductance of the solution in the cell was measured after each transfer at the desired temperature.

Apparatus

The conductance measurements were performed using a digital AMEL conductivity apparatus, model 60 in a water bath thermostated at a constant temperature 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.

Results

The variations of molar conductance (Λ_m) versus the ligand to the cation molar ratio ($[\text{L}]_t/[\text{M}]_t$) for complexation of A18C6 with Ag^+ , Hg^{2+} and Pb^{2+} cations in DMSO– H_2O binary systems were studied at different temperatures. $[\text{L}]_t$ is the total concentration of A18C6

and $[\text{M}]_t$ is the total concentration of the metal cations. Four typical series of molar conductance values as a function of ligand/metal cation mole ratios in pure DMSO, in DMSO– H_2O binary systems and pure H_2O are shown in Figures 1–4, respectively.

The conductometric method for the determination of the stability constants of complexes of crown ethers with metal cations has been used by several investigators. The 1:1 binding of a metal cation (M^+) with crown ethers can be represented by following equilibrium equation [16]:

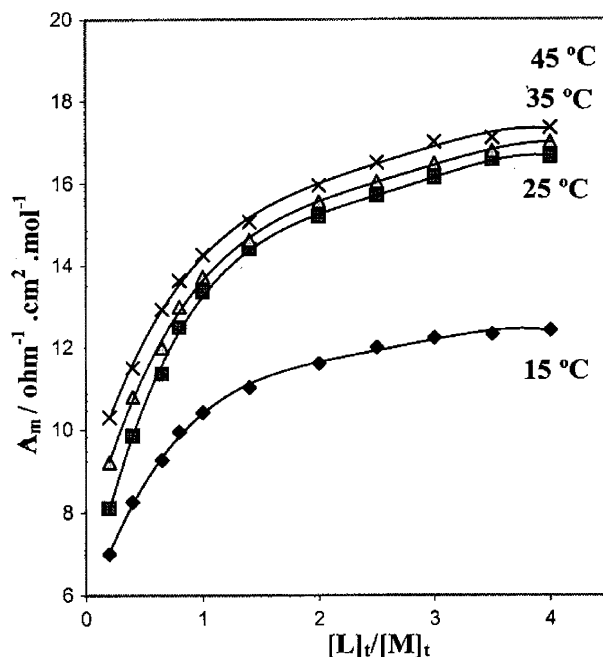


Figure 1. Molar conductance–mole ratio plots for A18C6– Hg^{2+} complex in pure DMSO at different temperatures.

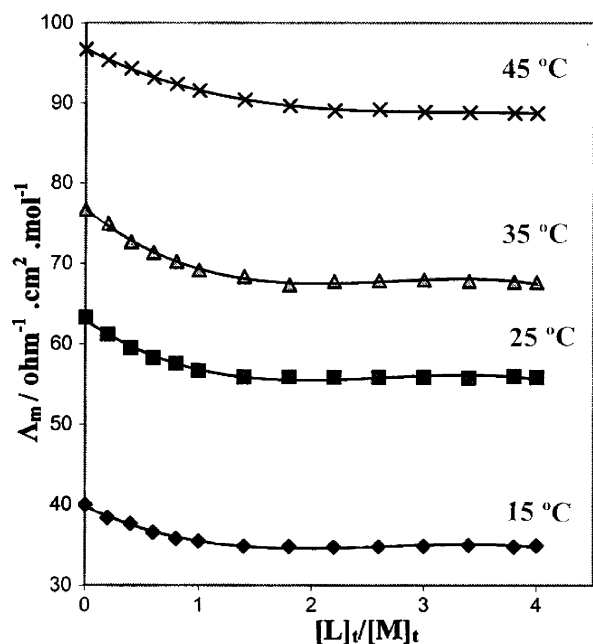


Figure 2. Molar conductance–mole ratio plots for the A18C6– Pb^{2+} complex in DMSO– H_2O binary mixture (mol% DMSO = 80) at different temperatures.

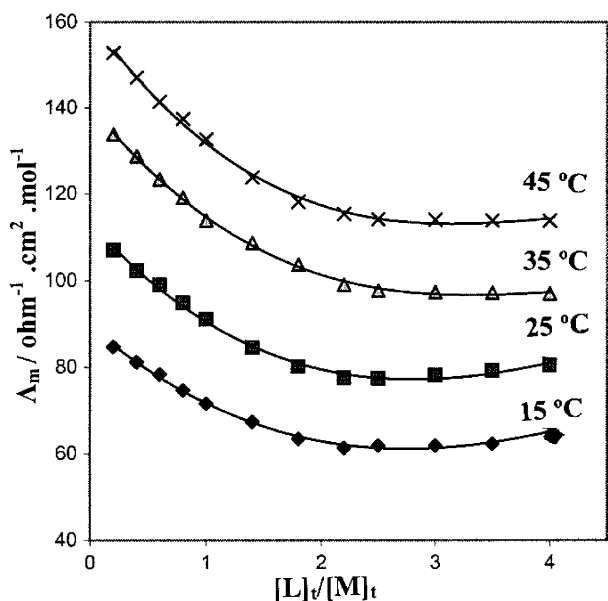


Figure 3. Molar conductance-mole ratio plots for the A18C6-Pb²⁺ complex in pure H₂O at different temperatures.

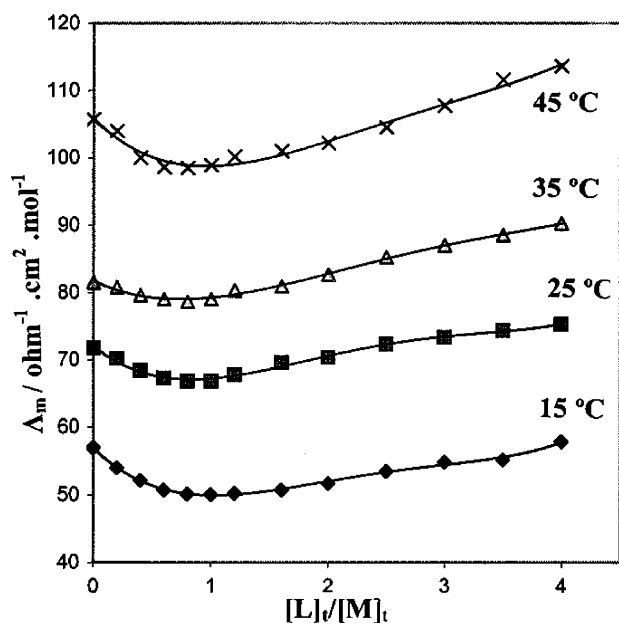


Figure 4. Molar conductance-mole ratio plots for the A18C6-Ag⁺ complex in DMSO-H₂O binary mixture (mol% DMSO=20) at different temperatures.



$$\alpha[M]_t \quad [L]_t - (1 - \alpha)[M]_t \quad (1 - \alpha)[M]_t$$

where M⁺, L, ML⁺ and α are the metal ion, the crown ether, the complex and the fraction of the free metal ion, respectively. The complex formation constant in terms of the molar concentration can be expressed as:

$$K_{ML^+} = \frac{[ML^+]}{[M^+][L]} = (1 - \alpha) / \alpha[L] \quad (3)$$

The observed conductivity, *k*, at each point in the titration can be written as:

$$k = k_{MA} + k_{MLA} \quad (4)$$

where A⁻ denotes an anion, and *k*_{MA} and *k*_{MLA} are the conductivities of the metal salt and metal crown ether salt, respectively. The molar conductivities are given by:

$$\Lambda_{MA} = k_{MA} / [M^+] = k_{MA} / \alpha[M]_t \quad (5)$$

$$\Lambda_{MLA} = k_{MLA} / [ML^+] = k_{MLA} / (1 - \alpha)[ML]_t \quad (6)$$

where Λ_{MA} and Λ_{MLA} are the molar conductivities of the metal salt and metal crown ether salt, respectively. As a consequence of Equations (5) and (6), Equation (4) can be transformed into

$$\Lambda_{MA} = k / [M]_t = \alpha\Lambda_{MA} + (1 - \alpha)\Lambda_{MLA} \quad (7)$$

Substituting from Equation (7) in to Equation 3 gives the following equation:

$$K_{ML^+} = (\Lambda_{MA} - \Lambda) / (\Lambda - \Lambda_{MLA})[L] \quad (8)$$

where $[L] = \frac{[L]_t - [M]_t (\Lambda_{MA} - \Lambda)}{(\Lambda_{MA} - \Lambda_{MLA})}$. The procedure for obtaining the *K*_{ML⁺} value is as follows. The Λ_{MLA} value is estimated from the Λ values at points of large [L]_t / [M]_t ratios. The molar conductance data obtained from complexation studies were fitted non-linearly to the equation (8), using the Genplot package from Computer Graphic Service [17]. The *K*_{ML⁺} and the estimated Λ_{MLA} at large [L]_t / [M]_t ratios were used as variables until best convergence was obtained.

The values of the stability constants (log *K*_f) for the A18C6-M^{*n+*} (M^{*n+*} = Ag⁺, Hg²⁺ and Pb²⁺) complexes in various solvent systems are listed in Table 1. The van't Hoff plots of ln *K*_f versus 1/*T* for all of the investigated systems were constructed. The changes in the standard enthalpy (Δ*H*^o_c) for complexation reactions were obtained from the slope of the van't Hoff plots and the changes in standard entropy (Δ*S*^o_c) were calculated from the relationship Δ*G*^o_{c,298.15} = Δ*H*^o_{c} - 298.15 Δ*S*^o_{c}. The thermodynamic}}}

Table 1. Log K_f values of A18C6–Ag⁺, A18C6–Hg²⁺ and A18C6–Pb²⁺ complexes in DMSO–H₂O binary mixtures at different temperatures

Medium	Log $K_f \pm SD^a$			
	15 °C	25 °C	35 °C	45 °C
<i>A18C6.Pb²⁺</i>				
Pure DMSO	–	4.4 ± 0.1	4.4 ± 0.1	4.04 ± 0.07
80%DMSO–20%H ₂ O ^b	5.2 ± 0.3	4.9 ± 0.3	4.7 ± 0.2	3.9 ± 0.2
60%DMSO–40%H ₂ O	3.7 ± 0.1	3.7 ± 0.4	3.49 ± 0.08	3.35 ± 0.07
40%DMSO–60%H ₂ O	3.73 ± 0.08	3.72 ± 0.07	3.50 ± 0.08	3.50 ± 0.07
20%DMSO–80%H ₂ O	c	c	c	c
Pure H ₂ O	c	c	c	c
<i>A18C6.Hg²⁺</i>				
Pure DMSO	–	4.05 ± 0.07	3.98 ± 0.07	3.81 ± 0.06
80%DMSO–20%H ₂ O ^b	4.2 ± 0.2	3.62 ± 0.05	3.64 ± 0.06	3.41 ± 0.03
60%DMSO–40%H ₂ O	c	c	c	c
40%DMSO–60%H ₂ O	2.4 ± 0.1	2.38 ± 0.09	2.3 ± 0.1	2.3 ± 0.1
20%DMSO–70%H ₂ O	2.55 ± 0.07	2.47 ± 0.06	2.35 ± 0.07	2.31 ± 0.08
Pure H ₂ O	2.85 ± 0.07	2.83 ± 0.07	2.77 ± 0.07	2.6 ± 0.04
<i>A18C6.Ag⁺</i>				
Pure DMSO	–	3.9 ± 0.1	3.8 ± 0.1	3.7 ± 0.4
80%DMSO–20%H ₂ O ^b	4.8 ± 0.7	4.4 ± 0.7	4.3 ± 0.1	4.3 ± 0.1
60%DMSO–40%H ₂ O	4.3 ± 0.1	4.2 ± 0.1	4.09 ± 0.09	3.4 ± 0.1
40%DMSO–60%H ₂ O	4.9 ± 0.3	4.2 ± 0.1	4.2 ± 0.1	4.1 ± 0.2
20%DMSO–80%H ₂ O	c	c	c	c
Pure H ₂ O	c	c	c	c

^aSD = standard deviation.^bThe composition of each solvent system is expressed in mol% of each solvent.^cThe data cannot be fitted in equation.

data are summarized in Table 2. The changes of log K_f versus the mole fraction of DMSO for A18C6–Ag⁺ and A18C6–Hg²⁺ complexes in DMSO–H₂O binary systems at different temperatures are shown in Figures 5 and 6, and the changes of the stability constants (log K_f) of A18C6–Ag⁺, A18C6–Hg²⁺ and A18C6–Pb²⁺ complexes as a function of cationic radii in various DMSO–H₂O binary systems are shown in Figure 7.

Discussion

As is seen from Figure 1, addition of A18C6 to Hg²⁺ cation in pure DMSO at different temperatures results in an increase in molar conductivity which indicates that the A18C6–Hg²⁺ complex is more mobile than free solvated Hg²⁺ cation but, as seen from Figure 2, addition of A18C6 to Pb²⁺ cation in DMSO–H₂O (mol% DMSO = 80) binary systems at different tem-

Table 2. Thermodynamic parameters for A18C6–Ag⁺, A18C6–Hg²⁺ and A18C6–Pb²⁺ complexes in DMSO–H₂O binary mixtures

Complex	Medium DMSO–H ₂ O mixtures mol% DMSO	$\Delta G_c^\circ(25^\circ\text{C}) \pm SD^a$ kJ mol ⁻¹	$\Delta H_c^\circ \pm SD^a$ kJ mol ⁻¹	$\Delta S_c^\circ \pm SD^a$ J mol ⁻¹ K ⁻¹
A18C6–Pb ²⁺	100	–25.0 ± 0.8	–35 ± 6	b
	80	–27.9 ± 0.3	–72 ± 9	–148 ± 90
	60	–20.9 ± 0.4	–23 ± 2	b
	40	–21.1 ± 0.5	–15 ± 3	–20 ± 7
	100	–21.7 ± 0.4	–28 ± 3	b
A18C6–Ag ⁺	80	–25.0 ± 0.8	–30 ± 5	b
	60	–24.2 ± 0.8	–53 ± 10	–99 ± 30
	40	–23.8 ± 0.4	b	b
	100	–22.0 ± 0.4	–17 ± 3	18 ± 8
	80	–20 ± 1	–41 ± 7	–16 ± 8
A18C6–Hg ²⁺	40	–13.4 ± 0.4	–14.2 ± 0.7	31 ± 1
	20	–14.0 ± 0.3	–14 ± 1	b
	0	–16.0 ± 0.4	–7 ± 2	30 ± 4

^aSD = standard deviation.^bWith high uncertainty.

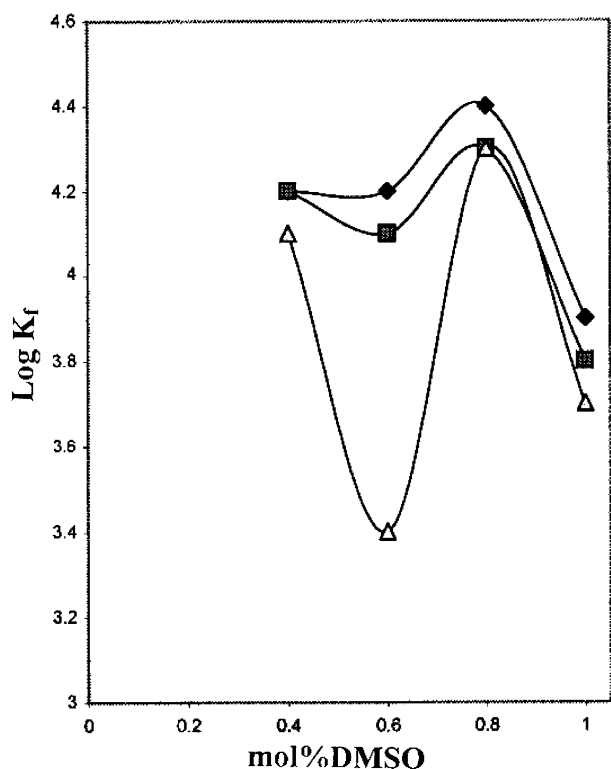


Figure 5. Variation of the stability constants of A18C6–Ag⁺ complex with the composition of the DMSO–H₂O binary mixture at different temperatures: 25 °C (◆), 35 °C(■) and 45 °C(Δ).

peratures results in a decrease in molar conductivity which indicates that the A18C6–Pb²⁺ complex in this solution is less mobile than free solvated Pb²⁺ cation. The slope of the corresponding molar conductivity versus [L]_t/[M]_t 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 (ML) between Hg²⁺ and Pb²⁺ cations with A18C6 in

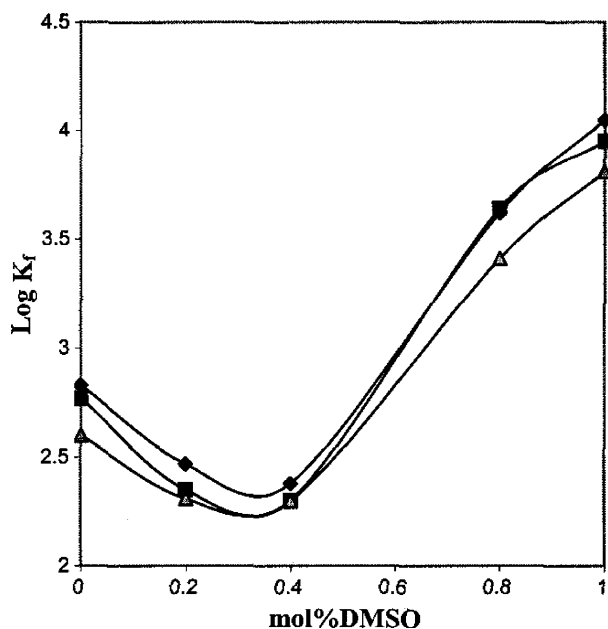


Figure 6. Variation of the stability constant of A18C6–Hg²⁺ complex with the composition of the DMSO–H₂O binary mixture at different temperatures: 25 °C (◆), 35 °C(■) and 45 °C(Δ).

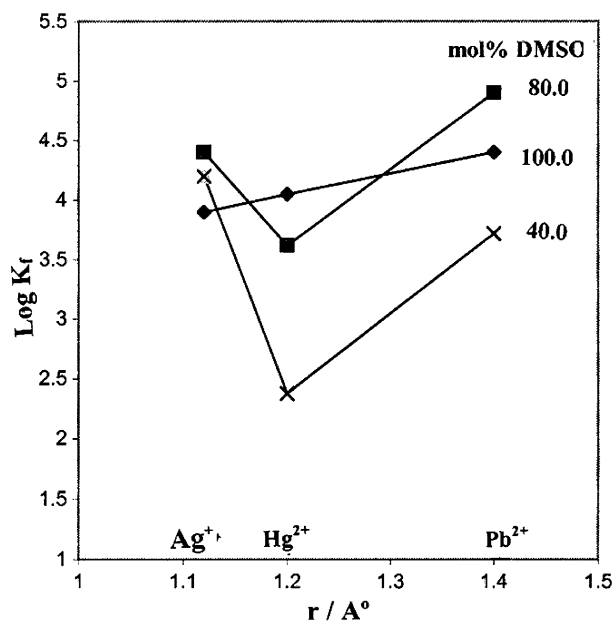
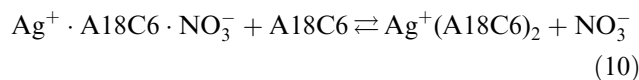
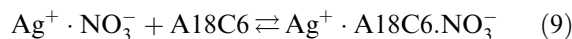


Figure 7. Variation of log K_f for A18C6–Ag⁺, A18C6–Hg²⁺ and 18C6–Pb²⁺ complexes vs. cationic radii in DMSO–H₂O binary solvent systems at 25 °C.

these solutions, but as evident from Figure 3, the slope of molar conductance mole ratio plots changes at the point where [L]_t/[M]_t is about 2 which indicates the formation of a 1:2 (ML₂) complex between Pb²⁺ cation and A18C6 in pure water. The results obtained in this study show that the stoichiometry of the metal cation-crown ether complexes may be changed by the nature of the solvent system.

It is evident from Figure 1 that the curvature of the molar conductivity plots of the A18C6–Hg²⁺ complex decreases as the temperature increases which is an evidence for formation of a weaker complex at higher temperatures. Similar behaviour was observed for A18C6–Hg²⁺, A18C6–Pb²⁺ and A18C6–Ag⁺ complexes in DMSO–H₂O mixtures, therefore, the complexation reactions between Ag⁺, Hg²⁺ and Pb²⁺ cations with A18C6 in these binary mixed solvents are exothermic.

As is obvious from Figure 4, addition of A18C6 to Ag⁺ cation in DMSO–H₂O (mol% DMSO = 20) binary solution, causes the molar conductivity initially decreases until the mole ratio reaches 1 and then to increase. Such behaviour may be described according to the following equilibria:



It seems that addition of the ligand to Ag⁺ solution results in formation of a relatively stable 1:1 complex which is present as an ion-pair (9), then addition of the

second ligand to the ion-pair complex, causes formation of a stable 1:2 complex with a sandwich structure (10) which decreases the space for diffusion and interaction of the NO_3^- ion with the Ag^+ cation and results in dissociation of the ion pair. Similar behaviour has been observed by Takeda and co-workers in their study of complex formation between 18C6 with Li^+ , K^+ and Rb^+ cations [18] and also for complexation reaction between DC18C6 with Tl^+ cation in AN-MeOH (mol% AN = 75) binary solutions [19].

As is evident from Table 2, the enthalpy and entropy values for complexation reactions vary with the nature and composition of the mixed solvents. The experimental values of ΔH_c° in Table 2, show that in all solvent systems used in this study, the complexation reactions between Ag^+ , Hg^{2+} and Pb^{2+} cations with A18C6 are enthalpy stabilized.

The variation of the $\log K_f$ of A18C6- Ag^+ and A18C6- Hg^{2+} complexes as a function of DMSO concentration in DMSO- H_2O binary systems are shown in Figures 5 and 6, respectively. As is evident from these Figures, the changes of the stability constants of A18C6- Ag^+ and A18C6- Hg^{2+} complexes versus the solvent composition are not linear. A non-linear behaviour was also observed for A18C6- Pb^{2+} complex in these binary solutions. This behaviour may reflect changes occurring in the structure of the solvent mixtures and, therefore, changing the solvation properties of the metal cations, the cyclic polyether and even the resulting complexes and also the preferential solvation of these species in the mixed solvent.

The solvation of crown ethers is of great importance during the complexation process of these macrocyclic ligands with the metal cations. The analysis of solvation enthalpy of some crown ethers in DMSO- H_2O and other mixed solvents has been studied by Jazwiak [20]. A non-linear behaviour has been observed between the solvation enthalpy of some crown ethers and the composition of DMSO- H_2O binary solutions. The observed behaviour has been discussed in terms of preferential solvation of the crown ether molecules which in turn depends quantitatively on the structural and energetic properties of the mixed solvent system.

The variations of $\log K_f$ of the A18C6- Ag^+ , A18C6- Hg^{2+} and A18C6- Pb^{2+} complexes vs. ionic radii in various DMSO- H_2O binary mixtures are shown in Figure 7. As is evident from this Figure, the order of stability of complexes in pure DMSO at 25 °C is: A18C6- Pb^{2+} > A18C6- Hg^{2+} > A18C6- Ag^+ . The Pb^{2+} cation forms a more stable complex with A18C6 than

the other two cations. This result seems reasonable, because the ionic size of the Pb^{2+} cation (1.4 Å) is very close to the cavity size of A18C6 (1.3–1.6 Å) [21, 22], therefore, it forms the most stable complex. But, since the ionic size of Ag^+ and Hg^{2+} cations are smaller than the size of the A18C6 cavity, they form weaker complexes compared to Pb^{2+} cation. It is interesting to note that the order of the stability of the complexes formed between A18C6 and these metal cations in DMSO- H_2O (mol% DMSO = 40 and 80) binary mixtures is: A18C6- Ag^+ > A18C6- Pb^{2+} > A18C6- Hg^{2+} . Therefore, a reversal in stabilities is observed in this binary solution. This reversal of stabilities indicates the possibility of changes in stabilities and, therefore, the reversal of cation selectivities for macrocyclic ligands obtained in certain composition of the mixed solvent systems.

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