



A Thermodynamic Study of Complex Formation between 18-Crown-6 with Tl^+ , Hg^{2+} and Ag^+ Metal Cations in Some Binary Mixed Non-aqueous Solvents Using the Conductometric Method

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(Received: 20 March 2002; in final form: 12 July 2003)

Key words: acetonitrile-methanol and benzonitrile-methanol binary mixtures, conductometry, 18-crown-6, Tl^+ , Hg^{2+} and Ag^+ cations

Abstract

The complexation reactions between Tl^+ , Hg^{2+} and Ag^+ metal cations with 18-Crown-6 (18C6) were studied in acetonitrile (AN)-methanol (MeOH) and benzonitrile (BN)-methanol (MeOH) 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 the case of the Tl^+ cation, in addition to a 1 : 1 complex, a 1 : 2 (ML_2) complex is 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. The stability of 18C6 complexes with Tl^+ , Hg^{2+} and Ag^+ cations is sensitive to solvent composition and in some cases, the stability order is changed with changing the composition of the mixed solvents. The values of the thermodynamic parameters (ΔH_c° , ΔS_c°) for formation of 18C6- Tl^+ , 18C6- Hg^{2+} and the 18C6- Ag^+ complexes were obtained from the temperature dependence of the stability constants and the results show that the thermodynamics of the complexation reactions is affected by the nature and composition of the mixed solvents and in most cases, the complexes are enthalpy destabilized but entropy stabilized.

Introduction

In 1967, Pedersen described the synthesis of macrocyclic polyethers and the formation of stable complexes between these ligands and various metal salts [1]. Today the chemistry of the crown compounds forms an important part of the literature [2, 3]. These studies mainly deal with the stability and selectivity of metal complexes of crown compounds and also with the thermodynamic and kinetics of complex formation in solutions. Most of these studies have been carried out in neat solvents [4, 5] or partly in mixtures of water and a few organic solvents [6, 7], consequently a little information is available about stability, selectivity and thermodynamics of complex formation in mixed non-aqueous solvents [8]. Studies of crown ethers complexation in different solvents show that the thermodynamic and kinetic parameters are affected by the nature and composition of the solvent systems [9]. Macrocyclic crown ethers which are similar to antibiotic ligands can be used as models for investigation of ion transport through membranes in biological systems [10], as a stationary phase in chromatography [11], and in the design of fiber optic chemical sensors [12].

A large number of physico-chemical techniques such as potentiometry [13], calorimetry [14], conductometry [15],

NMR spectroscopy [16], spectrophotometry [17] and polarography [18, 19] have been used for study of complexation reactions between crown ethers with different metal cations in solutions.

The goal of the present investigation is to study the effect of the nature of the cation, especially the solvent properties on the stability, selectivity and thermodynamic parameters of 18-Crown-6 complexes with Tl^+ , Hg^{2+} and Ag^+ cations in AN-MeOH and BN-MeOH binary systems using the conductometric technique.

Experimental

Reagents and solvents

18C6 (Aldrich), thallium nitrate (Prolabo), mercury(II) chloride (Aldrich), silver nitrate (Merck) were used without further purification. The solvents acetonitrile (Merck), benzonitrile (Riedel) and methanol (BDH) were used with the highest purity. The water content of the solvents was less than 100 ppm.

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, then a step-by-step

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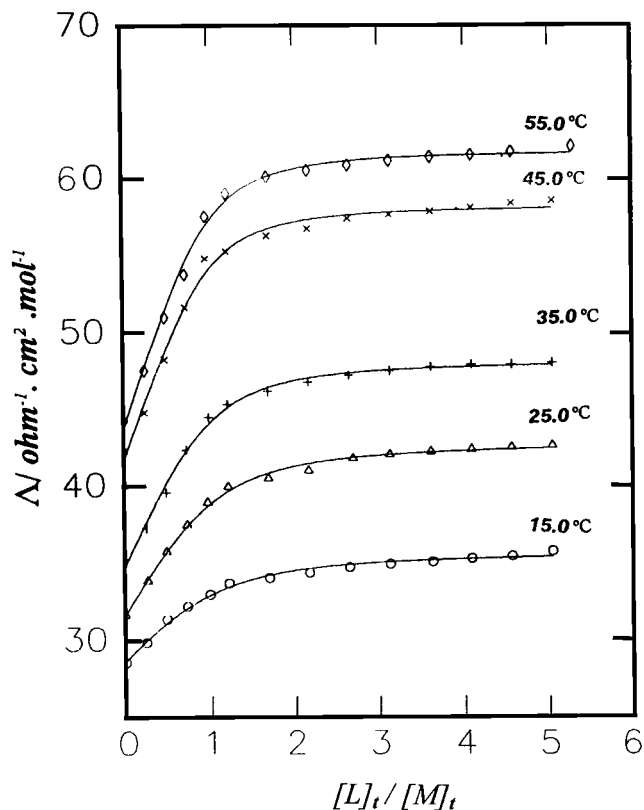


Figure 1. Molar conductance - mole ratio plots for the 18C6-Tl⁺ complex in BN-MeOH (mol% BN = 75) at different temperatures.

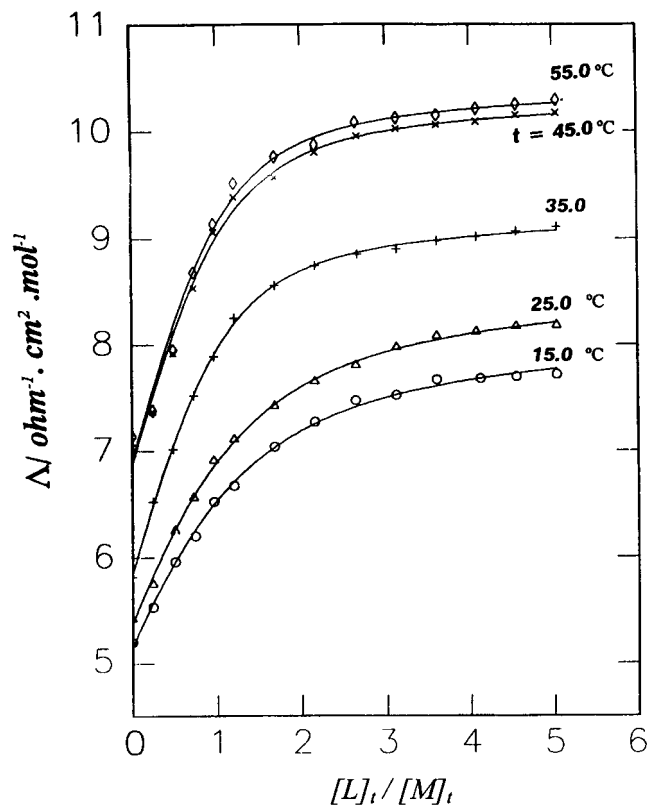


Figure 2. Molar conductance - mole ratio plots for the 18C6-Hg²⁺ complex in BN-MeOH (mol% BN = 75) at different temperatures.

increase in the crown ether concentration was carried out by a rapid transfer from crown ether solution prepared in the same solvent (3×10^{-2} 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.

Apparatus

The conductance measurements were performed on a digital AMEL conductivity apparatus, model 60 in a water bath thermostated with 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 0.79 cm^{-1} was used throughout the studies.

Results

The variations of molar conductance (Δ) versus the ligand to the cation molar ratio ($[L]_t/[M]_t$) for complexation of 18C6 with Tl⁺, Hg²⁺ and Ag⁺ cations in AN-MeOH and BN-MeOH binary systems were studied at different temperatures. Four typical series of molar conductance values as a function of Ligand/Metal Cation mole ratios in BN-MeOH (mol% BN = 75), BN-MeOH (mol% BN = 75) and AN-MeOH (mol% AN = 75) binary systems and in neat BN are shown in Figures 1-4, respectively.

The stability constants of the 18C6 crown ether complexes at each temperature were calculated from the vari-

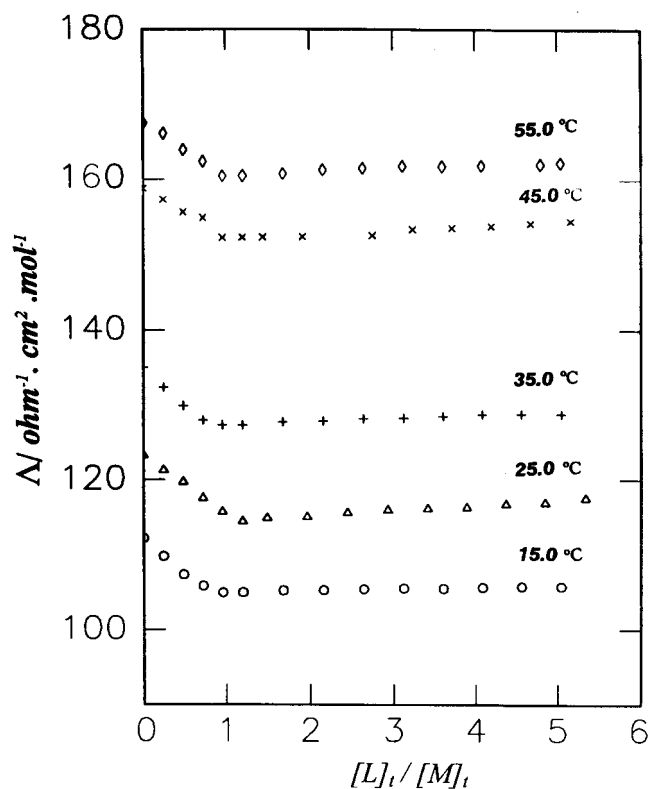


Figure 3. Molar conductance - mole ratio plots for the 18C6-Tl⁺ complex in AN-MeOH (mol% AN = 75) at different temperatures.

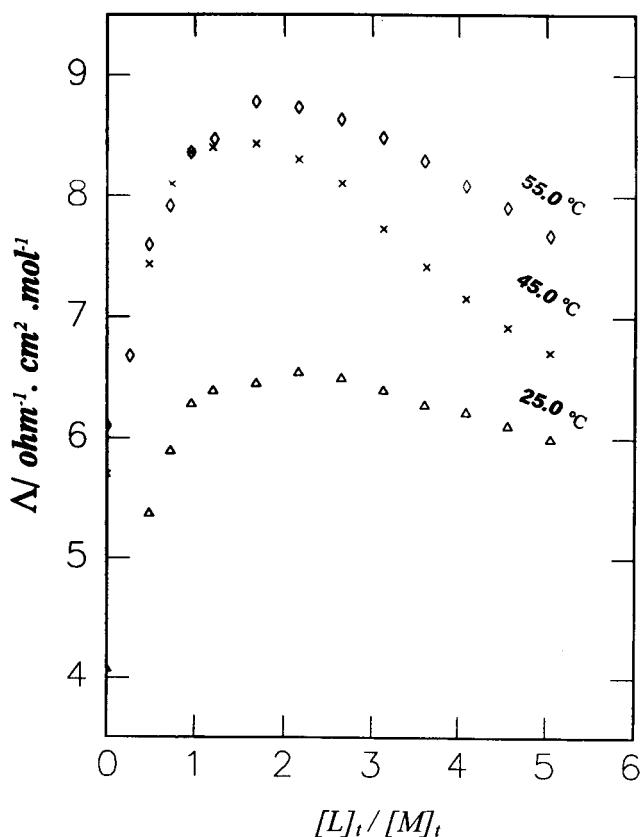


Figure 4. Molar conductance - mole ratio plots for the 18C6-Hg²⁺ complex in neat benzonitrile at different temperatures.

ation of the molar conductance as a function of Ligand/Mⁿ⁺ mole ratios using a GENPLOT computer program [20]. The details of the calculation of the stability constants of complexes by the conductometric method has been described elsewhere [18]. The values of the stability constants ($\log K_f$) for the 18C6-Mⁿ⁺ (Mⁿ⁺ = Tl⁺, Hg²⁺ and Ag⁺) complexes in various solvent systems are listed in Tables 1 and 2.

Assuming that the activity coefficients of the cation and complex have the same value, K_f is a thermodynamic equilibrium constant on the molar concentration scale, related to the Gibbs standard free energy of complexation reaction, ΔG_c^0 . The van't Hoff plots of $\log K_f$ versus $1/T$ for all of the investigated systems were constructed. A typical example of these plots is shown in Figure 5.

The changes in the standard enthalpy (ΔH_c^0) for the complexation reactions were obtained from the slope of the van't Hoff plots and the changes in standard entropy (ΔS_c^0) were calculated from the relationship $\Delta G_{c,298.15}^0 = \Delta H_c^0 - 298.15\Delta S_c^0$. The thermodynamic data are summarized in Tables 3 and 4.

The variations of $\log K_f$ versus the mole fraction of MeOH for (18C6.Hg)²⁺ complex in AN-MeOH and BN-MeOH binary systems at different temperatures are shown in Figures 6 and 7, and the variation of the stability constant ($\log K_f$) of the 18C6-Tl⁺, 18C6-Hg²⁺ and 18C6-Ag⁺ complexes as a function of cationic radii in various AN-MeOH binary systems is shown in Figure 8.

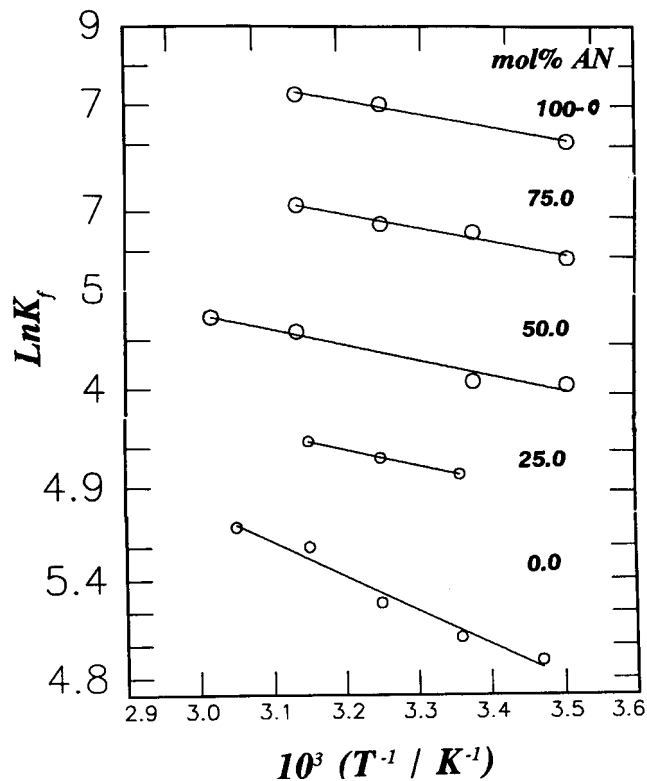


Figure 5. Van't Hoff plots for the 18C6-Hg²⁺ complex in AN-MeOH binary systems.

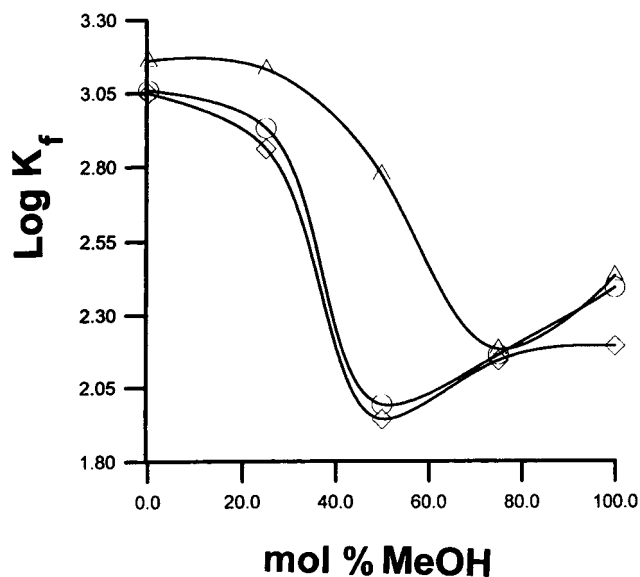


Figure 6. Variation of the stability constant of 18C6-Hg²⁺ with the composition of the AN-MeOH binary systems, at different temperatures.

Discussion

As seen from Figure 1, addition of 18C6 to thallium ion in BN-MeOH solutions at different temperatures results in an increase in molar conductivity which indicates that the 18C6-Tl⁺ complex in the BN-MeOH binary system is more mobile than free solvated Tl⁺ ion. The slope of the corresponding molar conductivity versus ligand/cation plots changes sharply at the point where the ligand to cation mole

Table 1. Log K_f values of 18C6-Hg²⁺, 18C6-Ag⁺ and 18C6-Tl⁺ complexes in AN-MeOH binary mixtures at different temperatures

Medium	Log $K_f \pm SD^a$				
	15°C	25°C	35°C	45°C	55°C
18C6-Hg ²⁺ ^b					
Pure AN	2.66 ± 0.04	3.05 ± 0.02	3.06 ± 0.01	3.16 ± 0.03	3.10 ± 0.07
75%AN-25%MeOH ^c	2.58 ± 0.08	2.86 ± 0.05	2.93 ± 0.04	3.13 ± 0.04	–
50%AN-50%MeOH	1.9 ± 0.2	1.9 ± 0.1	1.99 ± 0.08	2.77 ± 0.06	3.0 ± 0.1
25%AN-75%MeOH	~0	2.14 ± 0.05	2.16 ± 0.05	2.2 ± 0.1	~0
Pure MeOH	2.1 ± 0.1	2.2 ± 0.1	2.3 ± 0.1	2.4 ± 0.2	2.5 ± 0.1
18C6-Ag ⁺ ^b					
Pure AN	3.68 ± 0.07	3.54 ± 0.06	4.2 ± 0.1	4.5 ± 0.1	–
75%AN-25%MeOH ^c	2.2 ± 0.2	2.6 ± 0.1	3.0 ± 0.2	3.4 ± 0.1	3.47 ± 0.07
50%AN-50%MeOH	~0	~0	~0	~0	~0
25%AN-75%MeOH	1.6 ± 0.1	2.21 ± 0.02	2.38 ± 0.02	2.52 ± 0.05	2.63 ± 0.07
Pure MeOH	4.2 ± 0.2	4.6 ± 0.1	4.8 ± 0.1	4.9 ± 0.2	–
18C6-Tl ⁺					
Pure AN	d	d	d	d	d
75%AN-25%MeOH ^c	e	e	e	e	e
50%AN-50%MeOH	e	e	e	e	e
25%AN-75%MeOH	e	e	e	e	e
Pure MeOH	~0	~0	~0	~0	~0

^aSD= standard deviation.

^bThe concentration of each metal cation was 5.0×10^{-4} M.

^cComposition of binary mixtures is expressed in mole % for each solvent system.

^dThe salt is not dissolved.

^eThe data cannot be fitted in equations.

Table 2. Log K_f values of 18C6-Hg²⁺, 18C6-Ag⁺ and 18C6-Tl⁺ complexes in BN-MeOH binary mixtures at different temperatures

Medium	Log $K_f \pm SD^a$				
	15°C	25°C	35°C	45°C	55°C
18C6-Hg ²⁺ ^b					
Pure BN	e	e	e	e	e
75%BN-25%MeOH ^c	3.49 ± 0.04	3.52 ± 0.03	3.88 ± 0.06	3.94 ± 0.08	4.0 ± 0.1
50%BN-50%MeOH	3.02 ± 0.08	3.07 ± 0.06	3.38 ± 0.04	3.41 ± 0.05	3.5 ± 0.1
25%BN-75%MeOH	2.93 ± 0.01	3.01 ± 0.04	3.10 ± 0.06	3.13 ± 0.06	3.14 ± 0.05
Pure MeOH	2.1 ± 0.1	2.2 ± 0.1	2.3 ± 0.1	2.4 ± 0.2	2.5 ± 0.1
18C6-Ag ⁺ ^b					
Pure BN	3.2 ± 0.2	2.9 ± 0.1	2.8 ± 0.1	2.64 ± 0.05	2.59 ± 0.09
85%BN-15%MeOH ^c	~0	~0	~0	~0	~0
75%BN-25%MeOH ^c	~0	~0	~0	~0	~0
60%BN-40%MeOH	~0	~0	~0	~0	~0
50%BN-50%MeOH	3.38 ± 0.05	3.3 ± 0.2	2.92 ± 0.08	2.91 ± 0.09	2.76 ± 0.09
25%BN-75%MeOH	3.2 ± 0.7	3.05 ± 0.08	3.89 ± 0.09	2.8 ± 0.1	2.8 ± 0.2
Pure MeOH	4.2 ± 0.2	4.6 ± 0.1	4.8 ± 0.1	4.9 ± 0.2	–
18C6-Tl ⁺ ^b					
Pure BN	d	d	d	d	d
75%BN-25%MeOH ^c	3.87 ± 0.08	3.98 ± 0.06	4.15 ± 0.07	4.3 ± 0.1	4.34 ± 0.08
60%BN-40%MeOH	2.9 ± 0.1	3.13 ± 0.08	3.2 ± 0.1	3.4 ± 0.1	3.7 ± 0.1
50%BN-50%MeOH	2.8 ± 0.2	3.0 ± 0.1	3.2 ± 0.1	3.31 ± 0.08	3.44 ± 0.09
25%BN-75%MeOH	4.4 ± 0.2	5.2 ± 0.6	e	e	e
Pure MeOH	~0	~0	~0	~0	~0

^aSD = standard deviation.

^bThe concentration of each metal cation was 5.0×10^{-4} M.

^cComposition of binary mixtures is expressed in mole % for each solvent system.

^dThe salt is not dissolved.

^eThe data cannot be fitted in equations.

Table 3. Thermodynamic parameters for 18C6-Hg²⁺, and 18C6-Ag⁺ complexes in AN-MeOH binary mixtures

Medium	Log $K_f \pm SD^a$ 25°C	$-\Delta G_c^0 \pm SD^a$ (25°C) (KJ/mol)	$\Delta H_c^0 \pm SD^a$ (KJ/mol)	$\Delta S_c^0 \pm SD^a$ (J/mol K)
18C6-Hg ²⁺				
Pure AN	3.05 ± 0.02	17.4 ± 0.1	30 ± 3	163 ± 12
75%AN-25%MeOH ^b	2.86 ± 0.05	16.3 ± 0.3	29 ± 4	155 ± 12
50%AN-50%MeOH	1.9 ± 0.1	10.9 ± 0.8	54 ± 8	217 ± 29
25%AN-75%MeOH	2.14 ± 0.05	12.5 ± 0.6	17 ± 1	100 ± 4
Pure MeOH	2.2 ± 0.1	12.5 ± 0.4	17 ± 4	96 ± 12
18C6-Ag ⁺				
Pure AN	3.54 ± 0.06	20.2 ± 0.3	75 ± 12	321 ± 41
75%AN-25%MeOH ^b	2.6 ± 0.1	15.0 ± 0.8	58 ± 4	250 ± 12
25%AN-75%MeOH	2.21 ± 0.02	12 ± 1	26 ± 1	45 ± 4
Pure MeOH	4.6 ± 0.1	26.3 ± 0.8	25 ± 2	172 ± 2

^aSD = standard deviation.

^bComposition of binary mixtures is expressed in mole % for each solvent system.

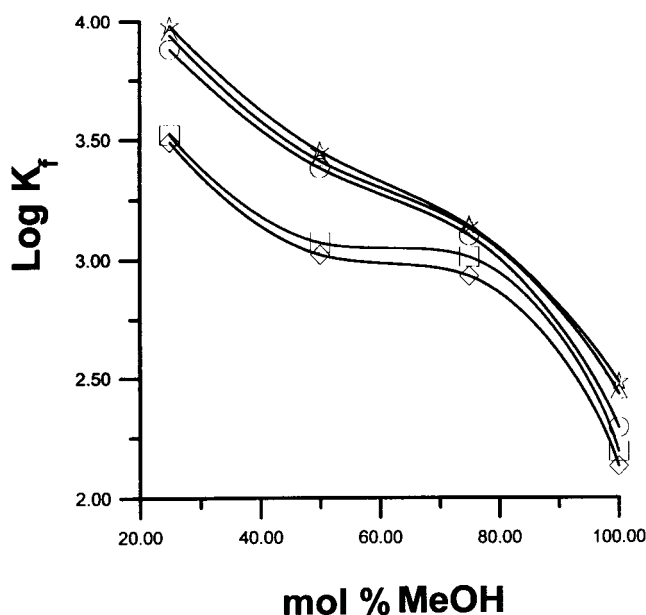


Figure 7. Variation of the stability constant of 18C6-Hg²⁺ with the composition of the AN-MeOH binary systems at different temperatures.

ratio is 1, which is evidence for formation of a relatively stable 1:1 complex.

It is evident from Figure 1, that the curvature of the plots of the 18C6-Tl⁺ complex increases as temperature increases which is evidence for formation of a stronger complex at higher temperatures. A similar behaviour is observed for the 18C6-Hg²⁺ complex in AN-MeOH and BN-MeOH binary mixtures and also for the 18C6-Tl⁺ in BN-MeOH binary systems, therefore, there is an endothermic reaction between Tl⁺ and Hg²⁺ ions with 18C6 in these binary mixed solvents, but in the case of the 18C6-Ag⁺ complex, the stability constant decreases with increasing temperature in BN-MeOH binary mixtures which is evidence for an exothermic reaction between Ag⁺ ion and 18C6 in these solvent systems.

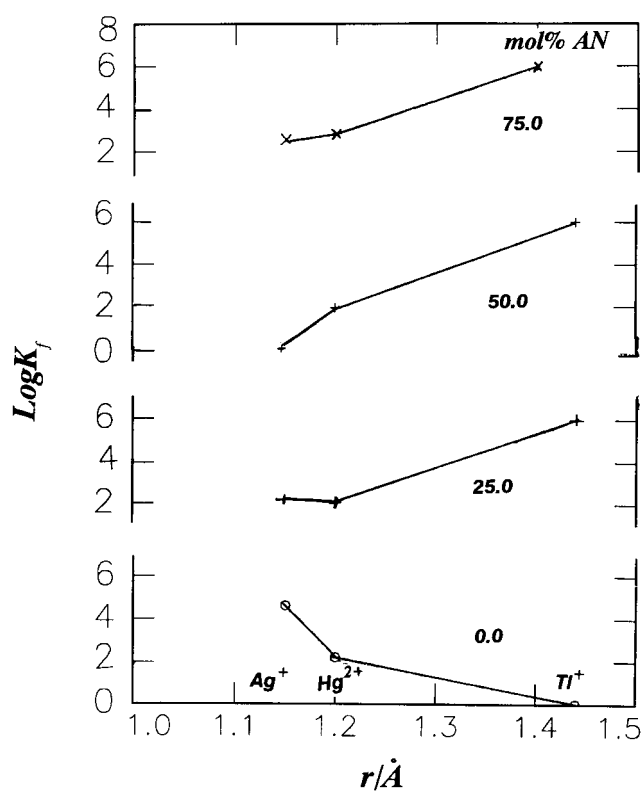


Figure 8. Variation of log K_f for the 18C6-Tl⁺, 18C6-Hg²⁺ and 18C6-Ag⁺ complexes vs cationic radii in AN-MeOH binary solvent systems at 25 °C.

As seen from Table 1, in most cases as the concentration of AN is increased in AN-MeOH binary mixtures, the stability of the complexes increases. These results seem reasonable, since in methanol with a relatively high Gutmann Donor Number (DN = 20), the solvation of the cations should be stronger than acetonitrile with lower solvating ability (DN = 14).

As is obvious from Figure 3, addition of 18C6 to thallium ion solution, causes the molar conductivity to initially de-

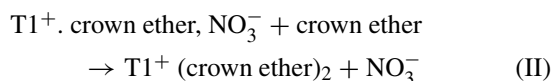
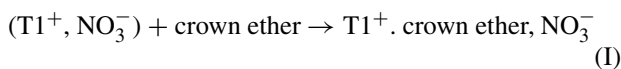
Table 4. Thermodynamic parameters for 18C6-Hg²⁺, 18C6-Ag⁺ and 18C6-Tl⁺ complexes in BN-MeOH binary mixtures

Medium	Log $K_f \pm SD^a$ 25°C	$-\Delta G_c^0 \pm SD^a$ (25°C) (KJ/mol)	$\Delta H_c^0 \pm SD^a$ (KJ/mol)	$\Delta S_c^0 \pm SD^a$ (J/mol K)
18C6-Hg ²⁺				
75%BN-25%MeOH ^b	3.52 ± 0.03	20.1 ± 0.2	25 ± 4	150 ± 12
50%BN-50%MeOH	3.07 ± 0.06	17.5 ± 0.4	21 ± 5	130 ± 12
25%BN-75%MeOH	3.01 ± 0.04	17.2 ± 0.2	9.6 ± 0.8	90 ± 2
Pure MeOH	2.2 ± 0.1	12.5 ± 0.4	17 ± 4	96 ± 12
18C6-Ag ⁺				
Pure BN	2.9 ± 0.1	16.7 ± 0.8	-29 ± 4	-42 ± 17
50%BN-50%MeOH ^b	3.3 ± 0.2	18.8 ± 0.8	-29 ± 2	-33 ± 8
25%BN-75%MeOH	3.05 ± 0.08	17.6 ± 0.4	-22 ± 3	-17 ± 8
Pure MeOH	4.6 ± 0.1	26.3 ± 0.8	25 ± 2	172 ± 2
18C6-Tl ⁺				
75%BN-25%MeOH ^b	3.98 ± 0.06	22.7 ± 0.3	23 ± 3	155 ± 12
60%BN-40%MeOH	3.13 ± 0.08	18.0 ± 0.4	33 ± 4	171 ± 12
50%BN-50%MeOH	3.0 ± 0.1	17.1 ± 0.4	28 ± 1	151 ± 4

^aSD = standard deviation.

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

crease until the mole ratio reaches 1 : 1 and then to increase. Such behaviour may be described according to the following equilibria:



It seems that addition of the ligand to thallium ion solution results in formation of a relatively stable 1 : 1 complex which is present as an ion-pair (I), then addition of the second ligand to the ion-pair complex, causes formation of a stable 1 : 2 complex with a sandwich structure (II) which decreases the space for diffusion and interaction of the NO₃⁻ ion with the Tl⁺ cation and results in dissociation of the ion pair. A similar behaviour has been observed by Takeda and co-workers in their study of complex formation between 18C6 with Li⁺, K⁺ and Rb⁺ cations and also for complexation reaction between DC18C6 with Tl⁺ cation in AN-MeOH (mol% AN = 50) binary system [21, 22].

It is interesting to note that in neat benzonitrile (a solvent with a low donicity; DN = 11.9) as the 18C6/Hg²⁺ mole ratio increases from 0 to 1, the molar conductivity increases, then further addition of the ligand causes the molar conductivity to decrease. This behaviour probably indicates a two step complexation, first the formation of a 1 : 1 complex then addition of the second ligand gives a 2 : 1 (ligand : metal ion) sandwich complex.

As is evident from Tables 3 and 4, the enthalpy and entropy values for the complexation reactions vary with the nature and composition of the mixed solvents. The experimental values of ΔH_c^0 and ΔS_c^0 show that in most cases,

except for the 18C6-Ag⁺ complex in BN-MeOH binary mixtures, the complexes are entropy stabilized but enthalpy destabilized, therefore, the entropies of complexation reactions are the principal driving forces for formation of these complexes. The variations of the log K_f of 18C6-Hg²⁺ complex as a function of MeOH concentration in AN-MeOH and BN-MeOH binary systems are shown in Figures 6 and 7, respectively. Investigation of these figures shows that the complexation process in these mixed non-aqueous solvents is quite sensitive to the solvent composition.

It is interesting to note that in BN-MeOH solutions, the variation of the stability constants of the 18C6-Hg²⁺ complex versus the solvent composition is not linear. A non-linear behaviour is also observed for this complex in AN-MeOH binary systems. This behaviour may reflect changes occurring in the structure of the solvent mixtures and, therefore, in the solvation properties of the cyclic polyether and cation or even complex in these solvent mixtures. Some structural changes probably occur in the structure of the solvents when they mix with one another. These structural changes may result in changing the interactions of those solvents with the solutes compared to the pure solvents. Prasad and co-workers have studied the interactions between acetonitrile and methanol molecules by excess adiabatic compressibility (β^E) and excess intermolecular free length (L_f^E) measurements at 303.15 K and they showed that these parameters become increasingly negative with increasing strength of interaction between the component molecules [23]. In addition, it has been shown that there is an interaction between acetonitrile and methanol molecules ($K_{ass} = 1.23$) via hydrogen bonding in their binary mixtures [24].

The variation of log K_f of the 18C6-Ag⁺, 18C6-Tl⁺ and 18C6-Hg²⁺ complexes vs the ionic radii in various AN-MeOH binary mixtures is shown in Figure 8. As is evident from this figure, the order of stability of complexes in 50-

50 mol% and 75-25 mol% of AN-MeOH binary mixtures is $18C6-T1^+ > 18C6-Hg^{2+} > 18C6-Ag^+$. The $T1^+$ cation forms a more stable complex with 18C6 than the other two cations. This result seems reasonable, because the ionic size of the $T1^+$ cation (1.47 Å) is very close to the size of the 18C6 cavity (1.3–1.6 Å) [25, 26]. In addition, the $T1^+$ ion is bound in the complex by an ion–dipole interaction with a covalent contribution [27]. Since the ionic size of the Ag^+ ion is smaller than the size of the 18C6 cavity, and it does not have a good fit condition, the Ag^+ ion forms a less stable complex compared to the $T1^+$ and Hg^{2+} ions.

It is interesting to note that the order of stability of complexes formed between 18C6 and these cations in neat methanol is $Ag^+ > Hg^{2+} > T1^+$, therefore, a reversal in stabilities is observed in neat MeOH compared with AN-MeOH binary mixed systems. This reversal of stabilities indicates the possibility of changes in stabilities and, therefore, reversal of cation selectivities which can be obtained in certain compositions of the mixed solvent systems.

Acknowledgement

The authors gratefully acknowledge the support of this research by National Research Council of I.R. Iran (NRCI) as a National Research Project under the grant number 265.

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