

# Conductance and Thermodynamic Study of Thallium and Silver Ion Complexes with Crown Ethers in Different Binary Acetonitrile–Water Solvent Mixtures

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(Received: 3 December 1996; in final form: 11 July 1997)

**Abstract.** The complexation reactions between  $\text{Ag}^+$  and  $\text{Tl}^+$  ions with 15-crown-5 (15C5) and phenyl-aza-15-crown-5 (PhA15C5) have been studied conductometrically in 90% acetonitrile-water and 50% acetonitrile - water mixed solvents at temperatures of 293, 298, 303 and 308 K. The stability constants of the resulting 1 : 1 complexes were determined, indicating that the  $\text{Tl}^+$  complexes are more stable than the  $\text{Ag}^+$  complexes. The enthalpy and entropy of crown complexation reactions were determined from the temperature dependence of the complexation constants. The enthalpy and entropy changes depend on solvent composition and the  $T\Delta S^0 - \Delta H^0$  plot shows a good linear correlation, indicating the existence of entropy – enthalpy compensation in the crown complexation reactions.

**Key words:** crown ether; thallium and silver nitrate; conductivity; formation constant; enthalpy; entropy.

## 1. Introduction

Pedersen's [1] discovery of macrocyclic polyethers (crowns) and their complexation with alkali and alkaline earth cations opened the door to several broad and fruitful areas of chemical investigation. During the past two decades, several hundreds of macrocyclic ligands have been synthesized and their complexation with a variety of metal ions and with neutral molecules have been studied by a number of different techniques [2–4].

The stability of crown complexes is the most significant feature of these complexes. This depends on several factors, including the relative size of the cation and the macrocyclic cavity, the number and nature of binding sites, the acid-base character of metal ions and the nature of the solvent. All the above mentioned factors affect the stability and selectivity of the crowns toward cations.

Interest in the study of the complexation of thallium and silver with crown ethers is due to their importance in biological and environmental processes [5,6]. Previous studies on the selective complexation between  $\text{Tl}^+$  and  $\text{Ag}^+$  with ionic radii 1.49

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Å and 1.15 Å, respectively, with different crown ethers showed the formation of relatively stable 1 : 1 complexes in various solvents. Literature studies [7–11] report the formation of 1 : 1 complexes between  $\text{Ag}^+$  and  $\text{Tl}^+$  cation with smaller sized crown ethers such as 12C4, 15C5, 18C6 and their substituted analogues. On the other hand, potentiometric studies [9, 11] of the complexation of 15C5 with  $\text{Tl}^+$  and  $\text{Ag}^+$  in PC solvent showed the formation of 2 : 1 complexes. It is obvious that the ion-in-the hole concept cannot explain the formation of the 1 : 1 complexes between large cations such as  $\text{Ag}^+$  and  $\text{Tl}^+$  with smaller size crown ethers such as 15C5 and it is clear that the solvent plays a fundamental role in determining the stoichiometry of the complexes.

Currently, there is increasing interest in the study of complexation phenomena in binary mixed solvent systems and their interpretation in terms of solute preferential solvation by one of the mixed solvent components [12–16]. In this paper we present the stability constants at different temperatures for  $\text{Tl}^+$  and  $\text{Ag}^+$  complexes with 15C5 and PhA15C5 in different  $\text{CH}_3\text{CN-H}_2\text{O}$  mixtures. Values of  $\Delta H^0$  and  $\Delta S^0$  at 298 K are also presented and their significance is discussed.

## 2. Experimental

Reagent grade thallium nitrate (BDH) and silver nitrate (Park) were of the highest commercial purity available, (98%) and (99.5%), respectively, and were used without further purification except for vacuum drying over  $\text{P}_2\text{O}_5$ . The crown ethers 15C5 (Fluka) and PhA15C5 (Merck) were of high purity, and were used as received. HPLC-grade acetonitrile,  $\text{CH}_3\text{CN}$ , was purchased from Gainleind Chemical Company, and used without further purification. Triply distilled water was used for the preparation of the solvent mixtures. The conductivities of the solvents were less than  $1 \times 10^{-7} \text{ S cm}^{-1}$ .

The conductance measurements were carried out with a Metrohm E 512 conductometer. A conductivity cell (Metrohm EA-645-2) with a cell constant of  $2.14 \text{ cm}^{-1}$  was used. This value was determined by measuring the conductivity of aqueous potassium chloride solutions of different concentrations [12]. In all measurements the cell was thermostatted at the required temperature ( $0.1^\circ\text{C}$ , using a Haak Mess-Technik GmbH U.Co., Type F3 thermostat).

Acetonitrile–water solutions of silver and thallium nitrates with concentrations of about  $(1.0\text{--}1.5) \times 10^{-4} \text{ mol. dm}^{-3}$  were used. These solutions, with the same total salt concentration, were also used as solvent for preparing the crown ether solutions.

In order to determine the complex formation constant of crown ethers with  $\text{Ag}^+$  and  $\text{Tl}^+$  ion, 25 mL of the desired metal nitrate solution was placed in a titration cell, thermostatted to the desired temperature and its conductance was measured. A known amount of the crown ether solutions of about  $(1.8\text{--}2.0) \times 10^{-3} \text{ M}$  was added in a stepwise manner using a microburette (with sensitivity  $\pm 0.01 \text{ cm}^3$ ). After stirring the mixture magnetically for about one minute, the cell was placed

in the thermostat and the conductivity was measured after about five minutes. This procedure was repeated in the same manner for each addition until the ligand to metal ion mole ratio was about 5 : 1.

The conductivity data were analyzed according to a nonlinear least squares curve fitting procedure based on a 1 : 1 metal to ligand complex formation model [17–18]. Least squares analysis of  $\log K$  vs  $1/T$  data was carried out using a linear fitting program.

### 3. Mathematical Treatment

The 1 : 1 binding of TI<sup>+</sup> and Ag<sup>+</sup> with the ligands 15C5 and ph-aza-15C5 can be described by the following equilibrium:



$M^+$ ,  $L$ ,  $ML^+$  and  $K_f$  represent the free solvated cation, the free ligand, the complex and the equilibrium constant, respectively. The thermodynamic equilibrium constant,  $K_f$ , for the association is given by the equation

$$K_f = \frac{[ML^+]f(ML^+)}{[M^+][L]f(M^+)f(L)} \quad (2)$$

where  $[ML^+]$ ,  $[M^+]$ ,  $[L]$  and  $f$  represent the equilibrium molar concentrations of the complex, the free cation, the free ligand and the activity coefficients of the species indicated, respectively. Under the dilute conditions used, where the ionic strength is less than 0.001 mol dm<sup>3</sup>, the activity coefficient of the uncharged ligand  $f(L)$  can be reasonably assumed to be unity. The use of the Deby–Hückel limiting law of electrolytes leads to the conclusion that  $f(ML^+) \cong f(M^+)$ , so the activity coefficients in Equation (2) cancel and this equation reduces to

$$K_f = \frac{[ML^+]}{[M^+][L]} \quad (3)$$

If  $\alpha$  is the fraction of total metal that is uncomplexed with the ligand, then the following equations result

$$[M^+] = \alpha[M]_t \quad (4)$$

$$[ML^+] = (1 - \alpha)[M]_t \quad (5)$$

$$[L] = [L]_t - (1 - \alpha)[M]_t \quad (6)$$

where  $[M]_t$ ,  $[L]_t$ ,  $[M^+]$ ,  $[ML^+]$  and  $[L]$  represent the concentration (mol dm<sup>-3</sup>) of total cation, total ligand, free uncomplexed cation, the complex and free solvated ligand respectively.

The dilute conditions used make it possible to neglect ion aggregation and corrections for viscosity changes. The molar conductivities,  $\Lambda$ , can be calculated by using the following equation

$$\Lambda (\text{Scm}^2, \text{mol}^{-1}) = \frac{10^3 \kappa}{[\text{M}]_t}, \quad (7)$$

where  $\kappa$  is the conductivity of the test solution in  $\text{S cm}^{-1}$ . On the other hand,  $\Lambda$  can be related to  $\alpha$  by the following equation

$$\Lambda = \alpha \Lambda_o + (1 - \alpha) \Lambda_c, \quad (8)$$

where  $\Lambda_o$  and  $\Lambda_c$  represent the molar conductivities of the ligand-free metal salt solution and the complexed cation solution at the same concentration, respectively. Substituting Equations (4) and (5) into Equation (3), gives the following equation

$$K_f = \frac{(1 - \alpha)}{\alpha [\text{L}]}. \quad (9)$$

The value of  $\alpha$  can be found from Equation (8) as given below

$$\alpha = \frac{\Lambda - \Lambda_c}{\Lambda_o - \Lambda_c}. \quad (10)$$

Substitution of Equation (10) into Equations (6) and (9) gives

$$[\text{L}] = [\text{L}]_t - \left\{ \frac{\Lambda_o - \Lambda}{\Lambda_o - \Lambda_c} \right\} [\text{M}]_t, \quad (11)$$

$$K_f = \frac{(\Lambda_o - \Lambda)}{[\text{L}](\Lambda - \Lambda_c)}. \quad (12)$$

Substitution of Equation (11) into Equation (12) results in the following equation

$$K = a_1 a_2 / (a_2 a_3 [\text{L}]_t - a_1 a_3 [\text{M}]_t), \quad (13)$$

where

$$a_1 = \Lambda_o - \Lambda \quad (14)$$

$$a_2 = \Lambda_o - \Lambda_c \quad (15)$$

$$a_3 = \Lambda - \Lambda_c. \quad (16)$$

Equation (13) can be rearranged to give a quadratic equation in  $\Lambda$  as follows

$$a\Lambda^2 + b\Lambda + c = 0, \quad (17)$$

where

$$a = K[M]_t \quad (18)$$

$$b = b_2(K[L]_t + 1) - [M]_t K(\Lambda_o + A_c) \quad (19)$$

$$c = [M]_t K \Lambda_o \Lambda_c - a_2([L]_t K \Lambda_c + A_o). \quad (20)$$

The solution of Equation (17) is given as

$$\Lambda_{\text{cal}} = \frac{-b}{2a} + \frac{(b^2 - 4ac)^{1/2}}{2a}. \quad (21)$$

$\Lambda_{\text{cal}}$  represents the calculated value of the molar conductivities in the simplex program which is to be compared with the experimental values we found. The calculation of  $K_f$  from the conductivity data is achieved by means of the simplex program listed elsewhere [17]. This program is based upon the fitting of the experimental data with the calculated data using Equation (21).

#### 4. Results and Discussion

The molar conductance of the nitrate salts of Tl<sup>+</sup> and Ag<sup>+</sup> in AN-H<sub>2</sub>O solvent mixtures was monitored as a function of the crown to metal ion mole ratio at various temperatures. The resulting molar conductance-mole ratio plots are shown in Figures 1 and 2. As can be seen, except for Tl<sup>+</sup> with both crowns in 90% AN-H<sub>2</sub>O solvent mixture, addition of crown ether to the metal ion solution causes a continuous increase in the molar conductance of the solutions. When the 90% AN-H<sub>2</sub>O solvent mixture was used both crown ethers showed the same behavior, where addition of crowns to Tl<sup>+</sup> solution causes a continuous decrease in the molar conductance of the resulting solutions, indicating a lower mobility of the thallium ion crown complex compared to the solvated cation. Figure 1 shows that in the 90% AN-H<sub>2</sub>O solvent, addition of crowns to the thallium solution results in a rather sharp decrease in the molar conductance which begins to level off at a mole ratio of about unity. The slope of the corresponding mole ratio plots changes at the point where the crown-to-cation mole ratio is equal to one, emphasizing the formation of a fairly stable 1 : 1 complex. However, the sharp decrease of the slope of the Tl<sup>+</sup>-15C5 system indicates that this complex is more stable than Tl<sup>+</sup>-PhA15C5. In contrast, the Ag<sup>+</sup>-crown solution showed opposite behavior, that is, the addition of crown to Ag<sup>+</sup> solution causes an increase in the molar conductance. This might indicate that the complex formed is more mobile than the solvated Ag<sup>+</sup>. However, the first addition of crown ether to the 90% AN-H<sub>2</sub>O solution of Ag<sup>+</sup> caused a relatively sharp increase in the conductivity. The second and subsequent additions of crown ether causes a slight increase in conductivity then levels off.

This behavior could be explained as follows: it is well known that Ag<sup>+</sup> strongly complexes with acetonitrile [19] and such a solvated cation will be highly ordered

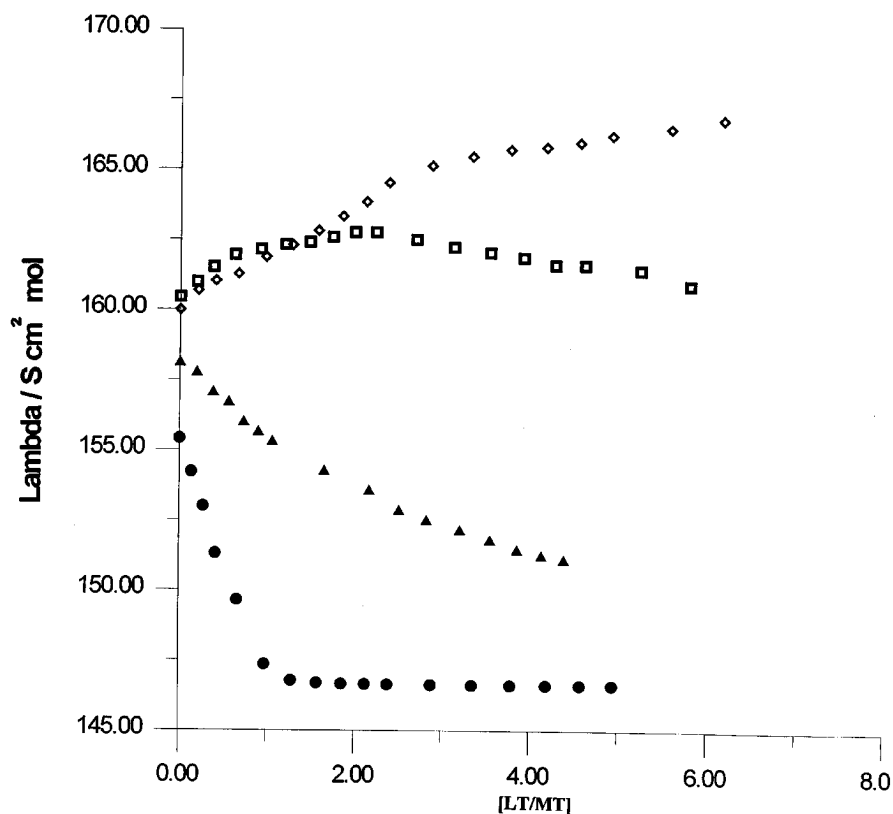


Figure 1. Molar Conductance vs.  $[LT]/[MT]$  curves for different thallium-crown complexes in various AN-H<sub>2</sub>O mixtures at 25 °C. ◇ 50% AN-H<sub>2</sub>O-15C5; □ 50% AN-H<sub>2</sub>O-PhA15C5; ▲ 90% AN-H<sub>2</sub>O-PhA15C5; ● 90% AN-H<sub>2</sub>O-15C5.

and sluggish. The first addition of crown ether will complex with  $Ag^+$  resulting in a more mobile system with relatively high conductivity. Further additions of crown ether to the relatively mobile system will cause a gradual increase in conductivity. However, the slope of the corresponding molar conductance-mole ratio plots change at the point where the crown to cation ratio is one and further additions of the crown cause no or very slight changes in the molar conductance. Such a conductance behavior is indicative of the formation of a 1 : 1 complex in solution.

The increase in the H<sub>2</sub>O percentage changed the properties of the solutions. In 50% AN-H<sub>2</sub>O solvent mixture both cations showed an increase in molar conductance with both crowns, which indicates that the mobility of the resulting crown ether complex is larger than that of the free solvated metal ion. The selectivity of both crowns for  $Tl^+$  in 90% AN-H<sub>2</sub>O solvent is signified by an appreciable curvature in the  $\Lambda$  vs  $[LT]/[MT]$  ratio as indicated in Figure 1.

However, an unusual conductance behavior was observed for the complexation of PhA15C5 with thallium nitrate in 50% AN-H<sub>2</sub>O solvent mixture. Figure 1

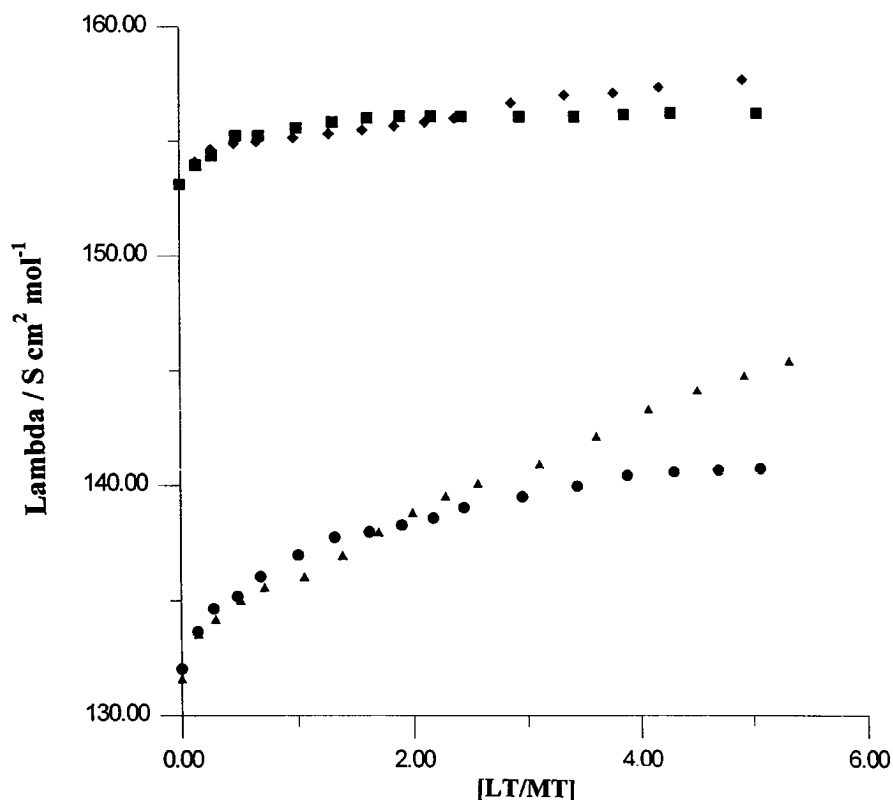


Figure 2. Molar conductance vs.  $[LT]/[MT]$  curves for different silver-crown complexes in various AN-H<sub>2</sub>O mixtures at 25 °C. ♦ 90% AN-H<sub>2</sub>O-15C5; ■ 90% AN-H<sub>2</sub>O-PhA15C5; ▲ 50% AN-H<sub>2</sub>O-PhA15C5; ● 50% AN-H<sub>2</sub>O-15C5.

shows that the molar conductance increases slightly and gradually until the molar ratio of crown to metal equals two. Further addition of the crown results in a very slight decrease in the molar conductance. This behavior probably results from the formation of a sandwich 2 : 1 (crown/Ti<sup>+</sup>) complex in addition to the 1 : 1 complex in agreement with the reported study by Farago et al. [7]. The small increase in the molar conductance of the above complex indicates that the mobility of this complex is slightly higher than the solvated Ti<sup>+</sup> cation. Evidence for the formation of a 1 : 1 complex comes from the change in the slope of the corresponding molar conductance-mole ratio plots. It changes at the point where the ligand to cation mole ratio is about one. Further additions of crown ethers will complex with the 1 : 1 complex producing the 2 : 1 complex. However, due to the limited capability of the program used we were able to calculate only the formation constant for the 1 : 1 complex as reported in Table I.

In order to achieve a better understanding of the thermodynamics of crown complexes, it is useful to consider the enthalpic and entropic contributions to these

Table I. Formation constants, enthalpies and entropies for different  $\text{Ti}^+$ -crown ether complexes.

System	Solvent	$\log K_f$				$\Delta H^0 f$ (kJ/mol)	$\Delta S^0$ (J/mol K)	Ref.
		20 °C	25 °C	30 °C	35 °C			
$\text{Ti}^+-15\text{C}5$	90% AN-H <sub>2</sub> O	6.21 ± 0.16	6.14 ± 0.15	6.07 ± 0.12	6.01 ± 0.12	23.2 ± 1.0	39.8 ± 1.5	This work
$\text{Ti}^+-15\text{C}5$	50% AN-H <sub>2</sub> O	5.08 ± 0.10	4.99 ± 0.11	4.90 ± 0.10	4.81 ± 0.09	31.1 ± 1.2	8.8 ± 0.6	This work
$\text{Ti}^+-\text{PhA}15\text{C}5$	90% AN-H <sub>2</sub> O	4.10 ± 0.07	4.05 ± 0.07	3.99 ± 0.06	3.94 ± 0.05	18.6 ± 1.0	14.8 ± 0.8	This work
$\text{Ti}^+-\text{PhA}15\text{C}5$	50% An-H <sub>2</sub> O*	3.60 ± 0.05	3.58 ± 0.04	3.56 ± 0.03	3.53 ± 0.03	7.9 ± 0.7	41.9 ± 1.7	This work
$\text{Ti}^+-15\text{C}5$	MeOH		3.91					[26]
$\text{Ti}^+-15\text{C}5$	DMF		0.91					[12]
$\text{Ti}^+-15\text{C}5$	PC		5.92					[11]

\*  $K_f$  values were calculated for a 1 : 1 crown to  $\text{Ti}^+$  complex.



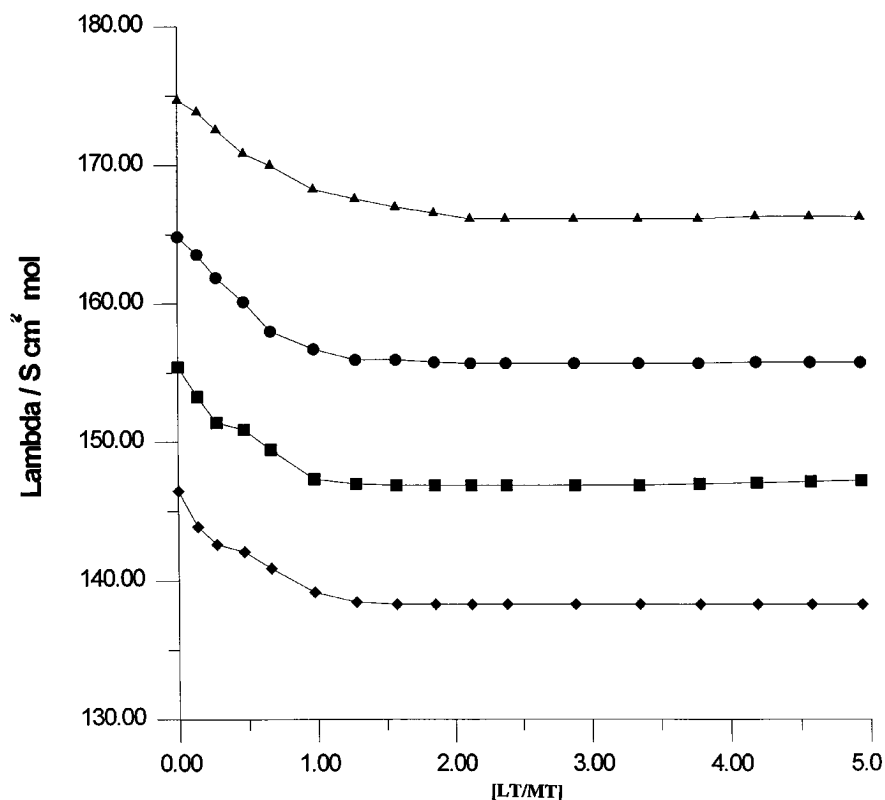


Figure 3. Molar conductance vs.  $[15C5]/[Tl^+]$  curves in 90% AN-H<sub>2</sub>O mixture at various temperatures. ▲ 35 °C; ● 30 °C; ■ 25 °C; ◆ 20 °C.

reactions. These thermodynamic parameters were evaluated from the temperature dependence of the formation constants of crown ether complexes. Figure 3 is an example which shows the effect of temperature on the stability constant, where  $K_f$  decreases as the temperature increases. This indicates that binding of Tl<sup>+</sup> and Ag<sup>+</sup> with both crowns is an exothermic process. Due to the lack of literature information on the complexation of PhA15C5 with Tl<sup>+</sup> and Ag<sup>+</sup>, we were not able to compare our results with literature values. However, a comparison of our results for the values of  $\log K_f$  for 1 : 1 complexes of 15C5 with Tl<sup>+</sup> and Ag<sup>+</sup> with literature values showed that our results are in agreement with the reported  $\log K_f$  values. For comparison purposes, some literature values of  $\log K$  for 15C5 complexes with Tl<sup>+</sup> and Ag<sup>+</sup> are included in Tables I and II [9–11].

The results in Tables I and II show that with 15C5 the  $-\Delta H^0$  values for Tl<sup>+</sup> complexes are higher than those of Ag<sup>+</sup> in both solvents indicating that the Tl<sup>+</sup> complexes with both crowns are more stable than the Ag<sup>+</sup> complexes. The fact that Tl<sup>+</sup> is weakly solvated compared to Ag<sup>+</sup>, will result in more exothermic complexes of Tl<sup>+</sup>.

Table II. Formation constants, enthalpies and entropies for different Ag<sup>+</sup>-crown ether complexes.

System	Solvent	log $K_f$			$\Delta H^0 f$ (kJ/mol)	$\Delta S^0$ (J/mol K)	Ref.
		20 °C	25 °C	35 °C			
Ag <sup>+</sup> -15C5	90% AN-H <sub>2</sub> O	5.00 ± 0.12	4.96 ± 0.10	4.91 ± 0.10	4.85 ± 0.08	17.3 ± 0.8	This work
Ag <sup>+</sup> -15C5	50% AN-H <sub>2</sub> O	4.59 ± 0.13	4.58 ± 0.08	4.56 ± 0.08	4.55 ± 0.07	4.8 ± 0.30	This work
Ag <sup>+</sup> -PhA15C5	90% AN-H <sub>2</sub> O	4.94 ± 0.10	4.93 ± 0.10	4.92 ± 0.10	4.91 ± 0.09	3.4 ± 0.2	This work
Ag <sup>+</sup> -PhA15C5	50% An-H <sub>2</sub> O	4.00 ± 0.08	3.99 ± 0.07	3.98 ± 0.08	3.97 ± 0.07	3.5 ± 0.1	This work
Ag <sup>+</sup> -15C5	MeOH		0.94				[10]
Ag <sup>+</sup> -15C5	DMF		3.62				[13]
Ag <sup>+</sup> -15C5	PC		6.24				[11]

Table III. The molar conductivities of thallium and silver complexes at 25 °C in different AN–H<sub>2</sub>O mixed solvents.

L	MA	$\Lambda_{MLA}$ ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )	$[MT] \times 10^4$ ( $\text{mol-dm}^{-3}$ )	Medium
15C5	TlNO <sub>3</sub>	148	2.0	90% AN–H <sub>2</sub> O
15C5	TlNO <sub>3</sub>	170	1.2	50% AN–H <sub>2</sub> O
PhA15C5	TlNO <sub>3</sub>	151	1.4	90% AN–H <sub>2</sub> O
PhA15C5	TlNO <sub>3</sub>	163	1.1	50% AN–H <sub>2</sub> O
15C5	AgNO <sub>3</sub>	161	1.2	90% AN–H <sub>2</sub> O
15C5	AgNO <sub>3</sub>	149	1.1	50% AN–H <sub>2</sub> O
PhA15C5	AgNO <sub>3</sub>	159	1.2	90% AN–H <sub>2</sub> O
PhA15C5	AgNO <sub>3</sub>	144	1.3	50% AN–H <sub>2</sub> O

On the other hand, the 15C5 complexes with Tl<sup>+</sup> and Ag<sup>+</sup> are more stable than those of PhA15C5. This unexpected behavior could be due to the formation of H-bonding between the nitrogen atom and protic solvents such as our system. This behavior has been reported by Parham and Shamsipur [16]. The  $\Delta S^0$  values do not correlate with the stability constant. It is worth noting that the  $\Delta S^0$  values of Ag<sup>+</sup> complexes are higher than those of Tl<sup>+</sup> complexes, emphasizing the conclusion that the Ag<sup>+</sup> cation is more solvated than Tl<sup>+</sup>.

The enthalpy–entropy compensation is observed in almost all systems studied. The unfavorable enthalpic contribution is compensated by large values of  $\Delta S^0$  resulting in large values of  $\log K$ .

It is very important to notice that the solvent plays a major role in the stability of the complexes. Except for the Tl<sup>+</sup>-PhA15C5 complex in the 90% AN–H<sub>2</sub>O mixed solvent, the stability of complexes increases with the weight percent of AN in the binary AN–H<sub>2</sub>O mixed solvent. The solvating power of a solvent expressed on the Gutmann scale plays an important role in the complexation process. Water as a solvent of high solvating power (DN = 33) strongly competes with the crown ethers. The addition of acetonitrile with low donor number (DN = 14.1) to water will decrease the solvation as a result of which the interaction between crown ethers and cations will increase [20–30]. The molar conductivities at 25 °C of the Tl<sup>+</sup> and Ag<sup>+</sup> complexes with both crown ethers are shown in Table III. The data indicate that complexes of Tl<sup>+</sup> with both crown ethers have lower mobilities in the 90% AN–H<sub>2</sub>O solvent compared to the mobilities of the same complexes in the 50% AN–H<sub>2</sub>O solvent. The Ag<sup>+</sup> complexes with both crown ethers showed opposite behavior, that is, the mobilities of Ag<sup>+</sup> complexes in 50% AN–H<sub>2</sub>O are higher than those of Ag<sup>+</sup> complexes in the 90% AN–H<sub>2</sub>O solvent. From the data in Table III, it is evident that Tl<sup>+</sup> is weakly solvated compared to Ag<sup>+</sup> in the 90% AN–H<sub>2</sub>O solvent. The above results also predict the previous conclusion, that the Tl<sup>+</sup> complexes are more stable than Ag<sup>+</sup> complexes in the 90% AN–H<sub>2</sub>O mixed solvent.

All the above mentioned results clearly indicate the role of solvent in the complexation process.

### Acknowledgements

Support from Yarmouk University is gratefully acknowledged (Project No. 27/95). Thanks are due to Dr. Yasir Al-Haj for help in preparing the figures.

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