Determination of the Stoichiometry, Stability Constant of Complexes Formation and Thermodynamic Parameters between 15-Crown-5, 1, 4, 8, 11-Tetrathiacyclotetradecane and 1, 7-Diaza-12-crown-4 Macrocyclic Ligands in Acetonitrile – Methanol Binary Solvent Mixtures

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The complex formation between Pb^{2+} and Ag^+ metal cations with 15-crown-5 (15C5), 1, 4, 8, 11-tetrathiacyclotetradecane (TTCTD) and 1, 7-diaza-12-crown-4 (DA12C4) macrocyclic ligands was studied in AN (acetonitrile) – MeOH (methanol) binary solvent mixtures using conductometric method. The stability constant of complexes obtained from fitting of molar conductivity data using GENPLOT computer program, also in all cases, the stoichiometry of the complexes was obtained 1: 1 [M: L]. The Pb^{2+} cation formed a more stable complex with 15C5 in AN–MeOH (mol% AN= 75 and 50) binary solvent mixtures than Ag^+ cation and the log K_f of $(TTCTD.Ag)^+$ complex derived bigger than $(TTCTD.Pb)^{2+}$ complex. A non-linear behavior was observed between the log K_f of the complexes versus the composition of a component of solvent in AN–MeOH mixtures. The values of standard enthalpy changes ($\Delta H°c$) for complexation reactions were obtained from the slope of the van't Hoff plots. The obtained results show that in most cases, the complexes are enthalpy destabilized but entropy stabilized and the positive values of entropy compensates of complex formation enthalpy.

1. INTRODUCTION

Nowadays, industrial world and poor management in various industries are two factors for the deterioration of environmental resources and human health. Lead and silver are classified as nonessential and hazardous elements [1].

Numerous methods have been employed for the determination lead and silver, namely, inductively coupled plasma atomic emission Spectrometry [2], reflection X-ray fluorescence [3], flame atomic absorption spectroscopy [4-6] and potentiometry [7, 8]. The selection of method to measuring these elements needs information about thermodynamic properties and stability constant of complex formation of them in chemical reactions.

The reaction between the ligand–cation is the type of ion–dipole and everything that strengthens this interaction, resulting in a stable complex. The complex stability depend on several factors such as the cavity size of the ligand, the diameter and nature of cation, type of donor atom in the ligand and the character of solvent [9-13]. The effect of solvent on the reactions of complex formation between the ligand and the cation is investigated through the study of stability of constant and thermodynamic parameters [14, 15] The influence of solvent in these reactions is mainly due to some physical and chemical properties of solvents such as polarity, hydrogen bond, donor/acceptor ability, polarizability, acidity/basicity and hydrophobicity/hydrophilicity; therefore, in this work, we studied the stoichiometry and stability of complexes formation between 15-crown-5 (15C5), 1, 4, 8, 11-tetrathiacyclotetradecane (TTCTD) and 1, 7-diaza-12-crown-4 (DA12C4) with Pb^{2+} and Ag^+ cations in AN(acetonitrile) – MeOH(methanol) binary solvent mixtures using conductometric method.

2. MATERIAL AND EXPERIMENTAL PROCEDURE

15-crown-5 (15C5), 1, 4, 8, 11-tetrathiacyclotetradecane (TTCTD) and 1, 7-diaza-12-crown-4 (DA12C4) are purcused all of Sigma-Aldrich (Saint Louis, USA) with high purity. The structure of these compounds has been shown in Scheme I.
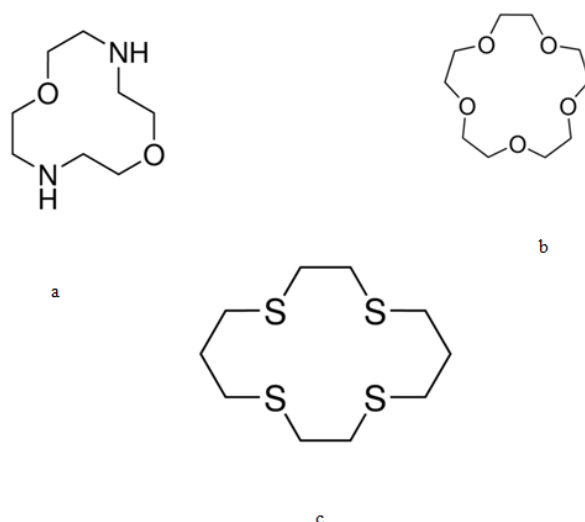
**Scheme I.** a) 15-crown-5 (15C5); b) 1, 4, 8, 11-tetrathiacyclotetradecane (TTCTD); c)1, 7-diaza-12-crown-4 (DA12C4)

Lead nitrate (Pb (NO$_3$)$_2$), silver nitrate (AgNO$_3$), methanol (MeOH) and acetonitrile (AN) all from Merck (Darmstadt, Germany) were used with analytical grade.

The experimental procedure to obtain the formation constants of complexes is as follow: a solution of Pb^{2+} or Ag^{+} metal salts (5×10^{-4} M) of was placed in a titration cell and conductance of the solution was measured, A required amount of solution of crown ether (2×10^{-3} M) (15-crown-5 (15C5), 1, 4, 8, 11-tetrathiacyclotetradecane (TTCTD) or 1, 7-diaza-12-crown-4 (DA12C4)) was quickly added to titration cell so that to increase step- by- step the crown ether concentration, and the conductance of the resulting solution was measured after each addition step at a desired temperature. The conductance measurements were performed on a digital El Metron conductivity apparatus, model cc-411, in a water – bath thermostated (Fanavaran Sahand Azar, model 4500) at a constant temperature maintained within of ±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 0.94 cm^{-1} was used throughout the studies.

3. RESULTS AND DISCUSSION

3.1. Conductance studies

In order to evaluate the influence of 15C5, TTCTD and DA12C4 ligands on the molar conductance of Ag^{+} and Pb^{2+} cations in acetonitrile(AN) – methanol (MeOH) binary solvent mixtures, the conductivity at a constant salt concentration (5×10^{-4} mol L^{-1}) was monitored while increasing the macrocycle concentration at each fixed temperature. Two typical of example molar conductance- mole ratio are shown in Figs 1 and 2.
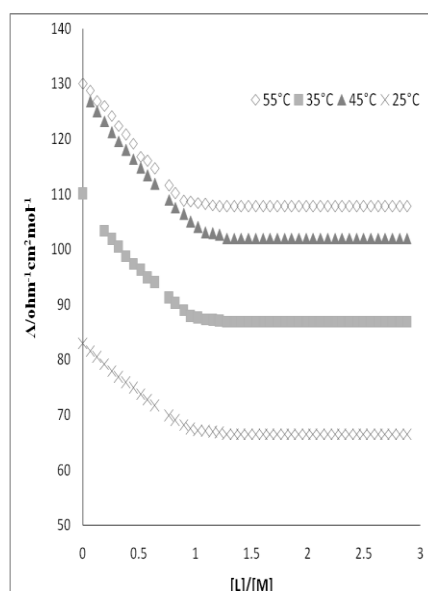

Figure 1. Molar conductance-mole ratio plots for (TTCTD.Ag)$^{+}$ complex in AN–MeOH(mol%AN=50).
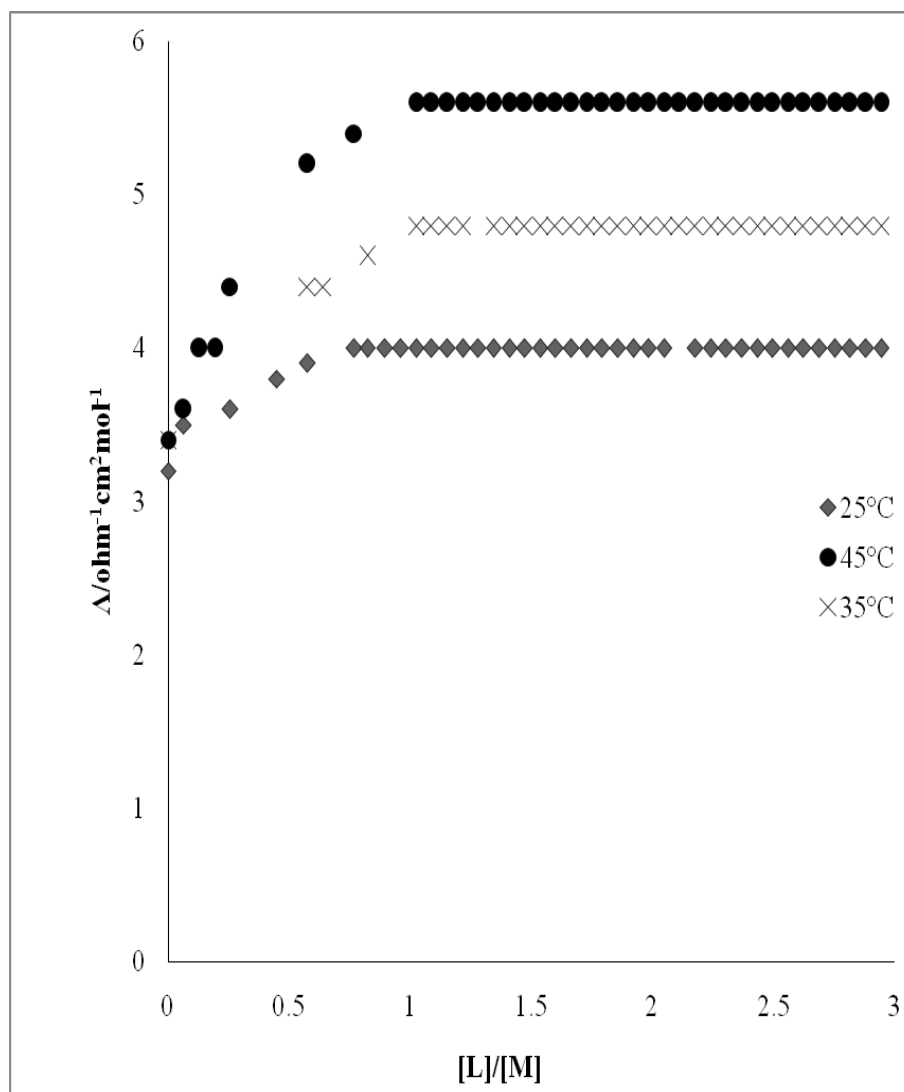
Figure 2. Molar conductance-mole ratio plots for $(15C5.Pb)^{2+}$ complex in AN–MeOH binary solutions (mol %AN=75).

According to Fig.1, addition of TTCTD to Ag^+ solutions in AN–MeOH (mol% AN=50) binary solvent mixtures decrease the molar conductivity with increasing in the ligand concentration at each different temperature, which indicates that the $(TTCTD.Ag)^+$ complex in these solutions is less mobile that the free solvated Ag^+ cation, similar behavior was observed for DA12C4 ligand with Ag^+ cation in AN– MeOH binary solvent mixtures, but addition of 15C5 to Ag^+ and Pb^{2+} solutions resulted in an increase in molar conductivity with an increase in the ligand concentration. This indicates that $(15C5.Ag)^+$ and $(15C5. Pb)^{2+}$ complexes in these binary solvent mixtures have higher mobility than free solvated Ag^+ and Pb^{2+} cations. Molar conductance-mole ratio plots for $(15C5.Pb)^{2+}$ complex in AN–MeOH (mol% AN=75) binary solvent mixtures is shown in Fig 3.

On the other hand, in most cases, the stoichiometry ratio for complex formation between 15C5, TTCTD and DA12C4 ligands with studied cations in AN- MeOH mixtures obtained 1:1 [M:L] complexes.
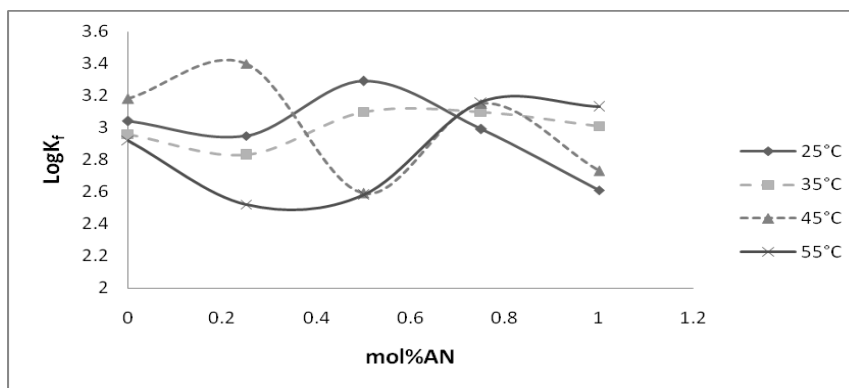
Figure 3. Variation of stability constant ($\log K_f$) of $(15C5.Pb)^{2+}$ complex with the composition of AN–MeOH binary solutions at different temperatures

Also, gradual changes in the molar conductance were observed for some of the studied metal cations upon addition of the ligand to their solutions, which does not show a considerable change in the curvature of the plots at mole ratio 1, indicating that a weaker 1:1 [M:L] complex is formed in solutions.

3.2. Theoretical Computation of Stability Constants of Complex Formation

The metal–ligand complexes have a 1:1 stoichiometry; the binding of the metal ions with ligand can be expressed by the following equilibrium:

$$M^{n+} + L \leftrightarrow ML^{n+} \qquad (1)$$
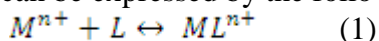
The corresponding equilibrium constant, K_f, is obtained by:

$$K_f = \{[ML^{n+}]/[M^{n+}][L]\}\{fML^{n+}/[M^{n+}][fL]\} \qquad (2)$$

Where $[ML^{n+}]$, $[M^{n+}]$, $[L]$ and f represent the equilibrium molar concentrations of the complex, free cation, free ligand and activity coefficient of the indicated species, respectively [16]. In this study, the highly dilute experimental conditions used; therefore, the activity coefficient of the uncharged ligand, f_L, assume to be unity [17]. Based on the Debye–Huckel limiting law, it can be stated $f_M{}^{n+} \sim f_{ML}{}^{n+}$ in Eq.2.

Mass balance equations of the ML type (Eqs. 3 and 4) used in computer GENPLOT need to be solved in order to obtain Eq.5 for the free ligand concentration [L].

$$C_M = [M^+] + [ML^+] \qquad (3)$$

$$C_L = [L] + [ML^+] \qquad (4)$$

Substitution of Eqs.3 and 4 into Eq.2 and rearrangement yields:

$$K_f[L]^2 + \{1 + K_f(C_M - C_L)\}[L] - C_L = 0 \qquad (5)$$

The complex formation constant in terms of the molar conductivity can be expressed as:

$$K_f = [ML^+]/[M^+][L] = (\Lambda_m - \Lambda_{obs})/[\Lambda_{obs} - \Lambda_{ML^+}][L] \qquad (6)$$

where

$$[L] = C_L - \{C_M(\Lambda_M - \Lambda_{obs})/(\Lambda_M - \Lambda_{ML^+})\} \qquad (7)$$

here, Λ_M, Λ_{obs} and Λ_{ML} are the molar conductivity of the cation solution before addition of the ligand, the molar conductivity of the titration solution and the molar conductivity of the complexes, respectively. Also, C_L and C_M are the analytical concentration of the ligand and cation, respectively.

The stability constants values of the complexes at each temperature were obtained from computer fitting of Eqs.6 and 7 to the molar conductivity–mole ratio data using a non–linear least–squares program, GENPLOT [18]. Rounghi et at [19] also used from this method for determination the stability constant of the dibenzo-18-crown-6 ligand with Ce^{3+}, Y^{3+}, UO_2^{2+} and Sr^{2+} cations.

Log K_f for 15C5, TTCTD and DA12C4 ligands with Ag^+ and Pb^{2+} cations in AN-MeOH binary solvent mixtures at different temperatures are listed in Table 1.

Table 1. Log K_f values of complex formation between 15C5, TTCTD, DA12C4 ligands with Pb^{2+} and Ag^+ cations in AN–MeOH binary solvent mixtures at different temperatures.

Medium	logK$_f$±SD[a]			
	25°C	35°C	45°C	55°C
(15C5.Pb)$^{2+}$				
AN	b	b	b	b
25%MeOH-75%AN	3.72±0.37	3.89 ±0.55	3.98±0.39	>6
50%MeOH-50%AN	4.07±0.49	4.14±0.13	4.26±0.09	4.34±0.48
75%MeOH-25%AN	c	c	c	c
MeOH	2.23±0.10	2.50±0.05	3.24±0.20	2.53±0.50
(15C5.Ag)$^+$				
AN	2.61±0.27	3.01±0.08	2.73±0.02	3.13±0.18
25%MeOH-75%AN	2.99±0.01	3.10±0.10	3.15±0.15	3.16±0.22
50%MeOH-50%AN	3.29±0.02	3.10±0.05	2.59±0.33	2.58±0.48
75%MeOH-25%AN	2.95±0.02	2.83±0.07	3.40±0.18	2.52±0.22
MeOH	3.04±0.03	2.96±0.02	3.18±0.18	2.92±0.34
(TTCTD.Pb)$^{2+}$				
AN	b	b	b	b
50%MeOH-50%AN	2.96±0.01	2.98 ±0.03	3.00±0.18	>6
75%MeOH-25%AN	3.17±0.04	3.02±0.02	2.89±0.09	2.57±0.30
MeOH	3.09±0.05	2.97±0.02	2.80±0.01	2.76±0.12
(TTCTD.Ag)$^+$				
AN	2.86±0.02	2.96±0.02	3.09±0.04	3.37±0.09
25%MeOH-75%AN	2.89±0.01	2.92±0.01	3.05±0.15	3.11±0.22
50%MeOH-50%AN	3.40±0.14	3.12±0.12	3.29±0.49	3.74±0.22
75%MeOH-25%AN	2.98±0.02	3.05±0.01	>6	>6
MeOH	3.05±0.02	3.28±0.15	>6	>6
DA12C4.Ag$^+$				
25%MeOH-75%AN	>6	>6	3.11±0.05	2.96±0.06
50%MeOH-50%AN	3.22±0.10	3.05±0.09	3.01±0.04	2.99±0.27
75%MeOH-25%AN	>6	>6	2.77±0.08	2.74±0.01

[a]SD: Standard deviation   [b] Pb(NO$_3$)$_2$ is not soluble in AN   [c] The complex is weak

3.3. Effect of Solvent Nature

As is evident from Fig. 3, the changes of the stability constant ($\log K_f$) of the $(15C5.Ag)^+$ complex with the variation of a component of solvent in AN–MeOH mixtures is nonlinear, and such nonlinear behavior was also observed for all of the obtained complexes. In solvent mixture, due to restructuring of solvent, the solvation ability is not the same for ligand, cation and the complexes; therefore, in many cases observe preferential solvation that, this type of solvation depend on solvent-solvent or ion- solvent interactions in binary solvent mixtures [20].

The obtained results in Table 1, show in most cases the order of stability constant of $(15C5.Ag)^+$ and $(TTCTD.Ag)^+$ complexes in pure organic solvents is: AN>MeOH. In AN solvent, Gutman Donor Number (DN= 14.1)[20] is smaller than MeOH (DN=20)[20]; therefore, the solvation of the metal cations must be weaker in AN than MeOH solvent.

As is evident from Table 1, the Pb^{2+} cation forms a more stable complex with 15C5 in AN–MeOH (mol% AN= 75 and 50) binary solvent mixtures than Ag^+ cation. Since, ionic size of Pb^{2+}(r= 1.19Å) [21] cation is close to the cavity size of this ligand (0.86–1.18Å) [21], and also, the Pb^{2+} cation is a hard lewis acid than Ag^+ [21]; therefore, based on the hard and soft acid- base concept, the interaction of Pb^{2+} cation with the oxygen atoms as hard base in 15C5 ligand is stronger than Ag^+ cation. Also, due to the presence of sulfur atoms(as soft atom) in TTCTD ligand, the log K_f of $(TTCTD.Ag)^+$ complex is bigger than $(TTCTD.Pb)^{2+}$ complex in AN–MeOH (mol% AN= 25, 50 and 75) binary solvent mixtures(Table 1).

Kazemi et al [22] revealed 1:1 [M: L] stoichiometry for complexation of Y^{3+}, La^{3+} and Hg^{2+} cations with macrocyclic ligands, dicyclohexyl-18-crown-6 (DCH18C6) and 15-crown-5(15C5) in acetonitrile (AN) – N, N-dimethylformamide(DMF) binary solvent mixtures. Therefore, the metal–solvent interaction competes with the metal cation– ligand interaction, and the stability of crown ether complexes in solution is expected to affect mainly by the solvent nature in combination with the relative size of the cation and crown ether cavity.

3.4 Thermodynamic Parameters Computation

The ΔH°_c values of complexation reaction between 15C5, TTCTD and DA12C4 ligands with Ag^+ and Pb^{2+} cations in AN–MeOH binary solvent mixtures were calculated from the temperature dependence of LnK_f using van't Hoff plots. In all cases, the plots of ln K_f versus 1/T were linear. van't Hoff plots for $(TTCD.Ag)+$ complex is given in Fig. 4. Also, the ΔS°_c values were determined from the relationship: $\Delta G^{\circ}_c = \Delta H^{\circ}_c - 298.15 \Delta S^{\circ}_c$.

The thermodynamic data are summarized in Table 2. As is clear from this table, the complexation reaction between 15C5, TTCTD and DA12C4 ligands with Ag^+ and Pb^{2+} cations in AN–MeOH binary solvent mixtures are enthalpy destabilized (in the most cases) and entropy stabilized and the values of standard enthalpy and standard entropy for these complexation processes change with the nature of binary solvent mixtures.
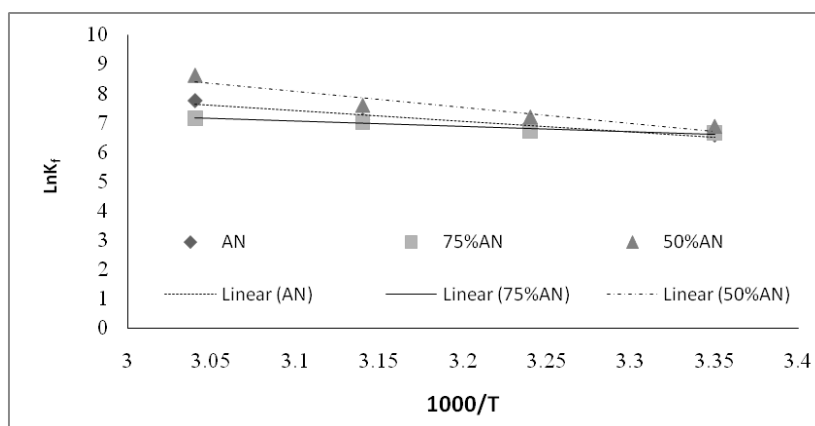
Figure 4. Vant' Hoff plots for $(TTCTD.Ag)^+$ complex in AN–MeOH binary solutions.

Table 2. Thermodynamic parameters of complex formation between 15C5, TTCTD, DA12C4 ligands with Pb^{2+} and Ag^+ cations in AN–MeOH binary solvent mixtures at 25°C.

Medium	$\Delta H^o_c \pm SD^a$ (J mol^{-1})	$\Delta S^o_c \pm SD^a$ (J mol^{-1}K^{-1})	$\Delta G^o_c \pm SD^a$ (KJ mol^{-1})
$(15C5.Pb)^{2+}$			
25%MeOH-75%AN	-23.06±0.09	71.00±0.11	-21.23±0.02
MeOH	-5.59±0.01	42.67±0.05	-12.73±0.04
$(15C5.Ag)^+$			
AN	30.65±0.11	50.06±0.01	-14.89±0.01
25%MeOH-75%AN	14.71±0.09	57.29±0.03	-17.07±0.02
50%MeOH-50%AN	-50.30±0.04	62.81±0.20	-18.78±0.05
75%MeOH-25%AN	-39.75±0.12	56.34±0.09	-16.84±0.06
MeOH	-11.84±0.01	58.16±0.11	-17.35±0.07
TTCTD.Pb)$^{2+}$			
50%MeOH-50%AN	3.55±0.04	56.68±0.11	-16.89±0.02
75%MeOH-25%AN	44.70±0.16	60.84±0.09	-18.09±0.07
$(TTCTD.Ag)^+$			
AN	20.53±0.06	54.82±0.12	-16.32±0.07
50%MeOH-50%AN	40.71±0.11	58.33±0.07	-17.35±0.03
DA12C4.Ag$^+$			
50%MeOH-50%AN	-6.15±0.08	61.62±0.04	-18.38±0.05

[a]SD: Standard deviation

Previous studies show, not only the loss of conformational entropy of ligand and complexation but also randomness of solvent molecules after desolvation of the ligand and cation affect on the values of ΔS°_c [23, 24].

4. CONCLUSION

The stability, selectivity, stoichiometry and thermodynamic parameters of the formation of crown ether complexes with metal cations depend on several factors such as the cavity size of the ligand, the diameter and nature of cation and the character of heteroatom in the polyether ring. The results obtained in this work show that the solvent nature and composition of binary solution are also important, since the stability and the order of selectivity of 15C5, TTCTD and DA12C4 ligands for Ag^+ and Pb^{2+} cations change in AN–MeOH binary solvent mixtures and conductometric measurement revealed the 1:1 [M: L] stoichiometry for all complexes. Also, in most cases, the complexes are enthalpy destabilized but entropy stabilized.

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