

# Complexation Study of Kryptofix22DD with Ag<sup>+</sup> cation in some Mixed non-aqueous binaries solutions

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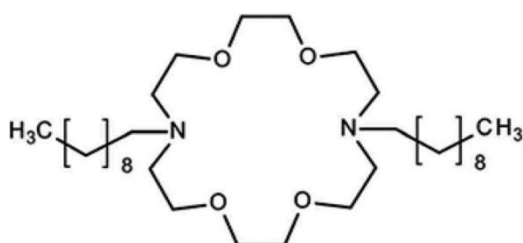
## I INTRODUCTION

**Abstract:** The complexation reactions between Kryptofix22DD, with Ag<sup>+</sup> cation, was studied in acetonitrile-dimethylformamide (AN-DMF), acetonitrile-tetrahydrofuran (AN-THF), methanol-tetrahydrofuran (MeOH-THF) and methanol-dimethylformamide (MeOH-DMF) binary non-aqueous dissolvable arrangements at various temperatures utilizing the conductometric strategy. The conductance information shows that in all cases, the complex stoichiometry framed between the macrocyclic ligand and the metal cation is 1:1 [ML]. The experimental results indicate that in any event, the complex stoichiometry formed between the Ag<sup>+</sup> and the Kryptofix22DD macrocyclic ligand is 1:1 (ML). The qualities the development constants of the complex have been amassed by plotting the molar conductivity bends-utilizing program, GENPLOT. A nonlinear relationship was observed between the complex's stability constant (log K<sub>f</sub>) and the binary solvent composition. The values standard thermodynamic parameters ( $\Delta H_c^\circ$  and  $\Delta S_c^\circ$ ) have been determined Dependence of the temperature of constant stability of the complex using van't Hoff plots. The results show that thermodynamic quantities are dependent on nature and Binary Solvent Composition solutions.

**Keywords:** Complexation Ag<sup>+</sup> metal cation; Kryptofix22DD; non-aqueous binary solvent; Conductometry.

Macrocyclic ethers crown [1, 2] are widely used for selective binding of metal particles (visitor) in their restricted cavity in different aqueous and non-aqueous solvents, Thanks to their excellent performance capacity as a neutral host. The earliest macrocyclic polyether was reported in 1937, but the importance of these compounds as neutral hosts began from 1967 with the synthesis of dibenzo-18-crown-6 (DB18C6) by Pedersen [3]. And Crown ethers are utilized in various fields such as extraction of metal cations from fluid arrangements into non-aqueous solvents [4, 5] and carrying these cations selectively through solvent-polymeric [6] liquid membranes [7, 8] and also the construction of chemical sensors [Ref]. Many of macrocyclic polyether's, which have been synthesized, form very strong and selective complexes with the heavy metal ions in solutions. Studies of crown ethers complexation with the metal cations in different media show that the coordination capacity and selectivity of these ligands with metal ions depend on various molecular factors such as ligand ring cavity size, ligand rigidity, the number and nature of the donor atoms in polyether ring, the charging density and polarizability cation and the cation diameter [9]. In addition, it has been indicated that the dissolvable additionally plays an extremely crucial role in binding selectivity and complex stability [10]. Although numerous studies upon complexation of cations of metal with macrocyclic ligand were made in watery and pure non-aqueous solvents, these complexation processes have been concentrated in the mixed non-aqueous solvent to a limited extend [11]. The solute-solvent and solvent-solvent interactions in mixed solvents, can create new solvent properties and, therefore, leading to the particular solvating Metal cation, ligand and even the complex in solution [12]. Recent experimental studies show

that the thermodynamic and kinetic parameters of the complexation reactions are affected by the nature and composition of the solvent system [13, 14]. The impact of dissolvable upon complexing coronary ethers with various metallic cations was studied using several different physicochemical techniques such as calorimetry [15], polarography [16, 17], potentiometry [18], NMR spectrometry [19], and conductometry [10]. Among these instrumental methods, conductometry has been recognized as a sensitive and cheap technique for such investigation [20]. In the present work, we report the aftereffects of a conductance investigation of the thermodynamics of  $\text{Ag}^+$  cation complexation with kryptofix22DD (Scheme 1) in acetonitrile-dimethylformamide



**Scheme 1. Chemical structure of kryptofix 22DD [ref]**

Acetonitrile-dimethylformamide (AN-DMF), acetonitrile-tetrahydrofuran (AN-THF), methanol-tetrahydrofuran (MeOH-THF) and methanol-dimethylformamide (MeOH-DMF) binary non-aqueous solvent solutions at different temperatures.

The mix of unadulterated solvents as blended solvents significantly expands the decent variety of response media. Examination of dissolvable consequences for thermodynamic and active capacities is intriguing both tentatively and the or ethically in substance and biochemical investigation. The investigation of dissolvable impacts on substance and physical procedures in binary solvent solutions is more confounded than in unadulterated solvents because the solute-solvent and solvent-solvent collaborations can make new dissolvable properties prompting particular solvation. In addition, by studying chemical systems in mixed non-aqueous solvents, we can obtain new information about the theory of solution chemistry. Macrocyclic crown ethers are comprehensively used as promising isolating operators for the metal cations, due to their great limit as a fair host for specific metal particles in arrangements. The coupling capacity also, Crown ethers are selective to metal ions rely upon a few

elements, for example, the size of an ether crown hole, the type of the donor atoms, metal ion radius, conformation of the ligand, polarity of the solvent, etc. These compounds assume a significant job in science [21-23].

## II EXPERIMENTAL RESULTS

### A. Reagents and solvents

Analytical-grade (4,13-Didecyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane), (Kryptofix22DD) (Merck) and silver (I) were used without further purification. The solvents: acetonitrile, dimethylformamide, methanol and tetrahydrofuran all from Merck chemical company, were used with the highest purity (>99 %).

### B. Apparatus procedure

To obtain the formation constant of (kryptofix22DD. $\text{Ag}$ )<sup>+</sup> complex, 20 ml solution of metal salt ( $1.0 \times 10^{-4}$  M) was set in a titration cell at a given temperature, and the conductance of the arrangement was estimated. At that point an answer of the ligand in the same solvent ( $2.0 \times 10^{-3}$  M), was added to the cell titration step by step using a micro burette, what's more, the conductance of the resulted solution was measured after each step at the desired temperature. The conductance measurements were performed on a digital conductometer (Jenway, model 4510), at a frequency of 1 kHz connected to a thermostated circulating water bath (LAUDA) with a precision of  $\pm 0.1^\circ\text{C}$ . 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  $0.98 \text{ cm}^{-1}$  was utilized all through the tests.

## III RESULTS AND DISCUSSION

### A. Conductance Studies

To study the influence of adding the solution of kryptofix22DD on the molar conductance of  $\text{Ag}^+$  cation in different solvents systems, the conductivity of the solutions containing ( $1.00 \times 10^{-4}$  M) concerning silver (I), was monitored with increasing the concentration of the ligands at four temperatures. Two typical series of molar conductance versus ligand/cation mole ratio plots for (kryptofix22DD. $\text{Ag}$ )<sup>+</sup> complex in AN-

THF (mol % AN=50) and MeOH-THF (mol % MeOH=50) binary solvent solutions at different temperatures are shown in Fig. 1 and 2, respectively. As it is evident in these Figures, the molar conductivity of the solutions increases after addition the ligand to the solution of  $\text{Ag}^+$  cation. Somewhat, Similar behaviour was found in all of the solvent systems analyzed for the complexation process.

It seems that the  $\text{Ag}^+$  cation is more solvated than its bulky complex and, therefore, the mobility of the solvated ( $\text{kryptofix22DD} \cdot \text{Ag}^+$ )<sup>+</sup> is more than solvated  $\text{Ag}^+$  in solutions and hence, the molar conductivity of the solutions increases upon addition of the ligand to the cation solution. As is shown in figure 1, the slope of the molar conductivity curves at different temperatures changes at  $[\text{L}]/[\text{M}]$  about 1, which is an evidence for the formation of a stable 1:1 complex (ML), between  $\text{Ag}^+$  cation and  $\text{kryptofix22DD}$  (AN-THF) binary mixed solvent but as indicated in Fig. 2, a slight increase in molar conductance of  $\text{Ag}^+$  cation is observed upon addition of the ligand in (MeOH-THF) binary solvent system (mol % MeOH = 50), which indicates the formation of a weak 1:1 complex between  $\text{kryptofix22DD}$  and  $\text{Ag}^+$  cation in this binary solvent solution. To make more clear the 1:1 [M:L] complexation model, in this solvent system, the fitting and experimental curves for ( $\text{kryptofix22DD} \cdot \text{Ag}^+$ )<sup>+</sup> complex at 25°C are shown in Fig. 3. As is evident in this Figure, there is a very good agreement between the fitting and experimental data, which is an evidence for formation a 1:1 complex between the  $\text{Ag}^+$  cation and the  $\text{kryptofix22DD}$  in solution. As we pointed out, the solvent has an important effect on the complexation processes. The complexation reaction for metal cation in solutions is a competitive reaction between the ligand and the solvent molecules. The formation constant of ( $\text{kryptofix22DD} \cdot \text{Ag}^+$ )<sup>+</sup> complex at each temperature was calculated, using a non-linear least-squares GENPLOT computer program[24]. The details of calculation the formation constants of complexes using the conductometric technique were described in reference[10]. Since the dielectric constants of the selected solvents AN ( $\epsilon = 36.64$ ), MeOH ( $\epsilon = 32.6$ ), THF ( $\epsilon = 7.6$ ) and DMF ( $\epsilon = 38.25$ ) are relatively high, therefore, an association of anion and cation into ion pair was considered to be negligible.

The values of formation constant ( $\log K_f$ ) of the complex that was formed between  $\text{Ag}^+$  cation and  $\text{kryptofix22DD}$  in various solvent systems are

listed in Table 1. Is it obvious from this Table, the complex stability changes with Nature and even the composition of mixed solvent systems. The changes of ( $\log K_f$ ) of complex to the structure of AN-THF and MeOH-THF binary solvent solutions are shown in figures 4 and 5, respectively. As is evident in these figures, It observes non-linear behaviour between the ( $\log K_f$ ) of the complex and the mole fraction of AN and MeOH in these mixed solvents. Somewhat similar behaviour is observed in MeOH-THF binary solvent system. This non-monotonic behaviour may be due to changes in the solvent-solvent interactions which result in changes in the structure of solvent systems and, therefore, changing the solvation properties of the ligand, metal cations and even the resulting complex in solutions. It is interesting to note that as shown in figure 4 and 5, the stability ( $\log K_f$ ) of the complex at all studied temperatures, reaches to its maximum values at certain compositions of the AN-THF and MeOH-THF binary solvent solutions. This behaviour may be attributed to the preferential settling of the dissolved species and the formation of mixed solvents in solutions, and solvent-solvent interactions in other binary mixed non-aqueous solvents between the constituent solvents. These experimental results clearly show that the stability order of the metal ion complexes may change with the composition of the binary mixed solvents as well as the chemical nature of the solvents.

### B. Thermodynamic Calculations

To study the thermodynamic properties of the complexing metallic cations reactions with ligands, it is useful to determine the contribution of enthalpy and entropy for the complexion processes. The standard Gibbs energy changes ( $\Delta G^\circ_c$ ) for the complexation reaction between  $\text{Ag}^+$  cation with  $\text{kryptofix22DD}$  was calculated from the relation:  $\Delta G^\circ_{c,298.15} = -RT \ln K_f$ . The changes in standard enthalpy for the complexation process were determined by the slant of the van't Hoff plots. An average-case of these plots for ( $\text{kryptofix22DD} \cdot \text{Ag}^+$ )<sup>+</sup> complex in AN-DMF binary systems is shown in Fig.6. Somewhat comparable to plots were gotten in other solvent systems. As is evident in the van't Hoff plot and from the experimental data in Table 1, the stability constant ( $\log K_f$ ) of the complex does not change with temperature within the experimental errors. Therefore, it seems that the complexation process between the  $\text{Ag}^+$  cation and the macrocyclic

ligand is thermic. ( $\Delta H_c^\circ = 0$ ). The changes in standard entropy for the complexation reaction were calculated from the equation:  $\Delta G_{c,298.15}^\circ = \Delta H_c^\circ - 298.15 \Delta S_c^\circ$ . The calculated standard thermodynamic parameters are summarized in Table 2. But as indicated in Table 2, the values of  $\Delta S_c^\circ$  are positive which show that the complex is being stabilized from entropy viewpoint. The thermodynamic data, which are summarized in Table 2, show that the thermodynamics of the complexation reaction is affected by nature and the composition of solvent systems and a non-monotonic behaviour is observed between the values of  $\Delta S_c^\circ$  and the composition of the studied mixed solvent solution.

#### IV CONCLUSION

In the present work, the complexation reaction between the macrocyclic ligand, (4,13-Didecyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane), (Kryptofix22DD) and  $Ag^+$  cation was concentrated in acetonitrile-dimethylformamide (AN-DMF), acetonitrile-tetrahydrofuran (AN-THF), methanol-tetrahydrofuran (MeOH-THF) and methanol-dimethylformamide (MeOH-DMF) binary mixtures at different temperatures using the conductivity measurements. The conductometric data indicate in all cases the complex created by stoichiometry is 1:1 [ML]. The experimental results indicate the stability constant ( $\log K_f$ ) of complex does not change monotonically with the composition of the respective studied mixed non-aqueous solvents and so that the complex stability order changes with nature and the binary composition solvent solutions. The outcomes show that ( $\log K_f$ ) of the complex, at all studied temperatures reaches to its maximum values at certain compositions of the binary mixed solvent solutions. Which was clarified as far as particular solvation and arrangement of blended solvates in arrangements and dissolvable collaborations. The obtained thermodynamic quantities show the complexation reaction between the  $Ag^+$  cation and the ligand is thermic, but positive values of entropy characterized the formation of the resulting complex in all solutions. For complexation processes, the normal thermodynamic parameters calculated show that in all solvent systems, the values of the standard enthalpy changes are negligible; therefore, it seems that the formation of the complexes between the ligand and the metal cation is athermic, but positive values characterized the

formation of these macromolecule complexes in solutions.

#### ACKNOWLEDGEMENTS

Express my gratitude for the support given to work at Ferdowsi University, Mashhad, with my efforts, and of my money.

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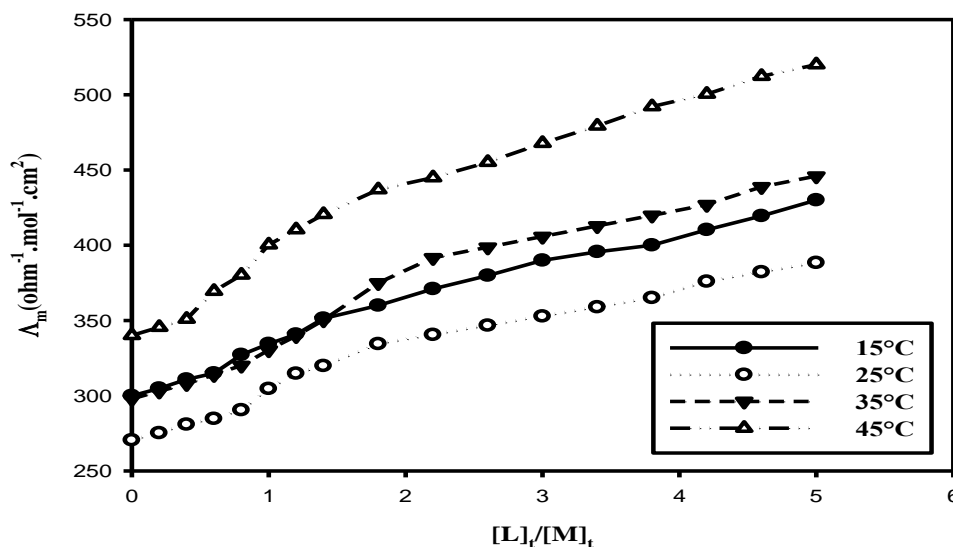


Figure 1. Molar conductance versus mole ratio plots for (kryptofix22DD.Ag)<sup>+</sup> complex in AN-THF binary solvent solution (mol %AN =50) at different temperatures.

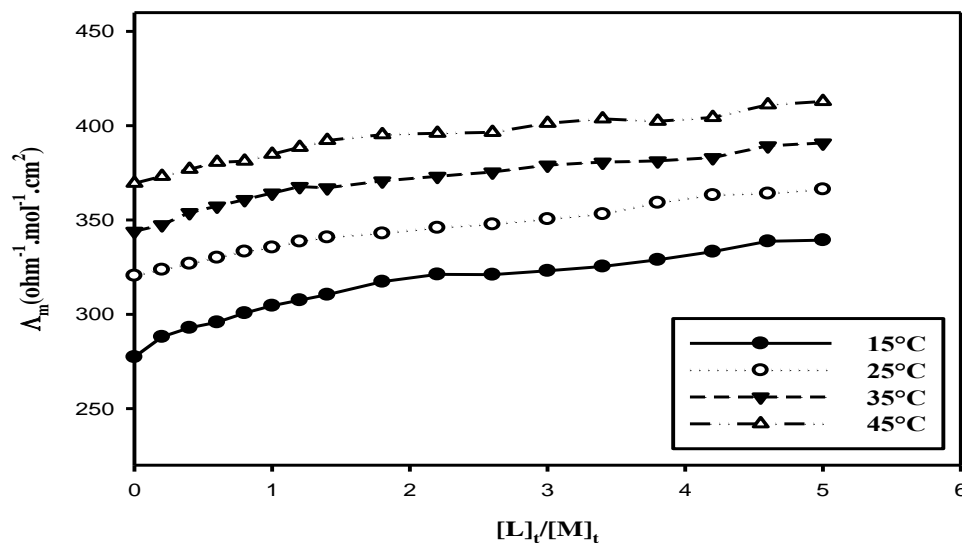


Figure 2. Molar conductance versus mole ratio plots for (kryptofix22DD.Ag)<sup>+</sup> complex in MeOH-THF binary solvent solution (mol %MeOH =50) at different temperatures.

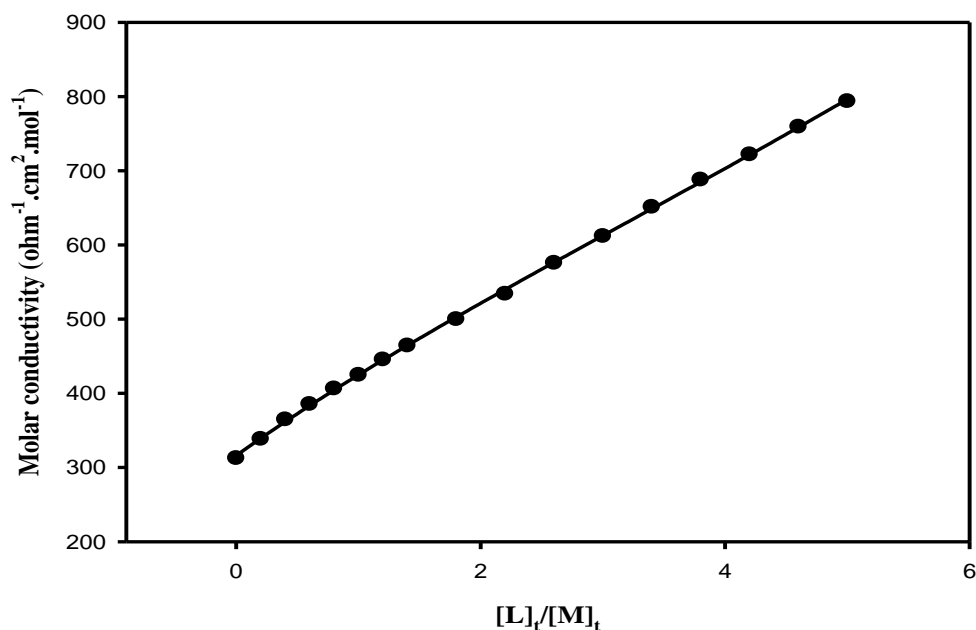


Figure 3. The fitting and experimental (filled circles) data for (kryptofix22DD.Ag)<sup>+</sup> complex in MeOH-THF (mol % MeOH=50) solvent system at 25 °C

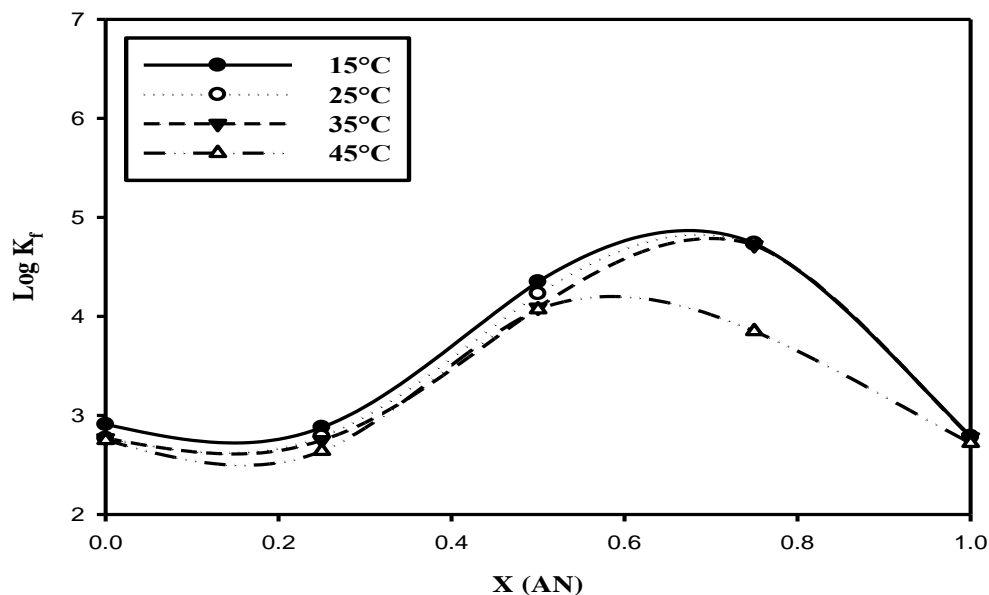


Figure 4. Changes of stability constants ( $\log K_f$ ) of (kryptofix22DD.Ag)<sup>+</sup> complex with the mole fraction of acetonitrile- tetrahydrofuran at different temperatures.

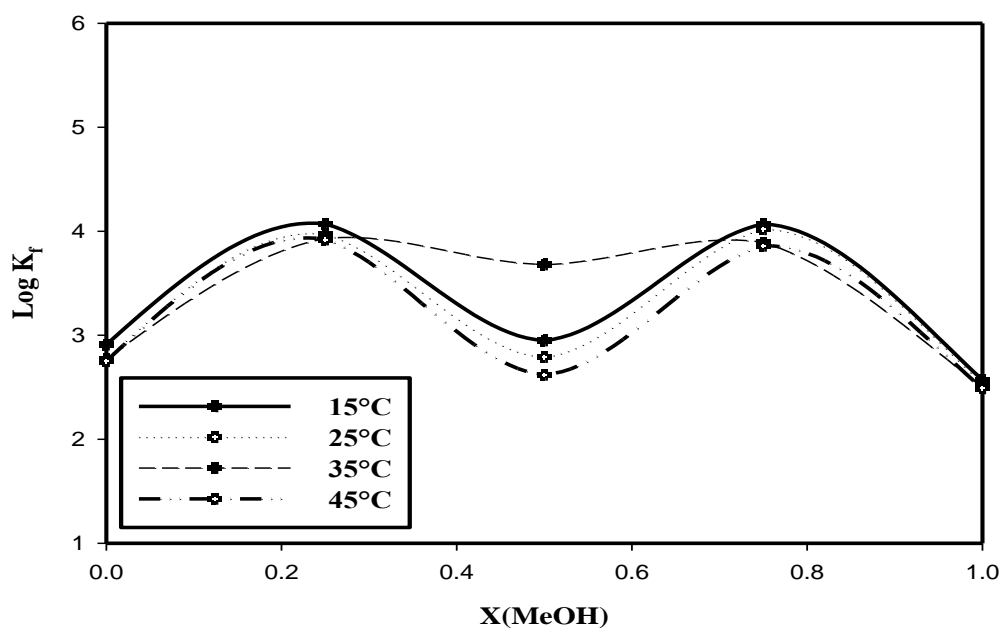


Figure 5. Changes of the stability constants ( $\log K_f$ ) of (kryptofix22DD.Ag)<sup>+</sup> complex with the mole fraction of methanol- tetrahydrofuran at different temperatures.

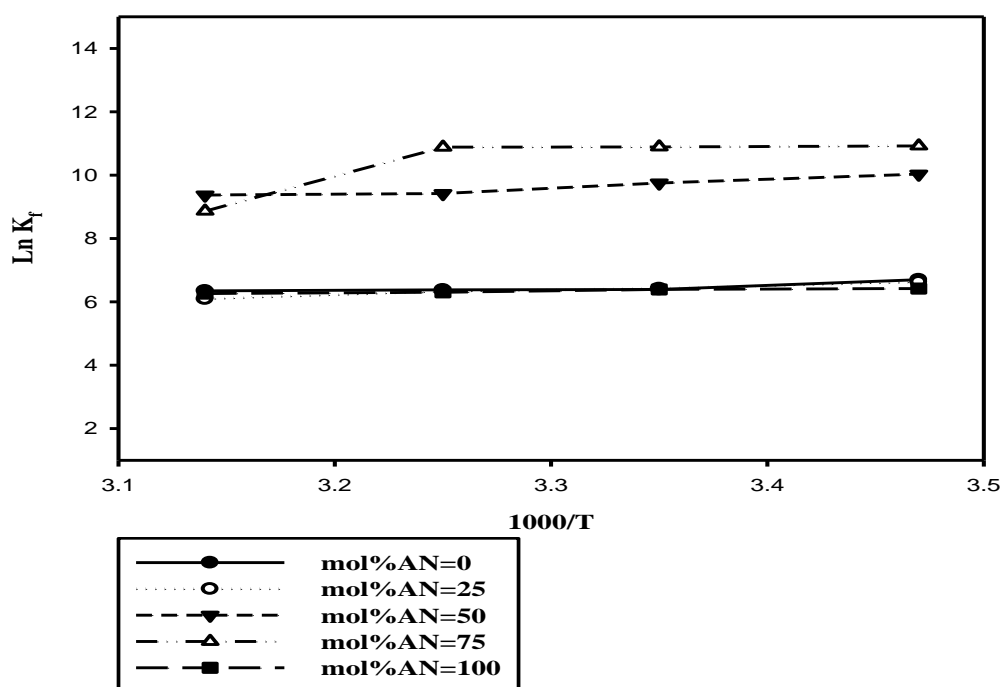


Figure 6. Van't Hoff plots for (kryptofix22DD.Ag)<sup>+</sup> complex in AN-THF binary system

**Table 1:** Formation constants (log K<sub>f</sub>) of (kryptofix22DD.Ag)<sup>+</sup> complex in various solvent systems at different temperatures.

Medium	Log K <sub>f</sub> ± SD <sup>a</sup>			
	15°C	25°C	35°C	45°C
<b>AN-MeOH</b>				
Pure AN	2.79 ± 0.08	2.78 ± 0.09	2.74 ± 0.13	2.72 ± 0.12
25% MeOH-75% AN <sup>b</sup>	4.16 ± 0.04	4.14 ± 0.03	3.81 ± 0.05	3.38 ± 0.07
50% MeOH -50% AN	2.77 ± 0.14	2.75 ± 0.15	2.72 ± 0.11	2.71 ± 0.12
75% MeOH-25% AN	4.12 ± 0.09	3.91 ± 0.05	3.74 ± 0.15	3.66 ± 0.08
Pure MeOH	2.57 ± 0.31	2.53 ± 0.17	2.50 ± 0.23	2.49 ± 0.22
<b>DMF-AN</b>				
Pure DMF	2.91 ± 0.06	2.77 ± 0.10	2.77 ± 0.08	2.75 ± 0.07
75% DMF-25% AN	2.88 ± 0.06	2.79 ± 0.09	4.75 ± 0.10	2.64 ± 0.05
50% DMF-50% AN	4.35 ± 0.05	4.23 ± 0.06	4.09 ± 0.04	4.07 ± 0.08
25% DMF-75% AN	4.74 ± 0.07	4.73 ± 0.07	4.72 ± 0.09	3.85 ± 0.08
Pure AN	2.79 ± 0.08	2.78 ± 0.09	2.74 ± 0.13	2.72 ± 0.12
<b>THF-AN</b>				
Pure THF	C	3.60 ± 0.04	3.51 ± 0.03	3.42 ± 0.04
25% THF-75% AN	3.20 ± 0.12	3.40 ± 0.09	3.70 ± 0.15	3.50 ± 0.20
50% THF-50% AN	2.40 ± 0.17	2.70 ± 0.13	2.70 ± 0.11	2.70 ± 0.17
75% THF-25% AN	3.10 ± 0.20	3.10 ± 0.06	3.00 ± 0.90	3.20 ± 0.06
Pure AN	2.75 ± 0.14	2.71 ± 0.13	2.72 ± 0.12	2.50 ± 0.26
<b>DMF-MeOH</b>				
Pure DMF	2.91 ± 0.06	2.77 ± 0.10	2.77 ± 0.08	2.75 ± 0.07
75% DMF-25% MeOH	4.0 ± 0.07	3.97 ± 0.06	3.93 ± 0.06	3.92 ± 0.05
50% DMF-50% MeOH	2.95 ± 0.03	2.79 ± 0.02	2.68 ± 0.09	2.62 ± 0.13
25% DMF-75% MeOH	4.07 ± 0.07	4.02 ± 0.09	3.89 ± 0.05	3.86 ± 0.03
Pure MeOH	2.57 ± 0.31	2.53 ± 0.17	2.50 ± 0.23	2.49 ± 0.22
<b>THF-MeOH</b>				
Pure THF	C	3.60 ± 0.04	3.51 ± 0.03	3.42 ± 0.04
25% THF-75% MeOH	3.70 ± 0.15	3.15 ± 0.16	3.50 ± 0.13	3.60 ± 0.13
50% THF-50% MeOH	3.47 ± 0.05	3.47 ± 0.05	3.46 ± 0.04	3.35 ± 0.06



75% THF-25% MeOH	3.47 ± 0.05	3.45 ± 0.05	3.36 ± 0.02	3.25 ± 0.03
Pure MeOH	2.57 ± 0.31	2.53 ± 0.17	2.50 ± 0.23	2.49 ± 0.22

<sup>a</sup>SD Standard deviation<sup>b</sup>Composition of the binary solvents is expressed in mol % for each solvent system<sup>c</sup>With high uncertainty**Table 2:** thermodynamic parameters for the formation of (kryptofix22DD.Ag)<sup>+</sup> complex in AN-MeOH, AN-DMF, AN-THF, MeOH-DMF, MeOH-THF binary solvent solution

Medium	$\Delta G^\circ_c \pm SD^a$ (25°C) (KJ mol <sup>-1</sup> )	$\Delta H^\circ_c \pm SD^a$ (KJ mol <sup>-1</sup> )	$\Delta S^\circ_c \pm SD^a$ J mol <sup>-1</sup> K <sup>-1</sup>
<b>AN-MeOH</b>			
75% AN-25% MeOH	-23.61 ± 0.19	≈ 0	79.19 ± 0.64
50% AN-50% MeOH	-15.71 ± 0.89	≈ 0	52.70 ± 3.00
25% AN-75% MeOH	-22.29 ± 0.26	≈ 0	74.75 ± 0.87
Pure AN	-15.85 ± 0.50	≈ 0	53.16 ± 1.67
<b>DMF-MeOH</b>			
75% DMF-25% MeOH	-22.67 ± 0.32	≈ 0	76.03 ± 1.08
50% DMF-50% MeOH	-15.93 ± 0.16	≈ 0	53.42 ± 0.54
25% DMF-75% MeOH	-22.93 ± 0.49	≈ 0	76.92 ± 1.63
Pure MeOH	-14.46 ± 0.97	≈ 0	48.50 ± 3.25
<b>THF-MeOH</b>			
75% THF-25% MeOH	-19.20 ± 0.31	≈ 0	64.41 ± 1.04
50% THF-50% MeOH	-19.79 ± 0.29	≈ 0	66.37 ± 0.98
25% THF-75% MeOH	-19.67 ± 0.28	≈ 0	65.96 ± 0.94
Pure MeOH	-14.46 ± 0.97	≈ 0	48.50 ± 3.25
<b>AN-DMF</b>			
75% AN-25% DMF	-26.99 ± 0.41	≈ 0	90.55 ± 1.40
50% AN-50% DMF	-24.16 ± 0.34	≈ 0	81.05 ± 1.14
25% AN-75% DMF	-15.91 ± 0.53	≈ 0	53.37 ± 1.77
Pure AN	-15.83 ± 0.57	≈ 0	53.10 ± 1.92
<b>AN-THF</b>			
75% AN-25% THF	-26.66 ± 0.50	≈ 0	89.41 ± 1.67
50% AN-50% THF	-21.70 ± 0.68	≈ 0	72.78 ± 2.28
25% AN-75% THF	-22.55 ± 0.31	≈ 0	75.63 ± 1.04
Pure THF	-20.56 ± 0.25	≈ 0	68.97 ± 0.84

<sup>a</sup>SD Standard deviation<sup>b</sup>Composition of the binary solvents is expressed in mol % for each solvent system<sup>c</sup>With high uncertainty