

## Thermodynamics of Complex Formation (Conductometrically) Between Cu (II) Ion and 4-Phenyl -1- Diacetyl Monoxime –3 -Thiosemicarbazone (BMPTS) in Methanol at Different Temperatures.

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### Research Article

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#### ABSTRACT

The association constant, formation constants and Gibbs free energies are calculated from the conductometric titration curves of CuCl<sub>2</sub> with 4-phenyl-2-diacetyl monoxime-3-thiosemicarbazone (BMPTS) in methanol at different temperatures (293.15 K, 298.15 K, 303.15 and 308.15 K). On drawing the relation between molar conductance and the ratio of metal to ligand concentrations, different lines are obtained indicating the formation of 1:2, 1:1 and 2:1 (M:L) stoichiometric complexes. The formation constants of different complexes in methanol follow the order:  $K_f(2:1) > K_f(1:1) > K_f(1:2)$  for (M:L). As the temperature increases, the formation constants and association constants of different complexes increase. The enthalpy and entropy of formation and association of CuCl<sub>2</sub> with (BMPTS) were also estimated and their values were also discussed.

#### INTRODUCTION

Transition metal ions have a strong role in bio-inorganic chemistry and redox enzyme systems and may provide the basis of models for active sites of biological systems [1]. Copper(II) ion is a biologically active, essential ion, chelating ability and positive redox potential allow participation in biological transport reactions. Cu(II) complexes possess a wide range of biological activity and are among the most potent antiviral, antitumor and anti-inflammatory agents [2]. The hydrazones and their metal complexes have many important applications in analytical chemistry and pharmacology [3,4,5]. Schiff bases hydrazone derivatives and their metal complexes have been studied for their interesting and important properties, e.g., antibacterial [6,7], antifungal [8], antioxidant [9], anticancer [10] and catalytic activity in oxidation of cyclohexene [11]. Moreover, Schiff bases hydrazone derivatives are versatile ligands and they offer the possibility of different modes of coordination towards transition metal ions. Also, some of these derivatives have been applied as iron chelator drugs in therapy of anemia [12] and treatment of neuropathic pain [13]. This work deals with the Determination of solvation free energies ( $\Delta G_s$ ), Enthalpy changes of solvation ( $\Delta H_s$ ) and the entropy of solvation ( $\Delta S$ ) from conductometric technique. Thus, thermodynamic studies of complexation reactions of this Schiff base with transition metal ions is important on the thermodynamics of complexation reaction, but also lead to a better understanding of the high selectivity of this ligand towards different metal cations.

The aim of this work is the evaluation the non-covalent behavior of CuCl<sub>2</sub> with (BMPTS) in absolute ethanol solutions at 294.15 K. These non-covalent interactions can help us for analysis of salts in bodies and environment [14,15,16].

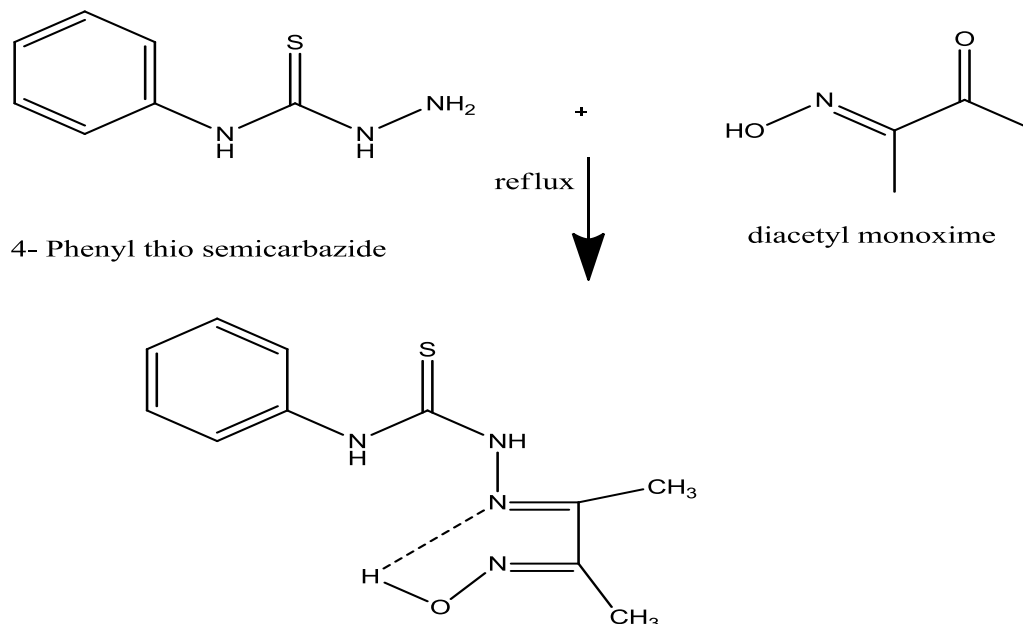
#### EXPERIMENTAL

##### Materials and Methods

All manipulations were performed under aerobic conditions. The copper chloride and the used reagents were Merck pure.

## Preparation of BMPTS

4-phenyl-1-diacetylmonoxime-3-thiosemicarbazone (BMPTS) was prepared by boiling an ethanol (EtOH) solution of 4-phenylthiosemicarbazone (1.7g) with an EtOH solution of diacetylmonoxime (1g) under reflux for two hours. The solution was then concentrated to one half of its volume and cooled. Yellowish white needles separated which were recrystallized from hot absolute EtOH. (M.p: 192 °C; yield 80%). The purity of the compound was checked by TLC.



**Scheme. (1):** The outline of the synthesis of 4-phenyl-1-diacetyl monoxime-3-thiosemicarbazone (BMPTS)

## Conductance measurement

The conductometric titration of the  $\text{CuCl}_2$  ( $1 \times 10^{-4}$  mole/L) against the ligand ( $1 \times 10^{-3}$  mole/l) in methanol was performed with 0.2 ml interval additions from (BMPTS) solution. The specific conductance values were recorded using conductivity bridge AdWa, AD 3000 with a cell constant equal to 1. The temperature was adjusted at 293.15 K, 298.15 K, 303.15 K and 308.15 K

## RESULTS AND DISCUSSION

The specific conductance values ( $K_s$ ) of different concentrations of  $\text{CuCl}_2$  in methanol were measured experimentally in absence and in the presence of ligand at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K).

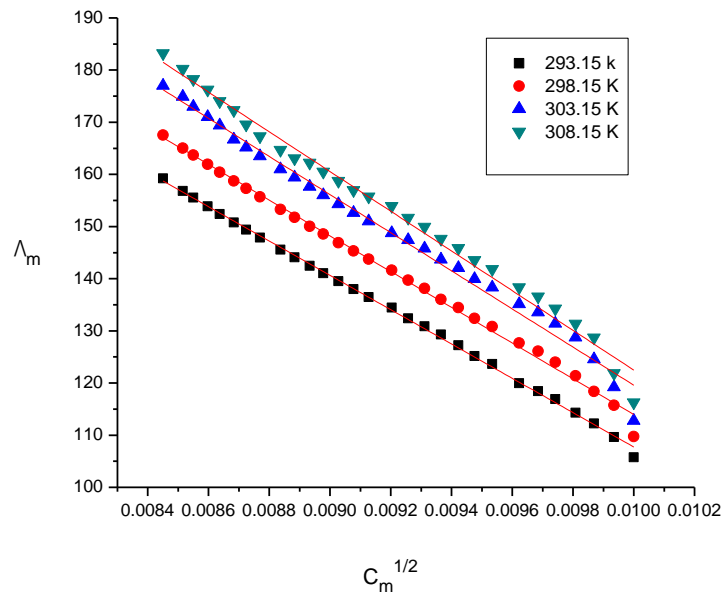
The molar conductance ( $\Lambda_m$ ) values were calculated [14,15,16] using equation:

$$\Lambda_m = (K_s - K_{\text{solv}})K_{\text{cell}} \times 1000/C \quad (1)$$

Where  $K_s$  and  $K_{\text{solv}}$  are the specific conductance of the solution and the solvent, respectively;  $K_{\text{cell}}$  is the cell constant and  $C$  is the molar concentration of the  $\text{CuCl}_2$  solutions.

The limiting molar conductances ( $\Lambda_m^\infty$ ) at infinite dilutions were estimated for  $\text{CuCl}_2$  in methanol in presence of the ligand at different temperatures by extrapolating the relation between  $\Lambda_m$  and  $C_m^{1/2}$  to zero concentration as shown in **Fig.(1)**.

Figure 1: The relation between molar conductance ( $\Lambda_m$ ) and ( $C_m^{1/2}$ ) of  $\text{CuCl}_2$  in presence of BMPTS at different temperatures (293.15K, 298.15 K, 303.15 K and 308.15 K).



By drawing the relation between molar conductance ( $\Lambda_m$ ) and the molar ratio of metal to ligand  $[M/L]$  concentrations (Fig. 2,3,4&5), different lines are obtained with sharp breaks indicating the formation of 1:2, 1:1 and 2:1  $[M:L]$  stoichiometric complexes.

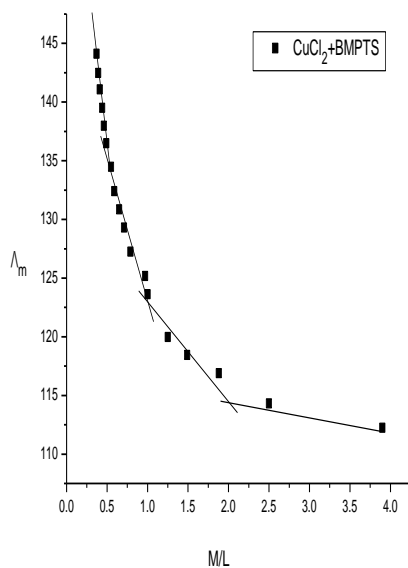


Figure 2: The relation between  $\Lambda_m$  and  $[M/L]$  at 293.15 K.

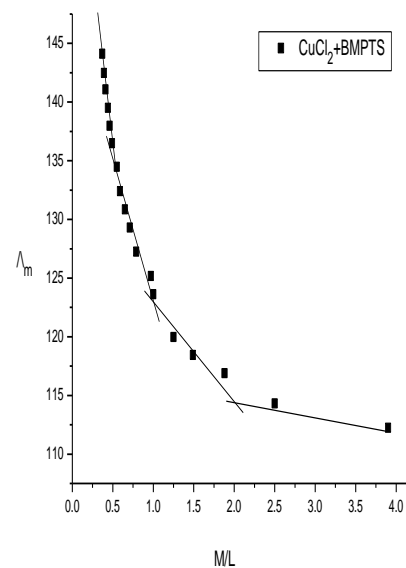


Figure 3: The relation between  $\Lambda_m$  and  $[M/L]$  at 298.15 K

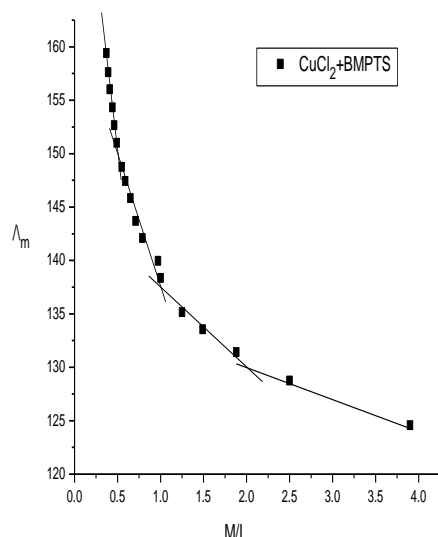


Figure 4: The relation between  $\Lambda_m$  and  $[M/L]$  at 303.15 K.

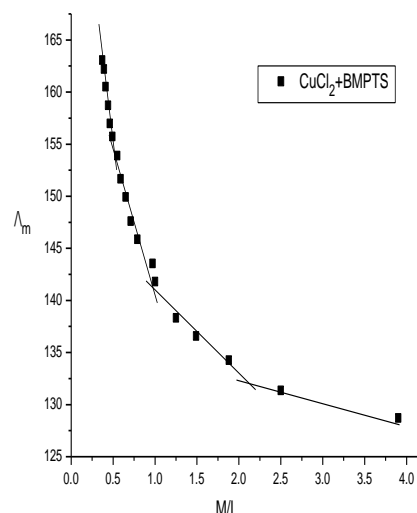


Figure 5: The relation between  $\Lambda_m$  and  $[M/L]$  at 308.15 K.

The experimental data of ( $\Lambda_m$ ) and ( $\Lambda_0$ ) were analyzed for the determination of association and formation constants for each type of the stoichiometric complexes.

The association constants of  $\text{CuCl}_2$  in the presence of ligand (BMPTS) in methanol at different temperatures ( 293.15 K , 298.15 K , 303.15K and 308.15 K) for 2:1 ,1:1 and 1:2 [M:L] were calculated by using equation [17,18]:

$$K_A = [\Lambda_0^2(\Lambda_0 - \Lambda_m)]/[4C_m^2 + \Lambda^3 S(z)] \quad (2)$$

Where ( $\Lambda_m, \Lambda_0$ ) are the molar and limiting molar conductance of  $\text{CuCl}_2$  in presence of BMPTS respectively;  $C_m$  is molar concentration of  $\text{CuCl}_2$ ,  $\gamma_{\pm}$  is activity coefficient  $S(z)$  is Fuoss-Shedlovsky factor, equal with unity for strong electrolytes [19]. The calculated association constants are shown in **Table (1)**.

**Table 1: Association constants of  $\text{CuCl}_2$  with (BMPTS) at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K) in methanol.**

$C_{\text{[ligand]}}$	$C_m[\text{CuCl}_2]$ Temp	$K_A$			
		293.15 K	298.15 K	303.15 K	308.15 K
4.76E-05	9.52E-05	1.05E+09	1.06E+09	1.08E+09	1.11E+09
6.25E-05	9.38E-05	9.89E+08	9.98E+08	1.01E+09	1.06E+09
7.41E-05	9.26E-05	9.17E+08	9.82E+08	9.94E+08	1.04E+09
9.09E-05	9.09E-05	9.12E+08	9.38E+08	9.53E+08	9.92E+08
1.12E-04	8.88E-05	8.55E+08	8.94E+08	9.12E+08	9.44E+08
1.33E-04	8.67E-05	8.26E+08	8.55E+08	8.75E+08	9.01E+08
1.53E-04	8.47E-05	7.79E+08	8.23E+08	8.56E+08	8.63E+08
1.67E-04	8.33E-05	7.76E+08	8.07E+08	8.40E+08	8.57E+08
1.85E-04	8.15E-05	7.51E+08	7.82E+08	8.14E+08	8.38E+08
2.02E-04	7.98E-05	7.27E+08	7.58E+08	7.88E+08	8.10E+08

The Gibbs free energies of association ( $\Delta G_A$ ) were calculated from the association constant [20, 21] by applying equation:

$$\Delta G_A = - R T \ln K_A \quad (3)$$

Where R is the gas constant (8.314 J) and T is the absolute temperature .The calculated Gibbs free energies were presented in **Table (2)**.

**Table 2: Gibbs free energies of association of CuCl<sub>2</sub> with (BMPTS) at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K) in methanol**

C <sub>[ligand]</sub>	C <sub>m[CuCl<sub>2</sub>]</sub> Temp	ΔG <sub>A</sub> (kJ/mol)			
		293.15 K	298.15 K	303.15 K	308.15 K
4.76E-05	9.52E-05	-50.6230	-51.5253	-52.4294	-53.3670
6.25E-05	9.38E-05	-50.4808	-51.3640	-52.2533	-53.2376
7.41E-05	9.26E-05	-50.2961	-51.3237	-52.2163	-53.1936
9.09E-05	9.09E-05	-50.2825	-51.2106	-52.1090	-53.0722
1.12E-04	8.88E-05	-50.1251	-51.0923	-51.9974	-52.9451
1.33E-04	8.67E-05	-50.0427	-50.9821	-51.8936	-52.8265
1.53E-04	8.47E-05	-49.9004	-50.8851	-51.8381	-52.7160
1.67E-04	8.33E-05	-49.8895	-50.8390	-51.7907	-52.6961
1.85E-04	8.15E-05	-49.8084	-50.7599	-51.7115	-52.6391
2.02E-04	7.98E-05	-49.7292	-50.6812	-51.6313	-52.5537

The formation constants (K<sub>f</sub>) for CuCl<sub>2</sub> complexes were calculated for each type of complexes (1:2), (1:1) and (2:1) (M: L) [22, 23] by using equation:

$$K_f = [\Lambda_M - \Lambda_{obs}] / [(\Lambda_{obs} - \Lambda_{ML})[L]] \quad (4)$$

Where  $\Lambda_M$  is the limiting molar conductance of the CuCl<sub>2</sub> alone,  $\Lambda_{obs}$  is the molar conductance of solution during titration and  $\Lambda_{ML}$  is the molar conductance of the complex.

The obtained values (K<sub>f</sub>) for CuCl<sub>2</sub>-ligand stoichiometric complexes are presented in **Tables (3,4 &5)**

**Table 3(a): Formation constants and Gibbs free energies of formation for 1:2(M/L) Complexes in absolute methanol at 293.15K**

$\Lambda_{obs}$ (cm <sup>2</sup> .Ohm <sup>-1</sup> )	[L]	$(\Lambda_{obs} - \Lambda_{ML})$ [L]	$(\Lambda_M - \Lambda_{obs})$	K <sub>f</sub>	Δ G <sub>f</sub> (kJ/mol)
136.495	1.67E-04	1.69E-04	133.1854	7.86E+05	-33.08508
137.985	1.76E-04	4.41E-04	131.69456	2.99E+05	-30.72652
139.509	1.85E-04	7.45E-04	130.1708	1.75E+05	-29.41866
141.067	1.94E-04	1.08E-03	128.613	1.19E+05	-28.47686
142.481	2.02E-04	1.41E-03	127.1988	8.99E+04	-27.80149

$\Lambda_{ML} = 135.48 \text{ cm}^2 \cdot \text{Ohm}^{-1}$ .

**Table 3(b): Formation constants and Gibbs free energies of formation for 1:2(M/L) Complexes in absolute methanol at 298.15 K**

$\Lambda_{obs}$ (cm <sup>2</sup> .Ohm <sup>-1</sup> )	[L]	$(\Lambda_{obs} - \Lambda_{ML})$ [L]	$(\Lambda_M - \Lambda_{obs})$	K <sub>f</sub>	Δ G <sub>f</sub> (kJ/mol)
143.7567	1.67E-04	1.45E-04	137.6333	9.51E+05	-34.1213
145.3203	1.76E-04	4.28E-04	136.0697	3.18E+05	-31.4071
146.9168	1.85E-04	7.45E-04	134.4733	1.81E+05	-30.0025
148.5473	1.94E-04	1.10E-03	132.8427	1.21E+05	-29.0118
150.0584	2.02E-04	1.45E-03	131.3316	9.07E+04	-28.2964

$\Lambda_{ML} = 142.89 \text{ cm}^2 \cdot \text{Ohm}^{-1}$ .

**Table 3(c): Formation constants and Gibbs free energies of formation for 1:2(M/L) Complexes in absolute methanol at 303.15 K**

$\Lambda_{obs}$ (cm <sup>2</sup> .Ohm <sup>-1</sup> )	[L]	$(\Lambda_{obs} - \Lambda_{ML})$ [L]	$(\Lambda_M - \Lambda_{obs})$	K <sub>f</sub>	Δ G <sub>f</sub> (kJ/mol)
151.019	1.67E-04	1.13E-04	141.2611	1.25E+06	-35.3748
152.655	1.76E-04	4.07E-04	139.6249	3.43E+05	-32.1212
154.324	1.85E-04	7.37E-04	137.9557	1.87E+05	-30.5968
156.028	1.94E-04	1.10E-03	136.2525	1.23E+05	-29.5488
157.636	2.02E-04	1.47E-03	134.6444	9.14E+04	-28.7894

$\Lambda_{ML} = 150.34 \text{ cm}^2 \cdot \text{Ohm}^{-1}$ .

**Table 3(d): Formation constants and Gibbs free energies of formation for 1:2(M/L) Complexes in absolute methanol at 308.15 K**

$\Lambda_{\text{obs}} (\text{cm}^2 \cdot \text{Ohm}^{-1})$	[L]	$(\Lambda_{\text{obs}}/\Lambda_{\text{ML}}) [\text{L}]$	$(\Lambda_{\text{M}}/\Lambda_{\text{obs}})$	$K_f$	$\Delta G_f$ (kJ/mol)
155.74	1.67E-04	9.85E-05	145.5003	1.48E+06	-36.3946
156.99	1.76E-04	3.24E-04	144.25	4.45E+05	-33.323
158.732	1.85E-04	6.63E-04	142.5082	2.15E+05	-31.4575
160.508	1.94E-04	1.04E-03	140.7322	1.35E+05	-30.272
162.213	2.02E-04	1.43E-03	139.0272	9.74E+04	-29.4294

$$\Lambda_{\text{ML}} = 155.15 \text{ cm}^2 \cdot \text{Ohm}^{-1}$$

**Table 4(a): Formation constants and Gibbs free energies of formation for 1:1(M/L) Complexes in absolute methanol at 293.15 K**

$\Lambda_{\text{obs}} (\text{cm}^2 \cdot \text{Ohm}^{-1})$	[L]	$(\Lambda_{\text{obs}}/\Lambda_{\text{ML}}) [\text{L}]$	$(\Lambda_{\text{M}}/\Lambda_{\text{obs}})$	$K_f$	$\Delta G_f$ (kJ/mol)
123.62	9.09E-05	6.82E-05	146.05999	2.14E+06	-35.52884
125.171	1.02E-04	2.35E-04	144.50884	6.16E+05	-32.48966
127.239	1.12E-04	4.89E-04	142.44064	2.91E+05	-30.66381
129.308	1.23E-04	7.92E-04	140.37244	1.77E+05	-29.45531
130.859	1.33E-04	1.06E-03	138.82129	1.31E+05	-28.71157

$$\Lambda_{\text{ML}} = 122.87 \text{ cm}^2 \cdot \text{Ohm}^{-1}$$

**Table 4(b): Formation constants and Gibbs free energies of formation for 1:1(M/L) Complexes in absolute methanol at 298.15 K**

$\Lambda_{\text{obs}} (\text{cm}^2 \cdot \text{Ohm}^{-1})$	[L]	$(\Lambda_{\text{obs}}/\Lambda_{\text{ML}}) [\text{L}]$	$(\Lambda_{\text{M}}/\Lambda_{\text{obs}})$	$K_f$	$\Delta G_f$ (kJ/mol)
130.8149	9.09E-05	4.77E-05	150.5751	3.16E+06	-37.0948
132.3851	1.02E-04	2.14E-04	149.0049	6.97E+05	-33.3523
134.4786	1.12E-04	4.69E-04	146.9114	3.13E+05	-31.3682
136.0487	1.23E-04	7.08E-04	145.3413	2.05E+05	-30.3202
138.1423	1.33E-04	1.04E-03	143.2477	1.37E+05	-29.3218

$$\Lambda_{\text{ML}} = 130.29 \text{ cm}^2 \cdot \text{Ohm}^{-1}$$

**Table 4(c): Formation constants and Gibbs free energies of formation for 1:1(M/L) Complexes in absolute methanol at 303.15K**

$\Lambda_{\text{obs}} (\text{cm}^2 \cdot \text{Ohm}^{-1})$	[L]	$(\Lambda_{\text{obs}}/\Lambda_{\text{ML}}) [\text{L}]$	$(\Lambda_{\text{M}}/\Lambda_{\text{obs}})$	$K_f$	$\Delta G_f$ (kJ/mol)
138.355	9.09E-05	3.23E-05	153.9247	4.77E+06	-38.7561
139.956	1.02E-04	2.00E-04	152.3238	7.63E+05	-34.1401
142.091	1.12E-04	4.58E-04	150.1893	3.28E+05	-32.0094
143.692	1.23E-04	7.00E-04	148.5885	2.12E+05	-30.9139
145.826	1.33E-04	1.04E-03	146.4539	1.41E+05	-29.8777

$$\Lambda_{\text{ML}} = 138 \text{ cm}^2 \cdot \text{Ohm}^{-1}$$

**Table 4(d): Formation constants and Gibbs free energies of formation for 1:1(M/L) Complexes in absolute methanol at 308.15K**

$\Lambda_{\text{obs}} (\text{cm}^2 \cdot \text{Ohm}^{-1})$	[L]	$(\Lambda_{\text{obs}}/\Lambda_{\text{ML}}) [\text{L}]$	$(\Lambda_{\text{M}}/\Lambda_{\text{obs}})$	$K_f$	$\Delta G_f$ (kJ/mol)
141.808	9.09E-05	1.89E-05	159.4317	8.42E+06	-40.8535
143.55	1.02E-04	1.99E-04	157.6896	7.93E+05	-34.7994
145.873	1.12E-04	4.79E-04	155.3667	3.25E+05	-32.5123
147.615	1.23E-04	7.40E-04	153.6246	2.08E+05	-31.3674
149.938	1.33E-04	1.11E-03	151.3017	1.36E+05	-30.2915

$$\Lambda_{\text{ML}} = 141.6 \text{ cm}^2 \cdot \text{Ohm}^{-1}$$

**Table 5(a): Formation constants and Gibbs free energies of formation for 2:1(M/L) Complexes in absolute methanol at 293.15K**

$\Lambda_{\text{obs}} (\text{cm}^2 \cdot \text{Ohm}^{-1})$	[L]	$(\Lambda_{\text{obs}}/\Lambda_{\text{ML}})$ [L]	$(\Lambda_{\text{M}}/\Lambda_{\text{obs}})$	$K_f$	$\Delta G_f$ (kJ/mol)
115.53	4.76E-05	4.43E-05	154.15	3.48E+06	-36.71271
116.024	4.94E-05	7.03E-05	153.656	2.18E+06	-35.57605
116.898	5.06E-05	1.16E-04	152.78163	1.31E+06	-34.33686
118.45	6.25E-05	2.41E-04	151.23048	6.29E+05	-32.5402
119.978	7.41E-05	3.99E-04	149.7016	3.76E+05	-31.28538

$$\Lambda_{\text{ML}} = 114.6 \text{ cm}^2 \cdot \text{Ohm}^{-1}$$

**Table 5(b): Formation constants and Gibbs free energies of formation for 2:1(M/L) Complexes in absolute methanol at 298.15K**

$\Lambda_{\text{obs}} (\text{cm}^2 \cdot \text{Ohm}^{-1})$	[L]	$(\Lambda_{\text{obs}}/\Lambda_{\text{ML}})$ [L]	$(\Lambda_{\text{M}}/\Lambda_{\text{obs}})$	$K_f$	$\Delta G_f$ (kJ/mol)
122.622	4.76E-05	3.34E-05	158.768	4.75E+06	-38.1092
123.347	4.94E-05	7.05E-05	158.043	2.24E+06	-36.2474
124.011	5.06E-05	1.06E-04	157.379	1.49E+06	-35.2304
126.1045	6.25E-05	2.62E-04	155.2855	5.94E+05	-32.954
127.6746	7.41E-05	4.26E-04	153.7154	3.60E+05	-31.717

$$\Lambda_{\text{ML}} = 121.92 \text{ cm}^2 \cdot \text{Ohm}^{-1}$$

**Table.5(c): Formation constants and Gibbs free energies of formation for 2:1(M/L) Complexes in absolute methanol at 303.15 K**

$\Lambda_{\text{obs}} (\text{cm}^2 \cdot \text{Ohm}^{-1})$	[L]	$(\Lambda_{\text{obs}}/\Lambda_{\text{ML}})$ [L]	$(\Lambda_{\text{M}}/\Lambda_{\text{obs}})$	$K_f$	$\Delta G_f$ (kJ/mol)
129.6777	4.76E-05	1.80E-05	162.6023	9.04E+06	-40.3707
130.5243	4.94E-05	6.05E-05	161.7557	2.67E+06	-37.2999
131.418	5.06E-05	1.07E-04	160.8619	1.50E+06	-35.8439
133.553	6.25E-05	2.66E-04	158.7273	5.97E+05	-33.5211
135.154	7.41E-05	4.34E-04	157.1265	3.62E+05	-32.2612

$$\Lambda_{\text{ML}} = 129.3 \text{ cm}^2 \cdot \text{Ohm}^{-1}$$

**Table.5(d): Formation constants and Gibbs free energies of formation for 2:1(M/L) Complexes in absolute methanol at 308.15 K**

$\Lambda_{\text{obs}} (\text{cm}^2 \cdot \text{Ohm}^{-1})$	[L]	$(\Lambda_{\text{obs}}/\Lambda_{\text{ML}})$ [L]	$(\Lambda_{\text{M}}/\Lambda_{\text{obs}})$	$K_f$	$\Delta G_f$ (kJ/mol)
133.375	4.76E-05	1.07E-05	167.865	1.57E+07	-42.4452
133.965	4.94E-05	4.03E-05	167.275	4.15E+06	-39.0437
134.259	5.06E-05	5.61E-05	166.981	2.98E+06	-38.1885
136.582	6.25E-05	2.14E-04	164.6581	7.68E+05	-34.7174
138.324	7.41E-05	3.83E-04	162.916	4.25E+05	-33.2022

$$\Lambda_{\text{ML}} = 133.15 \text{ cm}^2 \cdot \text{Ohm}^{-1}$$

**Table.6: The enthalpies ( $\Delta H_A$ ) and entropies ( $\Delta S_A$ ) of  $\text{CuCl}_2$  with BMPTS at different temperatures**

M:L	$(\Delta S_A)$ kJ/mol.K				$(\Delta H_A)$ KJ/mol
Temp	293.15 k	298.15 K	303.15 K	308.15 K	
1:2	0.1875	0.1876	0.1876	0.1875	5.0856
1:1	0.1852	0.1852	0.1852	0.1853	4.0214
2:1	0.1822	0.1821	0.1821	0.1822	2.7760

**Table.7: The enthalpies ( $\Delta H_f$ ) and entropies ( $\Delta S_f$ ) of  $\text{CuCl}_2$  with BMPTS at different temperatures**

M:L	$(\Delta S_f)$ kJ/mol.K				$(\Delta H_f)$ KJ/mol
Temp	293.15 k	298.15 K	303.15 K	308.15 K	
1:2	0.2241	0.2239	0.2243	0.2240	32.6345
1:1	0.3525	0.3519	0.3516	0.3527	67.8237
2:1	0.3894	0.3875	0.3886	0.3890	77.4379

Also the Gibbs free energies of complex formation were calculated using equation 95).

$$\Delta G_f = -RT \ln K_f \quad (5)$$

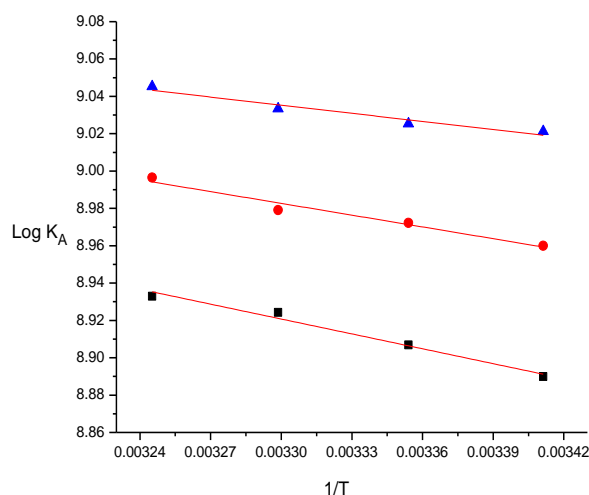
The calculated  $\Delta G_f$  values are presented also in **Tables (3,4&5)**.

The enthalpy ( $\Delta H_A$ ) for  $\text{CuCl}_2$  complexes were calculated for each type of complexes (1:2) , (1:1) and (2:1) (M:L) by using van 't Hoff equation [24,25] :

$$d \ln K / dT = \Delta H / RT^2 \quad (6)$$

Where  $R$  is the gas constant (8.314 J) and  $T$  is the methanol. By drawing the relation between  $\log K_A$  and  $1/T$ , different lines are obtained indicating the formation of 1:2,1:1 and 2:1 (M:L) stoichiometric complexes **Fig.(6)**.

**Figure 6: The relation between ( $\log K_A$ ) and ( $1/T$ ).**



From the relation between  $\log K$  and  $1/T$ ,  $\Delta H_A$  can be calculated for each type of complexes from the slope of each line ( $-\Delta H/2.303R$ ).The entropy ( $\Delta S_A$ ) for  $\text{CuCl}_2$  complexes were calculated for each type of complexes (1:2), (1:1) and (2:1) (M:L) by using equation :

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

Where (S) is the entropy of system.

The calculated values of ( $\Delta H_A$ ) and ( $\Delta S_A$ ) for  $\text{CuCl}_2$ -ligand stoichiometric complexes are presented in **Table (6)**.

By drawing the relation between  $\log K_f$  and  $1/T$ , different lines are obtained indicating the formation of 1:2,1:1 and 2:1 (M:L) stoichiometric complexes **Fig.(7)**.

The enthalpy ( $\Delta H_f$ ) for  $\text{CuCl}_2$  complexes were calculated for each type of complexes (1:2) , (1:1) and (2:1) (M:L) by using van 't Hoff equation .

The calculated values of ( $\Delta H_f$ ) and ( $\Delta S_f$ ) for  $\text{CuCl}_2$ -ligand stoichiometric complexes are presented in **Table (7)**.

Since the conductance of an ion depends mainly on its mobility, it is quite reasonable to treat the rate process taking place with the change of temperature on the basis of equation(8):

$$\Lambda_0 = A e^{-E_a/RT} \quad (8)$$

where  $A$  is the frequency factor,  $R$  is the gas constant and  $E_a$  is the Arrhenius activation energy of the transfer process. Consequently, from the plot of  $\log \Lambda_0$  vs.  $1/T$ , the  $E_a$  values can be evaluated [25] as shown in Fig (9), giving high activation energy value due to solvation behavior.



Figure 7: The relation between ( $\log K_f$ ) and ( $1/T$ ).

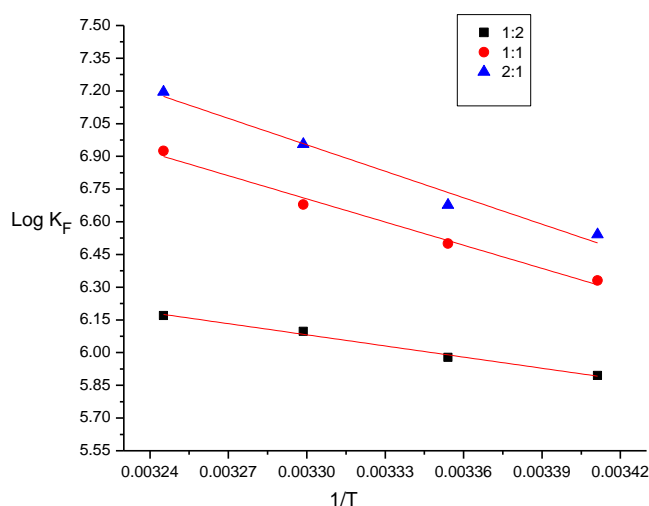
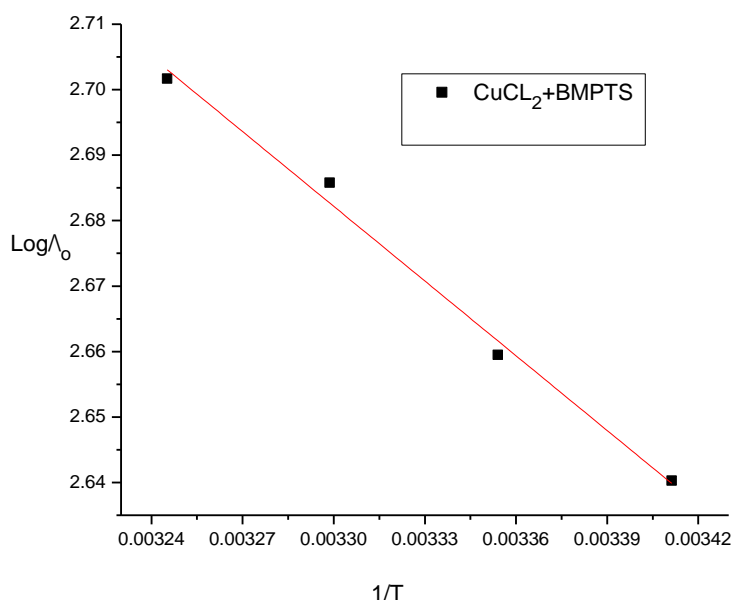


Figure 8: The relation between  $\log \Lambda_0$  and  $1/T$ .  $E_a=7.2853\text{KJ/mol}$



### CONCLUSION

According to the results presented in the article, one can be noticed that conductometry investigation of complexation in methanol at different temperatures( 293.15 K, 298.15 K , 303.15 and 308.15 K) could be obtained. Using the obtained data, selection of proper choice of parameter to predict selective and sensitive method.

The stability constants for the complexation of copper(II) ion with (BMPTS) were determined conductometrically at different temperatures. Thermodynamic parameters of complexation were determined from the temperature dependence of the formation constant. The negative values of  $\Delta G$  show the ability of the studied ligand to form stable complexes and the process tend to proceed spontaneously. However, the obtained positive values of  $\Delta H$  means that enthalpy is not the driving force for the formation of the complexes. Furthermore, the positive values of  $\Delta S$  indicate that entropy is responsible for the complexing process. As the temperature increases, the formation constants and association constants of different complexes increase.

## REFERENCES

1. MV Angelusiu, SF Barbuceanu, C Draghici, GL Almajan. *Eur J Med Chem.* 2010;45:2055–2062.
2. Vosburg WC, Cooper GR. *J Am Chem Soc.* 1941;63:437.
3. S Jayasree, KK Arvindakshan. *J Indian Chem Soc.* 1994;71:97.
4. RK Parashar, RC Sharma. *Inorg Chem Acta.* 1988;151:201.
5. MCR Arguelles, MB Ferrari, F Bisceglie, C Plizzi, G Pelosi, S Pinelli, M Sassi. *J Inorg Biochem.* 2004;98:313.
6. SM Emam, FA El-Saied, SA AbouEl-Enein, HA El-Shater. *Spectrochim Acta Part A.* 2009;72:291–297.
7. AR Yaul, VV Dhande, AS Aswar. *Rev Roum Chim.* 2010;55:537–542.
8. AS El-Tabl, FA El-Saied, W Plass, AN Al-Hakimi. *Spectrochim Acta Part A.* 2008;71:90–99.
9. Y Li, Z-Y Yang, M-F Wang. *J Fluoresc.* 2010;20:891–905.
10. SB Desai, PB Desai, KR Desai. *Heterocycl Commun.* 2001;7:83–90.
11. MS Niasari, A Amiri. *Appl Catal A.* 2005; 290:46–53.
12. MCR. Arguelles, MB Ferrari, F Bisceglie, C Plizzi, G Pelosi, S Pinelli, M Sassi. *J Inorg Biochem.* 2004;98:313–321.
13. P Yogeeswari, N Menon, A Semwal, M Arjun, D Sriram. *Eur J Med Chem.* 2011;46:2964–2970.
14. Zhibo Yang. Ph.D. thesis, Wayne State University, Detroit, Michigan, USA., 2005.
15. Kamal M Ibrahim, Magdy M Bekhit, Gaber M Abu EL-Reash. *Transition Met Chem.* 1991;16,189-192.
16. W Gryzbkowski, R Pastewski. *Electrochimica Acta.* 1980;25:279
17. NA El-Shishtawi, MA Hamada, EA Gomaa. *J Chem Eng Data.* 2010; 55:5422
18. MA Hamada, NA El-Shishtawi, EA Gomaa. *South Braz J Chem.* 2009;17:33
19. EA Gomaa. *Thermochimica Acta.* 1987;120:183
20. EA Gomaa. *Thermochimica Acta.* 1988;128:99
21. FI El-Doussoki. *J Mol Liq.* 2008;142:53
22. Farid I El-Dossoki. *J Mol Liq.* 2008;142:53-56.
23. M.Rahmi-Nasrabadi, F Ahmedi, SM Pourmor-Tazari, MR Ganjal, K Alizadeh. *J Mol Liq.* 2009;144:97.
24. PW Atkins . 1978. *Physical Chemistry*, Oxford University Press.
25. DJG Ives. 1971, *Chemical Thermodynamics*, University Chemistry, Macdonald Technical and Scientific, New York.