

## Thermodynamics of Complex Formation ( conductometrically) Between Cu(II) ion and 4-phenyl -1- diacetyl monoxime –3 -thiosemicarbazone (BMPTS) in Ethanol 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 absolute ethanol 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 absolute ethanol 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 [13,14,15].

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 [16].

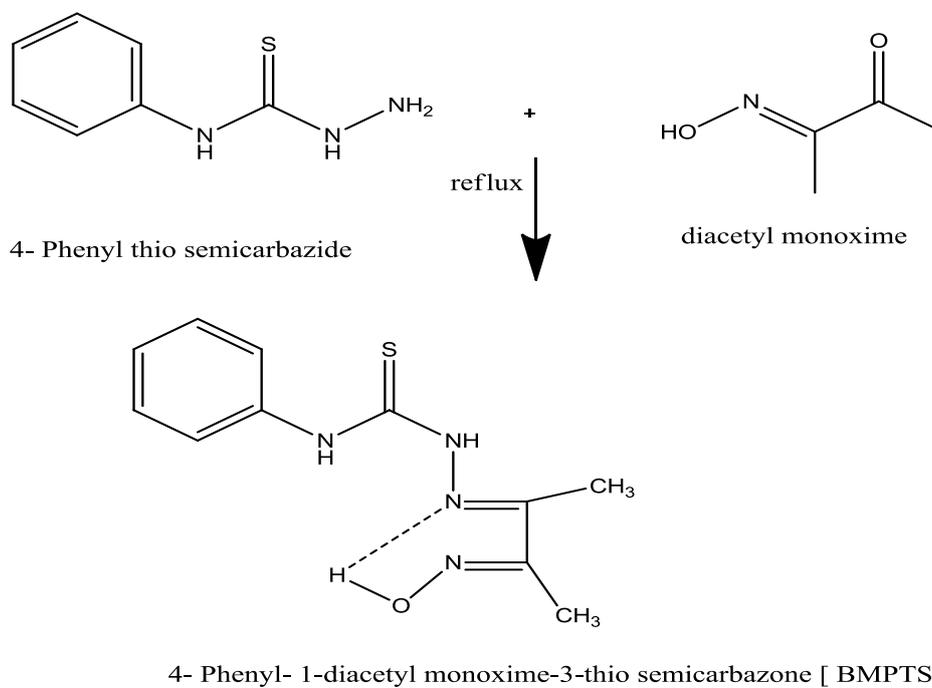
#### EXPERIMENTAL

##### Materials and Methods

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

## Preparation of PDMSC

4-phenyl-1-diacetylmonoxime-3-thiosemicarbazone (BMPTS) was prepared by boiling an EtOH solution of 4-phenylthiosemicarbazone (1.7g, 1mmole) with an EtOH solution of diacetylmonoxime(1g, 1mmole) 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-2-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 absolute ethanol 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  $1 \text{ cm}^{-1}$ . 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 absolute ethanol 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 [16] using equation:

$$\Lambda_m = \frac{(K_s - K_{solv})K_{cell} \times 1000}{C}$$

Where  $K_s$  and  $K_{solv}$  are the specific conductance of the solution and the solvent, respectively;  $K_{cell}$  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 absolute ethanol alone at different temperatures by extrapolating the relation between  $\Lambda_m$  and  $C_m^{1/2}$  to zero concentration as shown in Figure 1 .

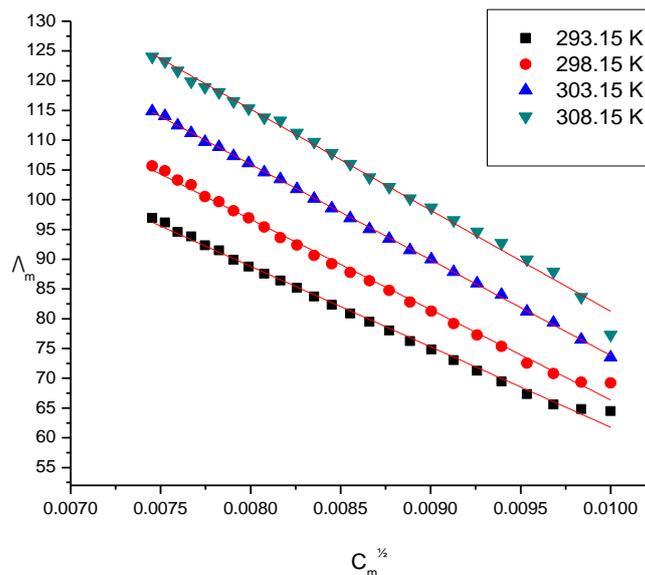


Figure 1: The relation between molar conductance ( $\Lambda_m$ ) and ( $C_m^{1/2}$ ) of  $\text{CuCl}_2$  alone in absolute ethanol at different temperatures (293.15K, 298.15 K, 303.15 K and 308.15 K).

The limiting molar conductances ( $\Lambda_0$ ) at infinite dilutions were estimated for  $\text{CuCl}_2$  in the presence of the ligand (BMPTS) by extrapolating the relation between  $\Lambda_m$  and  $C_m^{1/2}$  to zero concentration Figure 2.

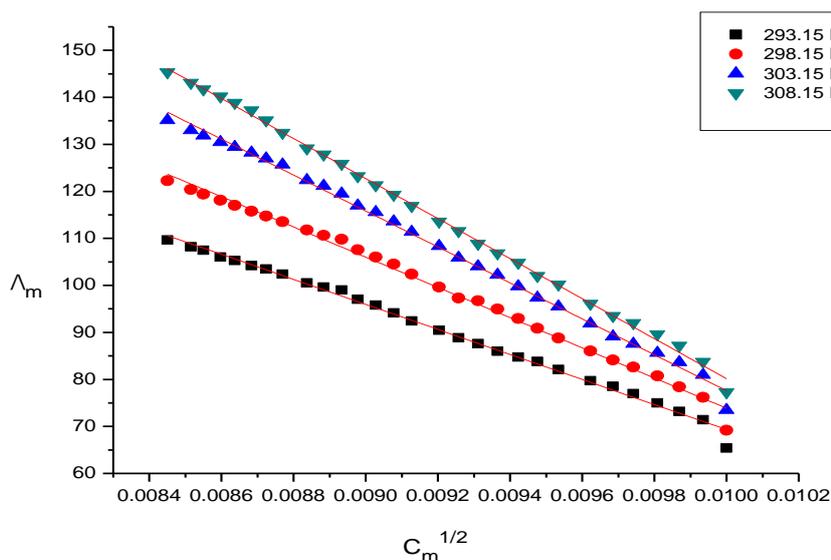


Figure 2: The relation between molar conductance ( $\Lambda_m$ ) and ( $C_m^{1/2}$ ) of  $\text{CuCl}_2$  in presence of BMPTS at different temperatures (293.15K, 298.15 K, 303.15 K and 308.15 K).

By drawing the relation between molar conductance ( $\Lambda_m$ ) and the molar ratio of metal to ligand (M/L) concentrations (Figure 3,4,5,6), different lines are obtained with sharp breaks indicating the formation of 1:2, 1:1 and 2:1 (M:L) stoichiometric complexes.

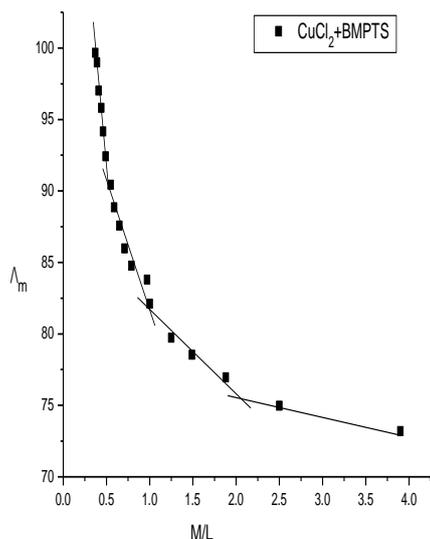


Figure 3: The relation between  $\Lambda_m$  and M/L at 293.15 K.

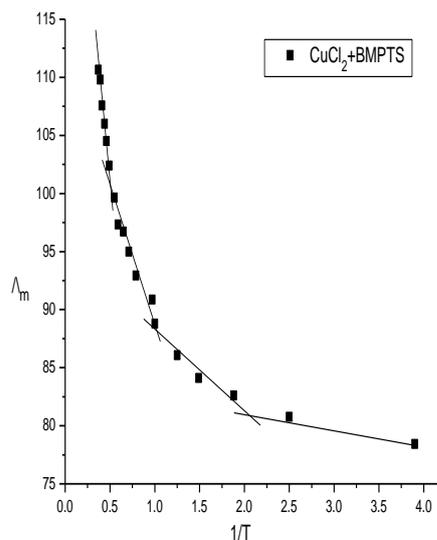


Figure 4: The relation between  $\Lambda_m$  and M/L at 298.15 K

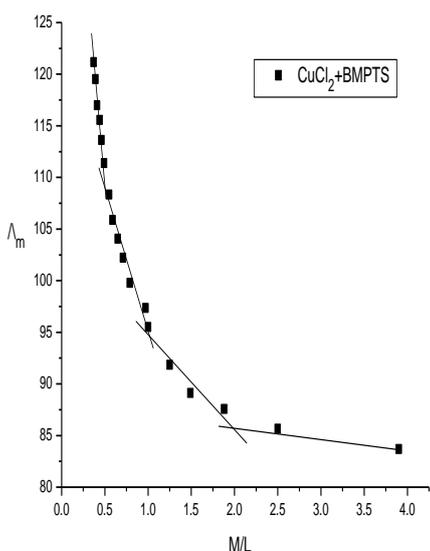


Figure 5: The relation between  $\Lambda_m$  and M/L at 303.15 K.

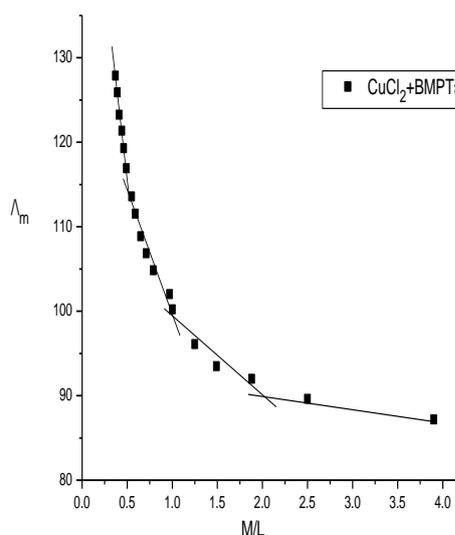


Figure 6: The relation between  $\Lambda_m$  and M/L at 308.15 K

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 absolute ethanol 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]:

$K_A =$	$\Lambda_0^2(\Lambda_0 - \Lambda_m)$
	$4C_m^2 \gamma_{\pm}^2 \Lambda_m^3 S(Z)$

Where ( $\Lambda_m, \Lambda_0$ ) are the molar and limiting molar conductance of  $\text{CuCl}_2$  in presence of HI 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).**

$C_{[\text{ligand}]}$	$C_{m[\text{CuCl}_2]}$	$K_A$			
		Temp	293.15 K	298.15 K	303.15 K
4.76E-05	9.52E-05	3.69E+09	3.92E+09	4.15E+09	4.24E+09
6.25E-05	9.38E-05	3.55E+09	3.80E+09	4.03E+09	4.14E+09
7.41E-05	9.26E-05	3.32E+09	3.57E+09	3.81E+09	3.94E+09
9.09E-05	9.09E-05	3.00E+09	3.25E+09	3.49E+09	3.53E+09
1.12E-04	8.88E-05	2.70E+09	2.95E+09	3.20E+09	3.25E+09
1.33E-04	8.67E-05	2.50E+09	2.75E+09	2.99E+09	2.98E+09
1.53E-04	8.47E-05	2.34E+09	2.51E+09	2.68E+09	2.69E+09
1.67E-04	8.33E-05	2.19E+09	2.37E+09	2.54E+09	2.56E+09
1.85E-04	8.15E-05	2.01E+09	2.19E+09	2.37E+09	2.40E+09
2.02E-04	7.98E-05	1.85E+09	2.03E+09	2.21E+09	2.25E+09

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

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

Where R is the gas constant (8.341 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  $\text{CuCl}_2$  with (BMPTS) at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K).**

$C_{[\text{ligand}]}$	$C_{m[\text{CuCl}_2]}$	$\Delta G_A(\text{kJ/mol})$			
		Temp	293.15 K	298.15 K	303.15 K
4.76E-05	9.52E-05	-53.6906	-54.7572	-55.8189	-56.7921
6.25E-05	9.38E-05	-53.5963	-54.6766	-55.7461	-56.7346
7.41E-05	9.26E-05	-53.4352	-54.5260	-55.6049	-56.6078
9.09E-05	9.09E-05	-53.1853	-54.2912	-55.384	-56.3235
1.12E-04	8.88E-05	-52.9313	-54.0533	-55.1606	-56.113
1.33E-04	8.67E-05	-52.7384	-53.8737	-54.9932	-55.8885
1.53E-04	8.47E-05	-52.5778	-53.6546	-54.7196	-55.6307
1.67E-04	8.33E-05	-52.4176	-53.5057	-54.5809	-55.501
1.85E-04	8.15E-05	-52.2145	-53.3169	-54.4048	-55.3361
2.02E-04	7.98E-05	-52.0098	-53.1256	-54.2260	-55.1679

The formation constants ( $K_f$ ) for  $\text{CuCl}_2$  complexes were calculated for each type of complexes (1:2), (1:1) and (2:1) (M: L) [21, 22] by using equation:

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

Where  $\Lambda_M$  is the limiting molar conductance of the  $\text{CuCl}_2$  alone,  $\Lambda_{obs}$  is the molar conductance of solution during titration and  $\Lambda_{ML}$  is the molar conductance of the complex.

The obtained values ( $K_f$ ) for  $\text{CuCl}_2$ -ligand stoichiometric complexes are presented in Table 3..

**Table 3: Formation constants for 1:2, 1:1 and 2:1 (M/L) complexes in 80%V ethanol at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K).**

		K <sub>f</sub>			
		1 : 2 (M/L)			
Cm	293.15 K	298.15 K	303.15 K	308.15 K	
8.33E-05	9.34E+05	1.60E+06	3.65E+06	6.07E+06	
8.24E-05	2.15E+05	2.41E+05	2.73E+05	2.87E+05	
8.06E-05	1.21E+05	1.31E+05	1.42E+05	1.47E+05	
7.98E-05	8.33E+05	8.81E+04	9.45E+04	9.57E+04	
7.89E-05	5.70E+04	5.96E+04	6.22E+04	6.51E+04	
		1 : 1 (M/L)			
Cm	293.15 K	298.15 K	303.15 K	308.15 K	
9.09E-05	1.51E+06	2.94E+06	7.20E+06	1.35E+07	
8.98E-05	4.78E+05	5.84E+05	6.95E+05	7.49E+05	
8.88E-05	2.10E+05	2.34E+05	2.57E+05	2.68E+05	
8.77E-05	1.39E+05	1.51E+05	1.63E+05	1.70E+05	
8.67E-05	9.99E+04	1.07E+05	1.14E+05	1.19E+05	
		2 : 1 (M/L)			
Cm	293.15 K	298.15 K	303.15 K	308.15 K	
9.52E-05	3.70E+06	5.76E+06	1.96E+07	4.05E+07	
9.51E-05	2.29E+06	4.72E+06	7.29E+06	2.13E+07	
9.49E-05	2.35E+06	3.34E+06	6.12E+06	1.70E+07	
9.38E-05	8.43E+05	9.82E+05	1.21E+06	1.39E+06	
9.26E-05	3.56E+05	3.87E+05	4.33E+05	4.78E+05	

The Gibbs free energies of formation for each stoichiometric complexes were calculated by using the equation:

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

The calculated  $\Delta G_f$  values are presented in Table 4..

**Table 4: Gibbs free energies of formation of CuCl<sub>2</sub> with (BMPTS) at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K).**

		$\Delta G_f$ (k J/mol)			
		1 : 2 (M/L)			
Cm	293.15 K	298.15 K	303.15 K	308.15 K	
8.33E-05	-33.5062	-35.4186	-38.6101	-40.0132	
8.24E-05	-29.9213	-30.7227	-31.5431	-32.1980	
8.06E-05	-28.5327	-29.2024	-29.9039	-30.4900	
7.98E-05	-27.6142	-28.2254	-28.8738	-29.4307	
7.89E-05	-26.6914	-27.2560	-27.8632	-28.3955	
		1 : 1 (M/L)			
Cm	293.15 K	298.15 K	303.15 K	308.15 K	
9.09E-05	-34.6947	-36.9222	-39.7946	-42.0630	
8.98E-05	-31.8704	-32.9142	-33.9037	-34.6531	
8.88E-05	-29.8736	-30.6410	-31.3942	-32.0260	
8.77E-05	-28.8655	-29.5576	-30.2505	-30.8484	
8.67E-05	-28.0579	-28.7026	-29.3582	-29.9335	
		2 : 1 (M/L)			
Cm	293.15 K	298.15 K	303.15 K	308.15 K	
9.52E-05	-36.9100	-38.5867	-42.3140	-44.8741	
9.51E-05	-35.7210	-38.6948	-39.8286	-43.2330	
9.49E-05	-35.8110	-37.2365	-39.3847	-42.6516	
9.38E-05	-33.3122	-34.2007	-35.2945	-36.2303	
9.26E-05	-31.2310	-31.8942	-32.712	-33.5029	

The enthalpy ( $\Delta H_A$ ) for CuCl<sub>2</sub> complexes were calculated for each type of complexes (1:2) , (1:1) and (2:1) (M:L) by using van 't Hoff equation [23,24]:

$$\frac{d \ln K}{dT} = \frac{\Delta H^\ominus}{RT^2} \quad (6)$$

Where  $R$  is the gas constant (8.341 J) and  $T$  is the absolute temperature. 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 Table 7.

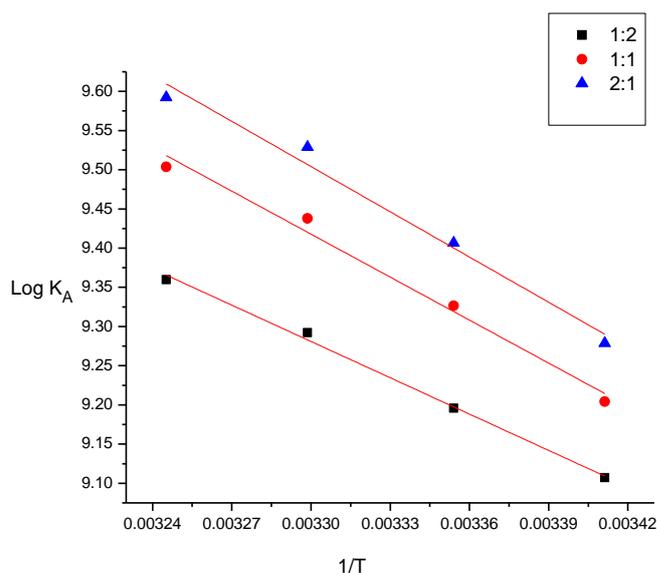


Figure 7: The relation between ( $\log K_A$ ) and ( $1/T$ ).

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 5:

Table 5: The enthalpies and entropies of association of complexes at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K).

M:L Temp	$(\Delta S_A)$ kJ/mol.K				$(\Delta H_A)$ kJ/mol
	293.15 K	298.15 K	303.15 K	308.15 K	
1:2	0.2752	0.2752	0.2754	0.2751	29.5695
1:1	0.2956	0.2960	0.2962	0.2956	35.0122
2:1	0.3033	0.3036	0.3039	0.3031	36.8291

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 Figure 8.

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 6:

Table 6: The enthalpies and entropies of formation of complexes at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K).

M:L Temp	$(\Delta S_f)$ kJ/mol.K				$(\Delta H_f)$ kJ/mol
	293.15 k	298.15 K	303.15 K	308.15 K	
1:2	0.4385	0.4356	0.4366	0.4383	95.3191
1:1	0.5311	0.5314	0.5296	0.5317	119.4839
2:1	0.5499	0.5532	0.5493	0.5513	121.8139

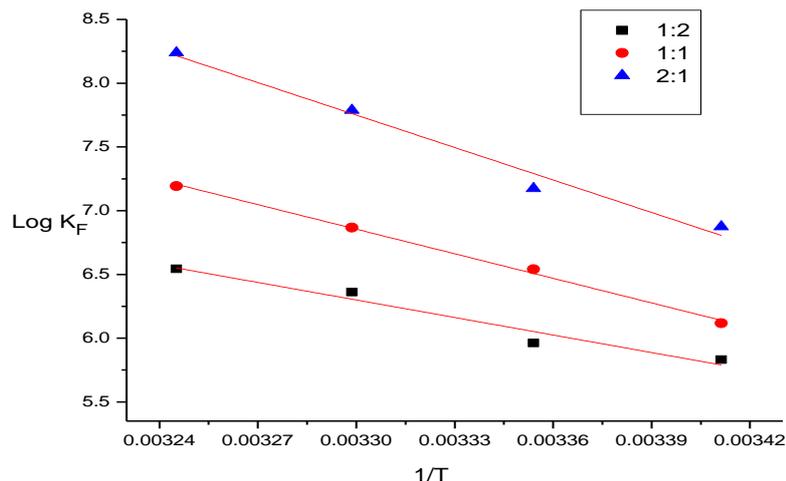


Figure 8: The relation between (log K<sub>f</sub>) and (1/T).

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<sub>a</sub> is the Arrhenius activation energy of the transfer process. Consequently, from the plot of log Λ<sub>0</sub> vs. 1/T, the E<sub>a</sub> values can be evaluated [25] as shown in Fig (9), giving high activation energy value due to solvation behavior.

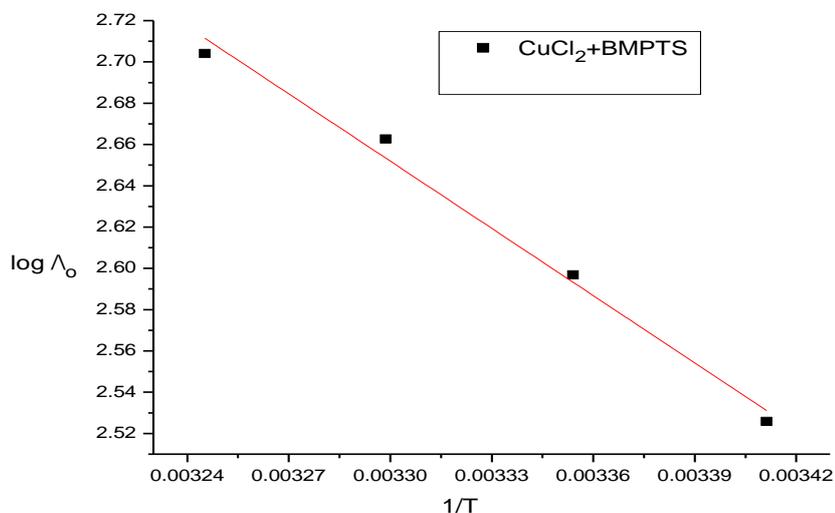


Figure 9: The relation between log Λ<sub>0</sub> and 1/T. E<sub>a</sub>=20.7985 kJ/mol

## CONCLUSION

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 ΔG show the ability of the studied ligand to form stable complexes and the process trend to proceed spontaneously. However, the obtained positive values of ΔH means that enthalpy is not the driving force for the formation of the complexes. Furthermore, the positive values of ΔS indicate that entropy is responsible for the complexing process. The formation constants and Gibbs free energies of different complexes follow that order: K<sub>f</sub> (2:1) > K<sub>f</sub> (1:1) > K<sub>f</sub> (1:2) for (M:L), and ΔG<sub>f</sub> (2:1) > ΔG<sub>f</sub> (1:1) > ΔG<sub>f</sub> (1:2) for (M:L)

## REFERENCES

1. MV Angelusiu, SF Barbuceanu, C Draghici, GL Almajan. New Cu(II), Co(II), Ni(II) complexes with aroyl-hydrazone based ligand. Synthesis, spectroscopic characterization and in vitro antibacterial evaluation. *Eur J Med Chem.* 2010;45(5):2055–2062. F.
2. Vosburg WC, Cooper GR. Complex Ions. I. The Identification of Complex Ions in Solution by Spectrophotometric Measurements. *J Am Chem Soc.* 1941;63(2):437-442.
3. TA Yousef, TH Rakha, Usama El Ayaan, GM Abu El Reash. Synthesis, spectroscopic characterization and thermal behavior of metal complexes formed with (Z)-2-oxo-2-(2-(2-oxoindolin-3-ylidene)hydrazinyl)-N-phenylacetamide (H2O). *J Mol Str.* 2012;1007:146-157.
4. RK Parashar, RC Sharma. Stability studies in relation to IR data of some schiff base complexes of transition metals and their biological and pharmacological studies. *Inorg Chem Acta.* 1988;151(3):201-208.
5. MCR Arguelles, et al. Synthesis, characterization and biological activity of Ni, Cu and Zn complexes of isatin hydrazones. *J Inorg Biochem.* 2004;98(3):313-321.
6. SM Emam, FA El-Saied SA. Abou El-Enein HA. El-Shater. Cobalt(II), nickel(II), copper(II), zinc(II) and hafnium(IV) complexes of N'-(furan-3-ylmethylene)-2-(4-methoxyphenylamino)acetohydrazide *Spectrochim Acta Part A.* 2009;72(2):291–297.
7. AR Yaul, VV Dhande, AS Aswar. Synthesis, characterization, electrical and biological studies of VO(IV), MoO2(VI), WO2(VI), Th(IV) and UO2(VI) complexes with hydrazone ligand. *Rev Roum Chim.* 2010;55:537–542.
8. AS El-Tabl, FA El-Saied, W Plass, AN Al-Hakimi. Synthesis, spectroscopic characterization and biological activity of the metal complexes of the Schiff base derived from phenylaminoacetohydrazide and dibenzoylmethane. *Spectrochim Acta Part A.* 2008;71(1):90–99.
9. Y Li, Z.-Y Yang, M.-F Wang. A Spectroscopic Study of 2-[4'-(Dimethylamino)phenyl]-benzothiazole Binding to Insulin Amyloid Fibrils. *J Fluoresc.* 2010;20(4):891–905.
10. SB Desai, PB Desai, KR Desai. Synthesis Of Some Schiff Bases, Thiazolidinones And Azetidines Derived From 2,6-Diaminobenzof[1,2-D:4,5-D'] Bisthiazole And Their Anticancer Activities. *Heterocycl Commun.* 2001;7:83–90.
11. MS Niasari, A Amiri. Synthesis and characterization of alumina-supported Mn(II), Co(II), Ni(II) and Cu(II) complexes of bis(salicylaldehyde)hydrazone as catalysts for oxidation of cyclohexene with tert-butylhydroperoxide. *Appl Catal A.* 2005;290:46–53.
12. MCR Arguelles, et al. Synthesis, characterization and biological activity of Ni, Cu and Zn complexes of isatin hydrazones. *J Inorg Biochem.* 2004;98:313–321.
13. P Yogeeswari, N Menon, A Semwal, M Arjun, D Sriram. Discovery of molecules for the treatment of neuropathic pain: Synthesis, antiallodynic and antihyperalgesic activities of 5-(4-nitrophenyl)furoic-2-acid hydrazones. *Eur J Med Chem.* 2011;46(7):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 metal complexes derived from 2-hydroxyimino-3-(2'-hydrazonopyridyl)-butane. *Transition Met Chem.* 1991;16(2):189-192.
16. Gryzybkowski W, Pastewski R. Conductometric studies of Co(II), Ni(II), and Cu(II) nitrates in dimethyl sulfoxide solutions at 25 °C. *Electrochimica Acta.* 1980;25(3):279-285.
17. El-Shishtawi NA, Hamada MA, Gomaa EA. *J Chem Eng Data.* 2010;55:5422.
18. Hamada MA, El-Shishtawi NA, Gomaa EA. Conductometric evaluation of association constant for aqueous solutions of CoCl2 in the absence and presence of magnetic field. *South Braz J Chem.* 2009;17:33.
19. Gomaa EA. Solute-solvent interactions of some univalent-univalent salts with various organic solvents at 25 °C. *Thermochimica Acta.* 1987;120:183-190.
20. Gomaa EA. Theoretical contribution of solvation of AgBr in some organic solvents at 25 °C. *Thermochimica Acta.* 1988;128:99-104.
21. Farid I El-Dossoki. Electric conductance and semi-empirical studies on two thiophene derivatives/metal cation complexation. *J Mol Liq.* 2008;142:53-56.
22. Rahmi-Nasrabadi M, Ahmedi F, Pourmor-tazari SM, Ganjal MR, Alizadeh K. Conductometric study of complex formations between some substituted pyrimidines and some metal ions in acetonitrile and the determination of thermodynamic parameters. *J Mol Liq.* 2009;144:97.
23. Atkins PW. 1978, *Physical Chemistry*, Oxford University Press.
24. Ives DJG. 1971, *Chemical Thermodynamics*, University Chemistry, Macdonald Technical and Scientific.