THE IJES

Evaluation of thermodynamic parameters (conductometrically) for the interaction of Cu(II) ion with 4-phenyl -1-diacetyl monoxime -3- thiosemicarbazone (BMPTS) in (60%V) ethanol (EtOH-H₂O) at different temperatures

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---ABSTRACT--
The association constant ,formation constants and Gibbs free energies are calculated from the conductometric titration curves of $CuCl_2$ with 4-phenyl-2-diacetyl monoxime-3-thiosemicarbazone (BMPTS) in 60 % by volume of ethanol (EtOH) - water 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 the interaction for $CuCl_2$ with (BMPTS) were also estimated and their values were discussed.

Key words: Association constants; formation constants; Gibbs free energies; solvation free energies; enthalpy and entropy of solvation.

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I.   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, cheating 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 [3-5]. 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 (ΔG)ₛ ,enthalpy changes of solvation(ΔH)ₛ and the entropy of solvation (ΔS) from conductometric technique. Thus, thermodynamic studies of complexation reactions of this Schiff base with transition metal ions not only result in important information 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 $CuCl_2$ with (BMPTS) in 60% V ethanol solutions at 294.15 K. These non-covalent interactions can help us for analysis of salts in bodies and environnement [16].

II.   EXPERIMENTAL

Materials and Methods

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

Preparation of BMPTS

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 ^{O}C; yield 80%). The purity of the compound was checked by TLC.
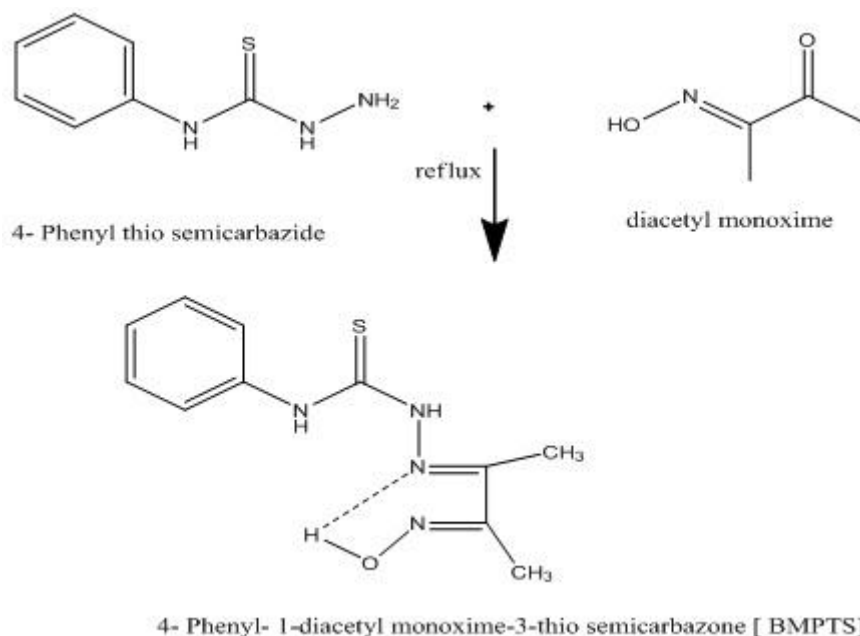
Scheme. (1): The outline of the synthesis of 4-phenyl-2-diacetyl monoxime-3-thiosemicarbazone (BMPTS)

Conductance measurement

The conductometric titration of the CuCl$_2$ (1x10^{-4}) mole/L against the ligand (1x10^{-3}) mole/L in 60%V of ethanol-water 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 cm^{-1}. The temperature was adjusted at 293.15 K, 298.15 K, 303.15 K and 308.15 K.

III.   RESULTS AND DISCUSSION

The specific conductance values (K$_s$) of different concentrations of 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 (Λ_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 CuCl$_2$ solutions.
The limiting molar conductances (Λ_m) at infinite dilutions were estimated for CuCl$_2$ in absolute ethanol alone at different temperatures by extrapolating the relation between Λ_m and C$_m^{1/2}$ to zero concentration .

The limiting molar conductances (Λ_o) at infinite dilutions were estimated for CuCl$_2$ in the presence of the ligand (BMPTS) by extrapolating the relation between Λ_m and C$_m^{1/2}$ to zero concentration **Fig. (1)**
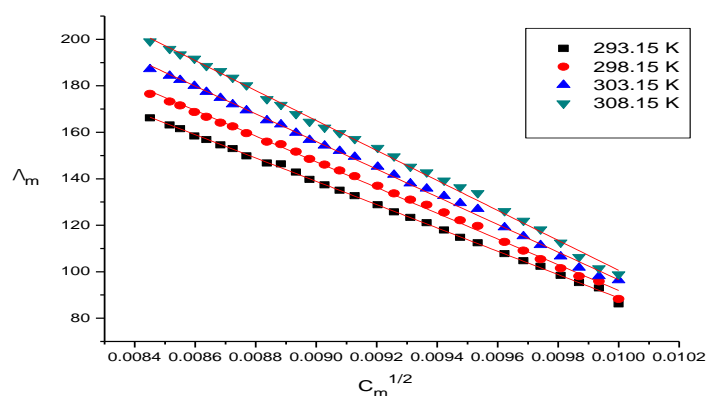
Fig. (1): : The relation between molar conductance ($\wedge_m$) and ($C_m^{1/2}$) of $CuCl_2$ in presence of BMPTS at different temperatures (293.15K, 298.15 K, 303.15 K and 308.15 K,) in EtOH 60%..

By drawing the relation between molar conductance ($\wedge_m$) 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.
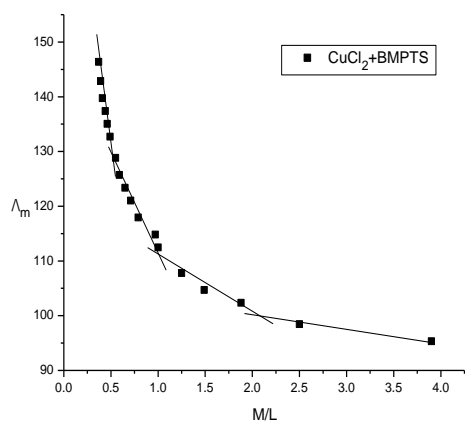

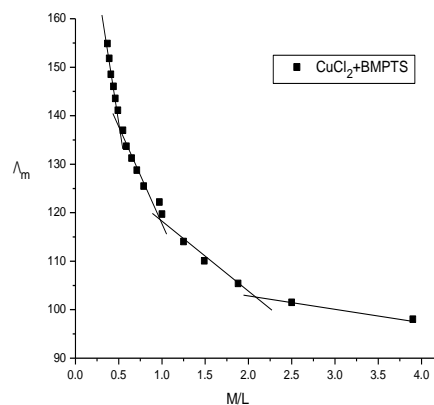**Fig. (2):** The relation between $\wedge_m$ and M/L at 293.15 K.
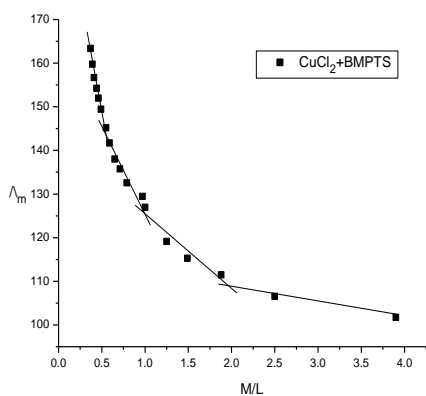

Fig. (3): The relation between $\wedge_m$ and M/L at 298.15 K

Fig. (4): The relation between $\wedge_m$ and M/L at 303.15 K
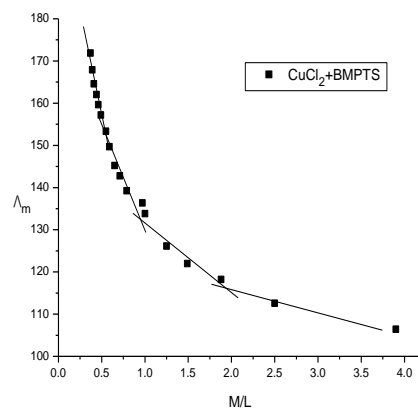
Fig. (5): The relation between $\wedge_m$ and M/L at 308.15 K

The experimental data of (Λ_M) and (Λ_o) were analyzed for the determination of association and formation constants for each type of the stoichiometric complexes.

The association constants of $CuCl_2$ in the presence of ligand (BMPTS) in 60% 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]:

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

(2)

Where (Λ_m, Λ_0) are the molar and limiting molar conductance of $CuCl_2$ in presence of Hl respectively; C_m is molar concentration of $CuCl_2$, $\gamma_{\pm}$ 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 $CuCl_2$ with (BMPTS) at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K) in 60% EtOH.

C[ligand]	Cm[CuCl2]	K_A			
	Temp	293.15 K	298.15 K	303.15 K	308.15 K
4.76E-05	9.52E-05	4.78E+09	5.48E+09	5.68E+09	5.96E+09
6.25E-05	9.38E-05	4.29E+09	5.00E+09	5.23E+09	5.54E+09
7.41E-05	9.26E-05	4.00E+09	4.60E+09	4.83E+09	5.11E+09
9.09E-05	9.09E-05	3.62E+09	3.95E+09	4.08E+09	4.38E+09
1.12E-04	8.88E-05	3.25E+09	3.55E+09	3.72E+09	4.04E+09
1.33E-04	8.67E-05	2.95E+09	3.24E+09	3.42E+09	3.82E+09
1.53E-04	8.47E-05	2.68E+09	2.93E+09	3.04E+09	3.25E+09
1.67E-04	8.33E-05	2.51E+09	2.75E+09	2.86E+09	3.09E+09
1.85E-04	8.15E-05	2.34E+09	2.57E+09	2.69E+09	2.92E+09
2.02E-04	7.98E-05	2.15E+09	2.36E+09	2.50E+09	2.71E+09

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

$\Delta G_A = - R T \ln K_A$ (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 $CuCl_2$ with (BMPTS) at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K) in 60%EtOH .

C[ligand]	Cm[CuCl2]	ΔG_A(k J/mol)			
	Temp	293.15 K	298.15 K	303.15 K	308.15 K
4.76E-05	9.52E-05	-54.3214	-55.5877	-56.6097	-57.6672
6.25E-05	9.38E-05	-54.0565	-55.3602	-56.3997	-57.4771
7.41E-05	9.26E-05	-53.8888	-55.1526	-56.1978	-57.2701
9.09E-05	9.09E-05	-53.6446	-54.7728	-55.7743	-56.876
1.12E-04	8.88E-05	-53.3838	-54.5112	-55.5408	-56.6682
1.33E-04	8.67E-05	-53.1410	-54.2803	-55.3309	-56.5236
1.53E-04	8.47E-05	-52.9094	-54.0356	-55.0327	-56.1081
1.67E-04	8.33E-05	-52.7518	-53.8776	-54.8774	-55.9858
1.85E-04	8.15E-05	-52.5796	-53.7052	-54.7251	-55.8408
2.02E-04	7.98E-05	-52.3678	-53.5017	-54.5386	-55.6505

The formation constants (K_f) for $CuCl_2$ complexes were calculated for each type of complexes (1:2), (1:1) and (2:1) (M: L) **[22, 23]** by using equation:

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

Where Λ_M is the limiting molar conductance of the $CuCl_2$ alone, Λ_{obs} is the molar conductance of solution during titration and Λ_{ML} is the molar conductance of the complex.

The obtained values (K_f) for $CuCl_2$-ligand stoichiometric complexes are presented in **Table (3)**

Table (3): Formation constants for 1:2, 1:1 and 2:1 (M/L) complexes in 60% ethanol at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K).

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K_f			
1 : 2 (M/L)			
[L]	**293.15 K**	**298.15 K**	**303.15 K**	**308.15 K**
1.67E-04	1.49E+06	4.31E+06	8.85E+06	1.94E+07
1.76E-04	2.37E+05	2.56E+06	2.58E+05	2.81E+05
1.85E-04	1.21E+05	1.23E+05	1.29E+05	1.34E+05
1.94E-04	7.76E+04	7.77E+04	8.02E+04	8.27E+04
2.02E-04	5.12E+04	5.13E+04	5.28E+04	5.35E+04
1 : 1 (M/L)			
[L]	**293.15 K**	**298.15 K**	**303.15 K**	**308.15 K**
9.09E-05	1.51E+06	2.94E+06	2.62E+07	5.70E+07
1.02E-04	4.78E+05	5.84E+05	5.41E+05	5.65E+05
1.12E-04	2.10E+05	2.34E+05	2.19E+05	2.38E+05
1.23E-04	1.39E+05	1.51E+05	1.24E+05	1.28E+05
1.33E-04	9.99E+04	1.07E+05	8.99E+04	9.16E+04
2 : 1 (M/L)			
[L]	**293.15 K**	**298.15 K**	**303.15 K**	**308.15 K**
4.76E-05	7.76E+06	2.93E+07	8.06E+07	1.74E+08
4.94E-05	2.29E+06	8.12E+06	3.06E+07	3.26E+07
5.06E-05	1.19E+06	6.37E+06	1.37E+07	2.12E+07
6.25E-05	4.91E+05	5.89E+05	6.16E+05	6.62E+05
7.41E-05	2.46E+04	2.54E+05	2.56E+05	2.65E+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 ΔG_f values are presented in **Table (4)**.

Table (4): Gibbs free energies of formation of $CuCl_2$ with HL at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K).

	ΔG_f (k J/mol)			
	1 : 2 (M/L)			
[L]	293.15 K	298.15 K	303.15 K	308.15 K
1.67E-04	-34.6388	-37.8594	-40.3174	-43.0038
1.76E-04	-30.1609	-30.8729	-31.4067	-32.1445
1.86E-04	-28.5191	-29.0660	-29.6586	-30.2487
1.94E-04	-29.4424	-27.9118	-28.4616	-29.0097
2.12E-04	-26.4282	-26.8863	-27.4075	-27.8933
	1 : 1 (M/L)			
[L]	293.15 K	298.15 K	303.15 K	308.15 K
9.09E-05	-34.4083	-40.5047	-43.0533	-45.7535
1.02E-04	-31.8618	-32.6760	-33.2730	-33.9330
1.12E-04	-29.7724	-30.3548	-30.9893	-31.7188
1.23E-04	-28.4612	-28.9613	-29.5555	-30.1289
1.33E-04	-27.6683	-28.1781	-28.9498	-29.2906
	2 : 1 (M/L)			
[L]	293.15 K	298.15 K	303.15 K	308.15 K
4.76E-05	-38.7100	-42.6212	-45.8830	-48.6180
4.94E-05	-35.7210	-39.4387	-43.4457	-44.3176
5.06E-05	-34.1022	-38.8350	-41.4165	-43.2132
5.25E-05	-31.9011	-32.9347	-33.6012	-34.3384
7.41E-05	-30.2030	-30.8510	-31.4157	-31.9936

The enthalpy (ΔH_A) for $CuCl_2$ 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]** :

$$\frac{d \ln K}{dT} = \frac{\Delta H^{\ominus}}{RT^2},$$ **(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 **Fig.(7).**
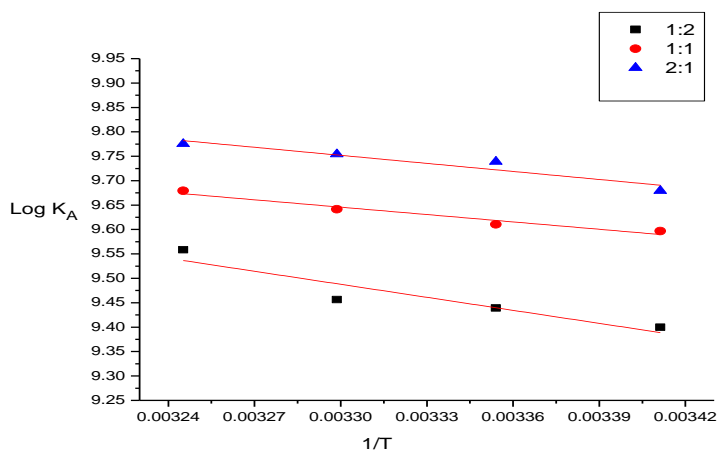

Fig. (7): The relation between (log K_A) and (1/T).

From the relation between log K and 1/T, ΔH_A can be calculated for each type of complexes from the slope of each line (-ΔH/2.303R).The entropy (ΔS_A) for $CuCl_2$ complexes were calculated for each type of complexes (1:2), (1:1) and (2:1) (M:L) by using equation :

$$\Delta G = \Delta H – T\Delta S \qquad (7)$$

Where (S) is the entropy of system.

The calculated values of (ΔH_A) and (ΔS_A) for CuCl$_2$-ligand stoichiometric complexes are presented in **Table (5):**

Table (5): : The enthalpies (ΔH_A) and entropies (ΔS_A) of CuCl$_2$ with BMPTS at different temperatures

M:L	(ΔS_A)kJ/mol.K				(ΔH_A)kJ/mol
Temp	293.15 k	298.15 K	303.15 K	308.15 K	
1:2	0.2418	0.2378	0.2372	0.2369	17.0193
1:1	0.159	0.2160	0.2158	0.2158	9.6328
2:1	0.2212	0.2217	0.2214	0.2212	10.5252

Table (6): : The enthalpies (ΔH_f) and entropies (ΔS_f) of CuCl$_2$ with BMPTS at different temperatures

M:L	(ΔS_f)kJ/mol.K				(ΔH_f)kJ/mol
Temp	293.15 k	298.15 K	303.15 K	308.15 K	
1:2	0.5509	0.5525	0.5515	0.5512	126.8636
1:1	0.6122	0.6157	0.6139	0.6128	143.0766
2:1	0.6629	0.6649	0.6647	0.6628	155.6284

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.(8).**
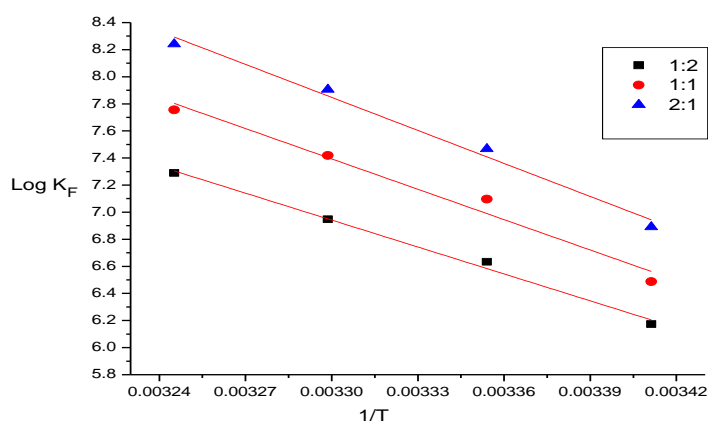

Fig. (8): The relation between (log K$_f$) and (1/T).

The enthalpy (ΔH_f) for 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 (ΔH_f) and (ΔS_f) for CuCl$_2$-ligand stoichiometric complexes are presented in **Table (6).**

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):

$$\Lambda_0 = A\ e^{-Ea/RT} \qquad (8)$$

where A is the frequency factor, R is the gas constant and Ea is the Arrhenius activation energy of the transfer process. Consequently, from the plot of logΛ_0 vs. 1/T, the Ea values can be evaluated [25] as shown in **Fig (9) .**

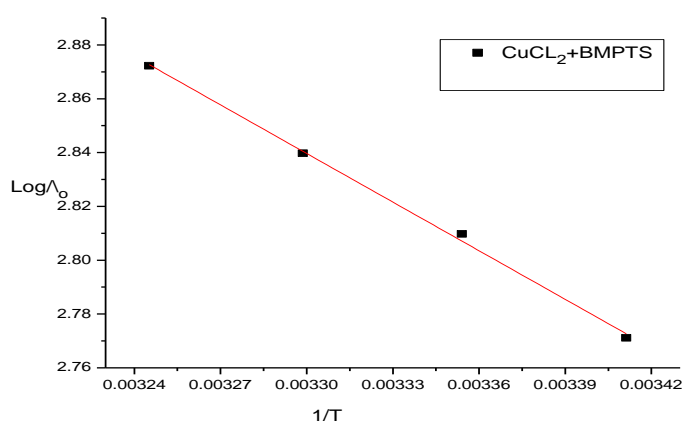**Fig. (9):** The relation between log Λ_0 and 1/T. Ea=10.34741KJ/mol

IV. CONCLUSION

The stability constants for the complexation of copper(II) ion with (BMPTS) in 60% V (EtOH) 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_f (2:1) › K_f (1:1) › K_f (1:2) for (M:L), and ΔG_f (2:1) › ΔG_f (1:1) › ΔG_f (1:2) for (M:L)

REFERENCES

[1.]   M.V. Angelusiu, S.F. Barbuceanu, C. Draghici, G.L. Almajan, Eur. J. Med. Chem. 45 (2010) 2055–2062. F.
[2.]   Vosburg W C and Cooper G R, J.Am. Chem. Soc., 1941, 63, 437.
[3.]   S. Jayasree, K.K. Arvindakshan, J. Indian Chem. Soc. 71 (1994) 97.
[4.]   R.K. Parashar, R.C. Sharma, Inorg. Chem. Acta 151 (1988) 201.
[5.]   M.C.R.Arguelles,M.B. Ferrari, F. Bisceglie, C. Plizzi,G. Pelosi, S. Pinelli, M. Sassi, J. Inorg. Biochem. 98 (2004) 313..
[6.]   S.M Emam, F.A. El-Saied, S.A. AbouEl-Enein, H.A. El-Shater, Spectrochim. Acta Part A 72 (2009) 291–297..
[7.]   A.R. Yaul, V.V. Dhande, A.S. Aswar, Rev. Roum. Chim. 55 (2010) 537–542.
[8.]   A.S. El-Tabl, F.A. El-Saied,W. Plass, A.N. Al-Hakimi, Spectrochim. Acta Part A 71 (2008) 90–99.
[9.]   Y. Li, Z.-Y. Yang, M.-F.Wang, J. Fluoresc. 20 (2010) 891–905.
[10.]   S.B. Desai, P.B. Desai, K.R. Desai, Heterocycl. Commun. 7 (2001) 83–90.
[11.]   M.S. Niasari, A. Amiri, Appl. Catal. A 290 (2005) 46–53.
[12.]   M.C.R. Arguelles,M.B. Ferrari, F. Bisceglie, C. Plizzi, G. Pelosi, S. Pinelli,M. Sassi, J. Inorg. Biochem. 98 (2004) 313–321.
[13.]   P. Yogeeswari, N.Menon, A. Semwal,M. Arjun, D. Sriram, Eur. J.Med. Chem. 46 (2011) 2964–2970.
[14.]   Zhibo Yang, , Ph.D. thesis, Wayne State University, Detroit, Michigan, USA., 2005.
[15.]   Kamal M.Ibrahim, Magdy M.Bekhit and Gaber M.Abu EL-Reash (1991) Transition Met .Chem, 16,189-192.
[16.]   Gryzybkowski, W. and Pastewski, R. (1980) *Electrochimica Acta* 25, 279
[17.]   El-Shishtawi, N.A , Hamada, M.A. and Gomaa, E.A. (2010) *J. Chem. Eng. Data* 55, 5422
[18.]   Hamada, M.A. , El-Shishtawi, N.A. and Gomaa, E.A. , (2009), *South . Braz . J.Chem.* 17, 33
[19.]   Gomaa, E.A. (1987) *Thermochimica Acta* 120, 183
[20.]   Gomaa, E.A. (1988) *Thermochimica Acta* 128, 99
[21.]   El-Doussoki, F.I. (2008) *Journal of Molecular Liquids* 142, 53
[22.]   Farid I. El-Dossoki, , Journal of Molecular Liquids, vol.142, pp.53-56, 2008.
[23.]   Rahmi-Nasrabadi, M., Ahmedi, F., Pourmor-tazari, S.M., Ganjal, M.R. and Alizadeh, K. (2009) *Journal of Molecular Liquids* 144, 97
[24.]   Atkins, P.W. (1978), Physical Chemistry, Oxford University Press.
[25.]   Ives, D.J.G. (1971), Chemical Thermodynamics, University Chemistry, Macdonald Technical and Scientific.