Conductometric Study of Complex Formation Between 
Cu (II) Ion and 
2-hydroxyimino-3-(2'-hydazonopyridyl)-butane (HL)

E A. Gomaa*, K. M. Ibrahim , N. M. Hassan
Chemistry Department, Faculty of Science, Mansoura University, 35516 , Mansoura, Egypt

Abstract The association constant, formation constants and Gibbs free energies are calculated from the conductometric titration curves of CuCl₂ with 2-hydroxyimino-3-(2'-hydazonopyridyl)-butane (HL) in absolute ethanol at different temperatures (293.15 K, 298.15 K, 303.15 K 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 CuCl₂ with HL were also estimated and their values were also discussed. The solvation free energies (\( \Delta G_s \)), enthalpy changes of solvation (\( \Delta H_s \)) and the entropy of solvation (\( \Delta S_s \)) were also calculated from solubility measurements for 2-hydroxyimino-3-(2'-hydazonopyridyl)-butane (HL) at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K).

Keywords Association Constants, Formation, Gibbs Free Energies, Solvation Free Energies, Enthalpy Changes of Solvation

1. Introduction

Schiff bases hydrazone derivatives and their metal complexes have been studied for their interesting and important properties, e.g., antibacterial[1,2], antifungal[3], antioxidant[4], anticancer[5] and catalytic activity in oxidation of cyclohexene[6]. 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 chelate or drugs in therapy of anaemia[7] and treatment of neuropathic pain[8].

Therefore it prompted us to study Schiff base transition metal complexes. 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[9]. Copper (II) ion is a biologically active, essential ion, cleaving 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[10]. Schiff base transition metal complexes have been extensively studied because of their potential use as catalysts in a wide range of oxidation reactions[11–14]. In recent years many copper, nickel and manganese complexes of Schiff bases were prepared and characterized by several techniques[15, 16].

2. Objectives

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 (\( \Delta S_s \)) from solubility measurements and identification of coordination behaviour of Schiff base ligand HL towards CuCl₂ and the determination of the thermodynamic stability constants and thermodynamic functions using the 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 CuCl₂ with 2-hydroxyimino-3-(2'-hydazonopyridyl)-butane (HL) in absolute ethanol solutions at 294.15 K. These non-covalent interactions can help us for analysis of salts in bodies and environment[17].

* Corresponding author:
esam_1947@hotmail.com (E. A. Gomaa )
Published online at http://journal.sapub.org/fs
Copyright © 2012 Scientific & Academic Publishing. All Rights Reserved
3. Methods

3.1. Materials

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

3.2. Preparation of HL

2-hydroxyimino-3-(2'-hydrazonopyridyl)-butane (HL) (scheme 1) was prepared by boiling an EtOH solution of 2-hydrazino pyridine (Aldrich) with 2, 3-butanedione monoxime (1:1) under reflux. The product was recrystallised from hot absolute EtOH[ 18]. (M.p: 220°C; yield 80%). The purity of the compound was checked by TLC.

3.4. Conductometric Measurement

The conductometric titration of the CuCl₂ (1x10⁻⁴) mole/L against the ligand (1x10⁻³) mole/L in absolute ethanol was performed with 0.2 ml interval additions from HL 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.

3.5. Solubility Measurement

Saturated solutions of HL were prepared by dissolving an excess amount of the solid substances in 10 ml. of the corresponding solvent mixtures, using closed test tubes. The solutions were vigorously shaken in a thermostatic water-bath at the desired temperature. The molal solubilities of the HL were analysed by drying 1ml. of the saturated solutions in small aluminium dishes. Evaporation of the solvent was performed carefully and slowly under a tungsten lamp to prevent any loss in salt weight. Solubility value was taken as an average of three consecutive independent measurements.

4. Results and Discussion

4.1. Association Constants

The specific conductance values (Kₕ) of different concentrations of CuCl₂ 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 (Λₘ) values were calculated[19] using equation (1):

$$\Lambda_m = \frac{(K_s - K_{solv})K_{cell} \times 1000}{C}$$  \hspace{1cm} (1),$$

where Kₕ and Kₕₛ₀ are the specific conductance of the solution and the solvent, respectively; Kₜ is the cell constant and C is the molar concentration of the CuCl₂ solutions.

The limiting molar conductances (Λₘ₀) at infinite dilutions...
were estimated for CuCl₂ in absolute ethanol alone at different temperatures by extrapolating the relation between \( \lambda_m \) and \( C_m^{\text{½}} \) to zero concentration as shown in Fig. (1).

The limiting molar conductances (\( \lambda_o \)) at infinite dilutions were estimated for CuCl₂ in the presence of the ligand (HL) by extrapolating the relation between \( \lambda_m \) and \( C_m^{\text{½}} \) to zero concentration Fig. (2).

By drawing the relation between molar conductance (\( \lambda_m \)) and the molar ratio of metal to ligand (M/L) concentrations (Fig. (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 1](image1.png)

**Figure 1.** The relation between molar conductance (\( \lambda_m \)) and \( C_m^{\text{½}} \) of CuCl₂ alone in absolute ethanol at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K).

![Figure 2](image2.png)

**Figure 2.** The relation between molar conductance (\( \lambda_m \)) and \( C_m^{\text{½}} \) of CuCl₂ in presence of HL in absolute ethanol at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K).

![Figure 3](image3.png)

**Figure 3.** The relation between \( \lambda_m \) and M/L(CuCl₂-HL) at 293.15 K.

![Figure 4](image4.png)

**Figure 4.** The relation between \( \lambda_m \) and M/L(CuCl₂-HL) at 298.15 K.

![Figure 5](image5.png)

**Figure 5.** The relation between \( \lambda_m \) and M/L(CuCl₂-HL) at 303.15 K.
The relation between $\Lambda_m$ and M/L (CuCl$_2$-HL) at 308.15K

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

The association constants of CuCl$_2$ in the presence of ligand (HL) in absolute ethanol at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K) for 2:1, 1:1 and 1:2 (M:L) were calculated by using equation (2):

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

where $\Lambda_m$ and $\Lambda_0$ are the molar and limiting molar conductance of CuCl$_2$ in presence of HL respectively; $C_m$ is molar concentration of CuCl$_2$, $S(Z)$ is Fuoss-Shedlovsky factor, equal with unity for strong electrolytes[22]. The calculated association constants are shown in Table (1).

### 4.2. Gibbs Free Energies of Association

The Gibbs free energies of association ($\Delta G_A$) were calculated from the association constant[23, 24] by applying equation:

$$\Delta G_A = -RT \ln K_A$$

where $R$ is the gas constant (8.341J) and $T$ is the absolute temperature. The calculated Gibbs free energies were presented in Table (2).

### 4.3. The Formation Constants for Complexes

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)[25, 26] by using equation:

$$K_f = \frac{\Lambda_M - \Lambda_{obs}}{\Lambda_{obs} - \Lambda_M}$$

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

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

#### Table 1. Association constants of CuCl$_2$ with HL at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K)

| $K_A$ | Cm   | 293.15 K | 298.15 K | 303.15 K | 308.15 K |
|-------|------|----------|----------|----------|----------|
| 9.52E-05 | 3.93E+01 | 4.63E+01 | 5.33E+01 | 5.60E+01 |
| 9.38E-05 | 3.66E+01 | 4.31E+01 | 4.94E+01 | 5.19E+01 |
| 9.26E-05 | 3.46E+01 | 4.09E+01 | 4.63E+01 | 4.84E+01 |
| 9.09E-05 | 3.18E+01 | 3.67E+01 | 4.20E+01 | 4.38E+01 |
| 8.88E-05 | 2.89E+01 | 3.31E+01 | 3.77E+01 | 3.88E+01 |
| 8.67E-05 | 2.61E+01 | 3.00E+01 | 3.40E+01 | 3.51E+01 |
| 8.47E-05 | 2.41E+01 | 2.72E+01 | 3.07E+01 | 3.19E+01 |
| 8.33E-05 | 2.27E+01 | 2.54E+01 | 2.84E+01 | 2.96E+01 |
| 8.15E-05 | 2.11E+01 | 2.32E+01 | 2.59E+01 | 2.71E+01 |
| 7.98E-05 | 1.96E+01 | 2.17E+01 | 2.40E+01 | 2.50E+01 |

#### Table 2. Gibbs free energies of association of CuCl$_2$ with HL at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K)

| $\Delta G_A$(kJ/mol) | Cm   | 293.15 K | 298.15 K | 303.15 K | 308.15 K |
|----------------------|------|----------|----------|----------|----------|
| 9.52E-05 | -8.95E+00 | -9.51E+00 | -1.00E+01 | -1.03E+01 |
| 9.38E-05 | -8.78E+00 | -9.33E+00 | -9.83E+00 | -1.01E+01 |
| 9.26E-05 | -8.64E+00 | -9.20E+00 | -9.66E+00 | -9.94E+00 |
| 9.09E-05 | -8.43E+00 | -8.93E+00 | -9.42E+00 | -9.68E+00 |
| 8.88E-05 | -8.19E+00 | -8.68E+00 | -9.15E+00 | -9.37E+00 |
| 8.67E-05 | -8.20E+00 | -8.43E+00 | -8.89E+00 | -9.12E+00 |
| 8.47E-05 | -7.75E+00 | -8.19E+00 | -8.63E+00 | -8.87E+00 |
| 8.33E-05 | -7.61E+00 | -8.02E+00 | -8.44E+00 | -8.68E+00 |
| 8.15E-05 | -7.43E+00 | -7.79E+00 | -8.20E+00 | -8.45E+00 |
| 7.98E-05 | -7.25E+00 | -7.62E+00 | -8.01E+00 | -8.25E+00 |
### 4.4. Gibbs Free Energies of Complex Formation

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

\[ \Delta G_f = - R \, T \, \ln K_f \]  \hspace{1cm} (5)

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

### 4.5. Enthalpies and Entropies

The enthalpy (\( \Delta H_A \)) 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 \([26,27]\):

\[ \frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \]  \hspace{1cm} (6)

where \( R \) is the gas constant 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).

### 4.6. Enthalpies and Entropies of Association

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 (\(-\Delta H/2.303 \, R\)). The entropy (\( \Delta S_A \)) for CuCl\(_2\) complexes were calculated for each type of complexes (1:2), (1:1) and (2:1) (M:L) by using equation:

\[ \Delta G = \Delta H - T \Delta S \]  \hspace{1cm} (7)

Where (S) is the entropy of the system.

The calculated values of (\( \Delta H_A \)) and (\( \Delta S_A \)) for CuCl\(_2\)-ligand stoichiometric complexes are presented in Table (5):

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).

### 4.7. Enthalpies and Entropies of Complex Formation

The enthalpy (\( \Delta H_f \)) 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 (\( \Delta H_f \)) and (\( \Delta S_f \)) for CuCl\(_2\)-ligand stoichiometric complexes are presented in Table (6):

### 4.8. Activation Energies

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):

\[ \ln \lambda = A e^{-E_a/RT} \]  \hspace{1cm} (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\([27]\) as shown in Fig (9).

\( E_a \) value is 14.6996 KJ/mol.

### 4.9. Solubility Measurement

The solubility (S) of 2-hydroxyimino-3-(2’-hydazonopyryl)butane (HL) in (EtOH-H\(_2\)O) mixtures at different temperatures (293.15, 298.15, 303.15 and 308.15 K) was determined by gravimetric technique. The results are illustrated in Table 1. Solubility was calculated as an average of the two experimental data. The molal solubility is...
calculated by using equation (9):

\[
\text{Molal solubility (S)} = \frac{W \times 1000}{d \times M} \text{g.mole /1000 g solvent} \quad (9),
\]

where \((W)\) is the weight of one ml. of saturated solution, after its complete evaporation in the aluminum dish under the effect of tungsten lamp, \((M)\) is the molecular weight of HL and \((d_0)\) is the density of pure solvent used as it shown in Table (7). Fig.(10) the molal solubility was increased with the increase of the content of the organic solvent used (EtOH). This can be explained on the basis of the fact that like dissolve like as well as the lower and higher ion-solvent interactions. The molal solubility of HL was increased with the increase of temperatures.

**Table 4.** Gibbs free energies of formation of CuCl₂ with HL at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K)

| Cm    | 293.15 K | 298.15 K | 303.15 K | 308.15 K |
|-------|----------|----------|----------|----------|
| 1:2   |          |          |          |          |
| 8.33E-05 | -32.7243 | -34.0278 | -36.9243 | -38.6072 |
| 8.24E-05 | -30.9752 | -31.8059 | -33.2027 | -34.1017 |
| 8.05E-05 | -29.0121 | -29.5208 | -30.1944 | -30.9637 |
| 7.98E-05 | -28.3917 | -28.9411 | -29.4929 | -30.1157 |
| 7.89E-05 | -27.7900 | -28.3702 | -28.9740 | -29.4305 |
| 1:1   |          |          |          |          |
| 9.09E-05 | -35.2606 | -36.3031 | -39.6971 | -42.4394 |
| 8.98E-05 | -33.1527 | -33.7523 | -34.7234 | -35.4580 |
| 8.88E-05 | -31.5954 | -31.9121 | -32.5605 | -33.1690 |
| 8.87E-05 | -30.4886 | -30.6951 | -31.2246 | -31.7554 |
| 8.67E-05 | -29.6959 | -29.9470 | -30.4239 | -30.9824 |
| 2:1   |          |          |          |          |
| 9.52E-05 | -38.5812 | -40.9373 | -43.3258 | -48.5997 |
| 9.51E-05 | -36.5700 | -38.4688 | -41.7124 | -44.9520 |
| 9.49E-05 | -35.9583 | -37.0661 | -40.1272 | -42.5507 |
| 9.38E-05 | -33.7636 | -34.7418 | -36.6154 | -36.0204 |
| 9.26E-05 | -32.0900 | -33.0054 | -34.5210 | -33.8937 |

**Figure 7.** The relation between \((\log K_A)\) and \((1/T)\)
### 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)

|       | Temp     | 293.15 K | 298.15 K | 303.15 K | 308.15 K |
|-------|----------|----------|----------|----------|----------|
| 1 : 2 | ΔHA      | 13.8326  | 13.8326  | 13.8326  | 13.8326  |
|       | ΔSA      | 0.07316  | 0.07329  | 0.07347  | 0.07305  |
| 1 : 1 | ΔHA      | 16.5043  | 16.5043  | 16.5043  | 16.5043  |
|       | ΔSA      | 0.08505  | 0.08530  | 0.08551  | 0.08497  |
| 2 : 1 | ΔHA      | 18.1299  | 18.1299  | 18.1299  | 18.1299  |
|       | ΔSA      | 0.09236  | 0.09270  | 0.09279  | 0.09138  |

### Figure 8. The relation between (log $K_f$) and (1/T)

### 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)

|       | Temp     | 293.15 K | 298.15 K | 303.15 K | 308.15 K |
|-------|----------|----------|----------|----------|----------|
| 1 : 2 | ΔHf      | 87.7317  | 87.7317  | 87.7317  | 87.7317  |
|       | ΔSf      | 0.4109   | 0.4083   | 0.4112   | 0.4099   |
| 1 : 1 | ΔHf      | 123.0207 | 123.0207 | 123.0207 | 123.0207 |
|       | ΔSf      | 0.5399   | 0.5360   | 0.5367   | 0.0536   |
| 2 : 1 | ΔHf      | 162.4927 | 162.4927 | 162.4927 | 162.4927 |
|       | ΔSf      | 0.6859   | 0.6823   | 0.6789   | 0.6850   |
Table 7. The Molal solubility (S) of HL at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K)

| Vol. % of EtOH | 293.15 K | 298.15 K | 303.15 K | 308.15 K |
|----------------|----------|----------|----------|----------|
| 0              | 0.0005   | 0.0007   | 0.0009   | 0.0011   |
| 10             | 0.0011   | 0.0015   | 0.0019   | 0.0021   |
| 20             | 0.0016   | 0.0019   | 0.0025   | 0.0030   |
| 30             | 0.0018   | 0.0024   | 0.0029   | 0.0033   |
| 40             | 0.0032   | 0.0044   | 0.0051   | 0.0057   |
| 50             | 0.0047   | 0.0063   | 0.0072   | 0.0081   |
| 60             | 0.0069   | 0.0076   | 0.0089   | 0.0115   |
| 70             | 0.0114   | 0.0125   | 0.0148   | 0.0179   |
| 80             | 0.0179   | 0.0199   | 0.0221   | 0.0246   |
| 90             | 0.0201   | 0.0229   | 0.0248   | 0.0275   |
| 100            | 0.0257   | 0.0278   | 0.0311   | 0.0339   |

Figure 9. The relation of \(\log /\sigma\) and \(1/T\)

Figure 10. Variation of the molal solubility (S) of HL with the mole fraction (Xs) of EtOH at different temperatures
### Table 8. The solvation free energies ($\Delta G_s$) of HL in EtOH-H2O mixture at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K)

| Vol. % of EtOH | ($\Delta G_s$)$_{293.15}$ (KJ/mol) | ($\Delta G_s$)$_{298.15}$ (KJ/mol) | ($\Delta G_s$)$_{303.15}$ (KJ/mol) | ($\Delta G_s$)$_{308.15}$ (KJ/mol) | ($\Delta H_s$)$_{293.15}$ (KJ/mol) | ($\Delta H_s$)$_{298.15}$ (KJ/mol) | ($\Delta H_s$)$_{303.15}$ (KJ/mol) | ($\Delta H_s$)$_{308.15}$ (KJ/mol) |
|---------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| 0             | 18.5286                          | 18.0104                          | 17.6789                          | 17.7005                          | 35.1255                          | 35.1255                          | 35.1255                          | 35.1255                          |
| 10            | 16.6066                          | 16.1209                          | 15.7953                          | 15.7994                          | 32.7945                          | 32.7945                          | 32.7945                          | 32.7945                          |
| 20            | 15.6932                          | 15.5348                          | 15.1035                          | 14.8854                          | 32.4435                          | 32.4435                          | 32.4435                          | 32.4435                          |
| 30            | 15.3393                          | 14.9045                          | 14.7294                          | 14.6412                          | 28.6884                          | 28.6884                          | 28.6884                          | 28.6884                          |
| 40            | 13.9657                          | 13.4528                          | 13.3063                          | 13.2407                          | 27.6306                          | 27.6306                          | 27.6306                          | 27.6306                          |
| 50            | 13.0406                          | 12.5629                          | 12.4370                          | 12.3403                          | 25.3114                          | 25.3114                          | 25.3114                          | 25.3114                          |
| 60            | 12.1305                          | 12.0978                          | 11.9026                          | 11.4422                          | 22.8197                          | 22.8197                          | 22.8197                          | 22.8197                          |
| 70            | 10.9065                          | 10.8642                          | 10.6206                          | 10.3085                          | 21.897                           | 21.897                           | 21.897                           | 21.897                           |
| 80            | 9.8067                           | 9.7113                           | 9.6099                           | 9.437                            | 19.020                           | 19.020                           | 19.020                           | 19.020                           |
| 90            | 9.5241                           | 9.3632                           | 9.3193                           | 9.2082                           | 17.336                           | 17.336                           | 17.336                           | 17.336                           |
| 100           | 8.9250                           | 8.8825                           | 8.7487                           | 8.6721                           | 15.199                           | 15.199                           | 15.199                           | 15.199                           |

### 4.10. Thermodynamics of Solvation

The solvation free energies $\Delta G_s$ of HL in EtOH-H2O mixture at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K) were calculated from the solubility measurements by using the following equation (10):

$$\Delta G_s = - 2.303 RT \log K_{sp}$$  (10)

The value of (log $K_{sp}$) depends mainly on the solvation of the solute in the solvent under investigation. In case of neutral compound (the activity coefficient is close to one), the values of (log $K_{sp}$) can be equal to log (S).

The enthalpy changes of solvation ($\Delta H_s$) of HL in EtOH-H2O mixtures were calculated from the plots of (log $K_{sp}$) versus (1/T), where the slope equals (-$\Delta H_s$/2.303 R) using the following equation (11):

$$\log K_{sp} = \frac{-\Delta H_s}{2.303 RT} + \text{constant}$$  (11)

### 5. Conclusions

The stability constants for the complexation of copper (II) ion with 2-hydroxyimino-3-(2'-hydazonopyridyl)-butane (HL) 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 trend 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. 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 $\Delta G_f (2:1) > \Delta G_f (1:1) > \Delta G_f (1:2)$ for (M:L)

### REFERENCES

[1] S.M. Emam, F.A. El-Saied, S.A. Abou El-Enein, H.A. El-Shater, Spectrochim. Acta Part A 72 (2009) 291–297.
[2] A.R. Yaul, V.V. Dhande, A.S. Aswar, Rev. Roum. Chim. 55 (2010) 537–542.
[3] A.S. El-Tabl, F.A. El-Saied, W. Plass, A.N. Al-Hakim, Spectrochim. Acta Part A 71 (2008) 90–99.
[4] Y. Li, Z.-Y. Yang, M.-F. Wang, J. Fluoresc. 20 (2010) 891–905.
[5] S.B. Desai, P.B. Desai, K.R. Desai, Heterocycl. Commun. 7 (2001) 83–90.
[6] M.S. Niasari, A. Amirizi, Appl. Catal. A 290 (2005) 46–53.
[7] M.C.R. Arguelles, M.B. Ferrari, F. Bisceglie, C. Plizzi, G. Pelosi, S. Pinelli, M. Sassi, J. Inorg. Biochem. 98 (2004) 313–321.
[8] P. Yogeeswari, N. Menon, A. Semwal, M. Arjun, D. Sriram, Eur. J. Med. Chem. 46 (2011) 2964–2970.
[9] M.V. Angelusiu, S.F. Barbuceanu, C. Draghici, G.L. Almajan, Eur. J. Med. Chem. 45 (2010) 2055–2062, F. W. C. Usborg and G.R. Cooper, J. Am. Chem. Soc., 1941, 63, 437.
[10] L. Canali, D.C. Sherrington, Chem. Soc. Rev. 28 (1999) 85–93.
[11] G.J. Kim, J.H. Shin, Catal. Lett. 63 (1999) 83–89.
[12] T. Katsuki, Coord. Chem. Rev. 140 (1995) 189–214.
[13] K.J. O’Connor, S.J. Wey, C.J. Burrows, Tetrahedron Lett. 33 (1992) 1001–1004.
[14] M.J. Samide, D.G. Peters, J. Electroanal. Chem. 443 (1998) 95–102.
[15] Losada, I. Del Peso, L. Beyer, Inorg. Chim. Acta 321 (2001) 107–115.
[16] Zhibo Yang, Ph.D. thesis, Wayne State University, Detroit, Michigan, USA., 2005.
[17] Kamal M. Ibrahim, Magdy M. Bekhit and Gaber M. Abu EL-Reash (1991) Transition Met. Chem., 16, 189-192.
[18] W. Gryzybkowski, and R Pastewski, (1980) Electrochimica Acta 25, 279

[19] N.A El-Shishawi, , M.A Hamada, , and E.A. Gomaa, (2010) J. Chem. Eng. Data 55, 5422

[20] M.A. Hamada, , N.A El-Shishawi, , and E.A. Gomaa, , (2009), South . Braz . J.Chem. 17, 33

[21] E.A. Gomaa, (1987) Thermochimica Acta 120, 183

[22] E.A. Gomaa , (1988) Thermochimica Acta 128, 99

[23] F.I. El-Doussoki, (2008) Journal of Molecular Liquids 142, 53

[24] Farid I. El-Doussoki, , Journal of Molecular Liquids, vol.142, pp.53-56, 2008.

[25] M., Rahmi-Nasrabadi, F.Ahmedi, , S.M., Pourmor-tazari, M.R. Ganjal, and K Alizadeh,, (2009) Journal of Molecular Liquids 144, 97

[26] P.W. Atkins, (1978), Physical Chemistry, Oxford University Press.

[27] C. Burgdorff, T. Kircher, Photo physical properties of tetracene derivatives in solution, Spectrochim. Acta part A, 44, 11 (1988), 1137–1141.