

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

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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 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 CuCl_2 with HL were also estimated and their values were also discussed. The solvation free energies (ΔG_s), Enthalpy changes of solvation (ΔH_s) and the entropy of solvation (ΔS_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, 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[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 (ΔG_s), enthalpy changes of solvation (ΔH_s) and the entropy of solvation (ΔS_s) from solubility measurement and identification of coordination behaviour of Schiff base ligand HL towards CuCl_2 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.

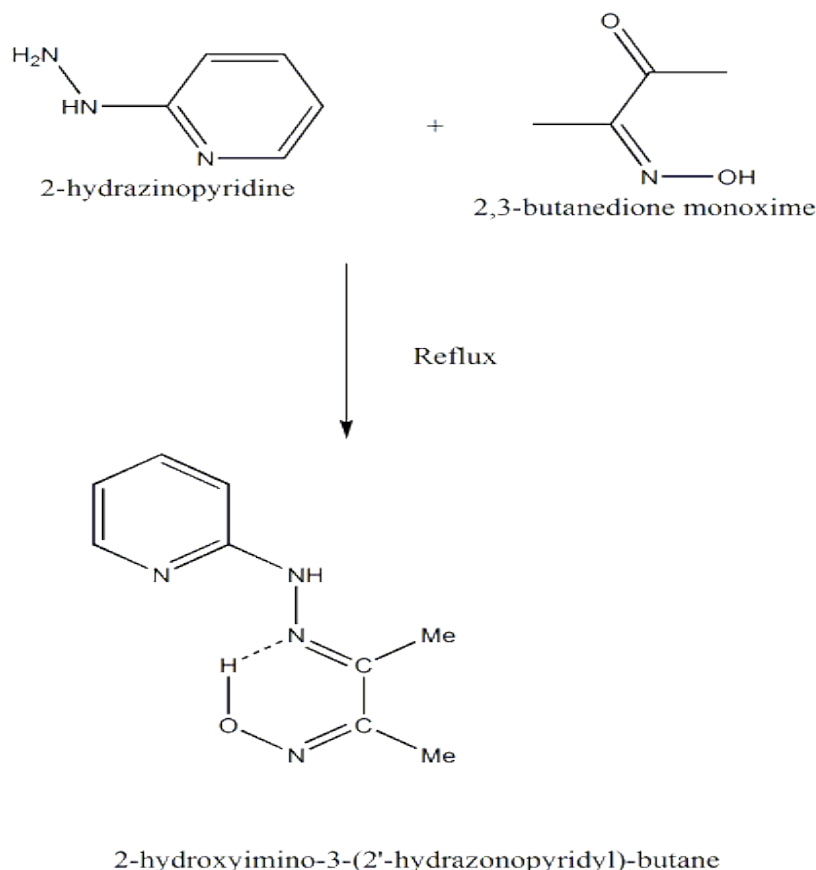
The aim of this work is the evaluation of the non-covalent behavior of CuCl_2 with 2-hydroxyimino-3-(2'-hydazonopyridyl)-butane (HL) in absolute ethanol solutions at 294.15 K. These non-covalent interactions can help us for analysis of salts in bodies and environment[17].

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Scheme 1. The outline of the synthesis of 2-hydroxyimino-3-(2'-hydrazonopyridyl)-butane (HL)

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 CuCl_2 (1×10^{-4} mole/L) against the ligand (1×10^{-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 (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 [19] using equation (1):

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

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 as shown in Fig.(1) .

The limiting molar conductances (Λ_0) at infinite dilutions were estimated for CuCl_2 in the presence of the ligand (HL) by extrapolating the relation between Λ_m and $C_m^{1/2}$ to zero concentration Fig. (2)

By drawing the relation between molar conductance (Λ_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.

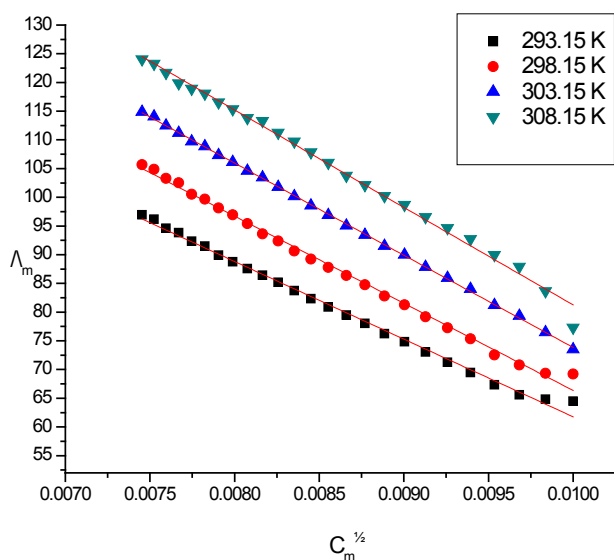


Figure 1. The relation between molar conductance (Λ_m) and ($C_m^{1/2}$) of CuCl_2 alone in absolute ethanol at different temperatures (293.15K, 298.15 K, 303.15 K and 308.15 K)

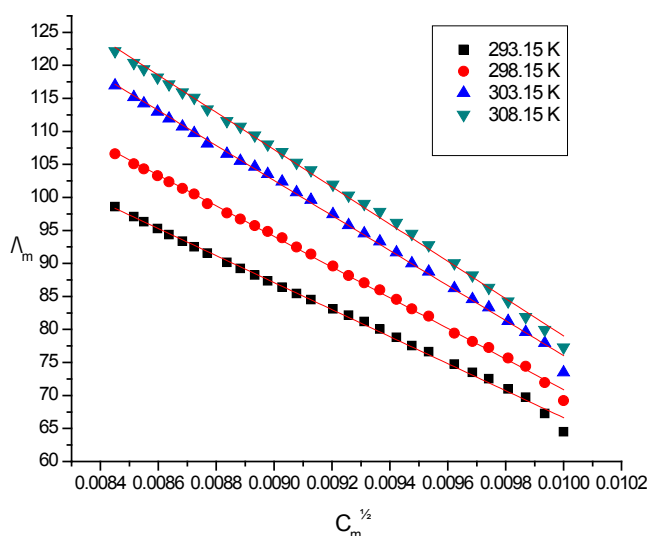


Figure 2. The relation between molar conductance (Λ_m) and ($C_m^{1/2}$) of CuCl_2 in presence of HL in absolute ethanol at different temperatures (293.15K, 298.15 K, 303.15 K and 308.15 K)

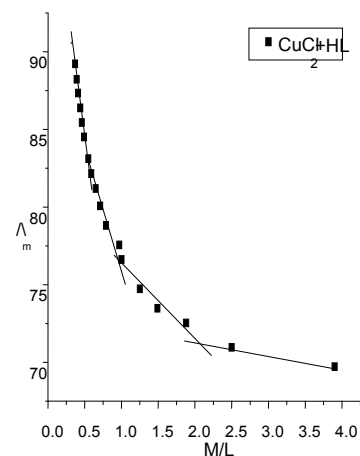


Figure 3. The relation between Λ_m and M/L (CuCl_2 -HL) at 293.15 K

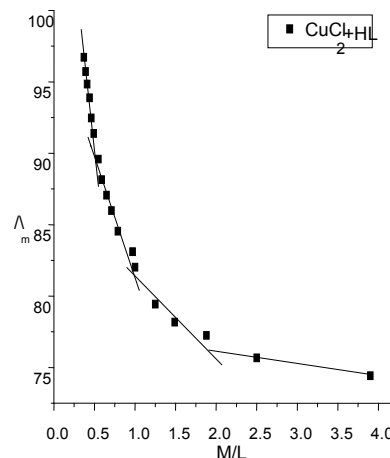


Figure 4. The relation between Λ_m and M/L (CuCl_2 -HL) at 298.15 K

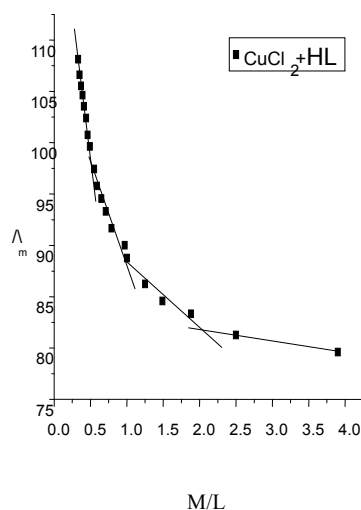


Figure 5. The relation between Λ_m and M/L (CuCl_2 -HL) at 303.15 K

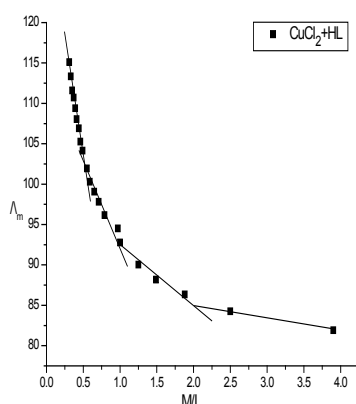


Figure 6. The relation between Λ_m and M/L ($\text{CuCl}_2\text{-HL}$) at 308.15K

The experimental data of (Λ_m) and (Λ_0) 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 (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[20,21]:

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

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 , $S(Z)$ 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 (ΔG_A) were calculated from the association constant[23, 24] by applying equation:

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

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).

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:

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

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 1. Association constants of CuCl_2 with HL at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K)

Cm	K _A			
	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)

Cm	ΔG_A (kJ/mol)			
	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

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

		K _f			
		1 : 2 (M/L)			
Cm		293.15 K	298.15 K	303.15 K	308.15 K
8.33E-05		6.78E+05	9.16E+05	2.30E+06	3.50E+06
8.24E-05		3.31E+05	3.74E+05	5.26E+05	6.04E+05
8.06E-05		1.48E+05	1.49E+05	1.60E+05	1.77E+05
7.98E-05		1.15E+05	1.18E+05	1.21E+05	1.27E+05
7.89E-05		8.95E+04	9.34E+04	9.83E+04	9.75E+04
		1 : 1 (M/L)			
Cm		293.15 K	298.15 K	303.15 K	308.15 K
9.09E-05		1.31E+06	2.81E+06	6.92E+06	1.56E+07
8.98E-05		6.00E+05	8.19E+05	9.62E+05	1.02E+06
8.88E-05		3.29E+05	3.90E+05	4.08E+05	4.19E+05
8.77E-05		2.13E+05	2.39E+05	2.40E+05	2.42E+05
8.67E-05		1.56E+05	1.77E+05	1.75E+05	1.79E+05
		2 : 1 (M/L)			
Cm		293.15 K	298.15 K	303.15 K	308.15 K
9.52E-05		7.50E+06	1.49E+07	2.92E+07	1.73E+08
9.51E-05		3.28E+06	5.49E+06	1.54E+07	4.17E+07
9.49E-05		2.56E+06	3.12E+06	8.21E+06	1.63E+07
9.38E-05		1.04E+06	1.22E+06	2.04E+06	1.27E+06
9.26E-05		5.23E+05	6.06E+05	8.88E+05	5.57E+05

4.4. Gibbs Free Energies of Complex Formation

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

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

The calculated ΔG_f values are presented in **Table (4)**.

4.5. Enthalpies and Entropies

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[26,27] :

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

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 $1/T$, ΔH_A can be calculated for each type of complexes from the slope of each line ($-\Delta H/2.303 R$). 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 :

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

Where (S) is the entropy of the system.

The calculated values of (ΔH_A) and (ΔS_A) for CuCl_2 -lig and 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 (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)**:

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) :

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

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[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'-hydazonopyridyl)-butane (HL) in (EtOH-H₂O) 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):

$$\text{Molal solubility (S)} = \frac{W \cdot 1000}{d_0 \cdot M} \text{ g.mole /1000 g . solvent} \quad (9),$$

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 CuCl_2 with HL at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K)

		ΔG_f (kJ/mol)			
		1 : 2 (M/L)			
Cm		293.15 K	298.15 K	303.15 K	308.15 K
8.33E-05		-32.7243	-34.0278	-36.9243	-38.6072
8.24E-05		-30.9752	-31.8059	-33.2027	-34.1017
8.06E-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 (M/L)			
Cm		293.15 K	298.15 K	303.15 K	308.15 K
9.09E-05		-35.2606	-36.8031	-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
8.77E-05		-30.4886	-30.6951	-31.2246	-31.7554
8.67E-05		-29.6959	-29.9470	-30.4239	-30.9824
		2 : 1 (M/L)			
Cm		293.15 K	298.15 K	303.15 K	308.15 K
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	-36.0169
9.26E-05		-32.0900	-33.0054	-34.5210	-33.8937

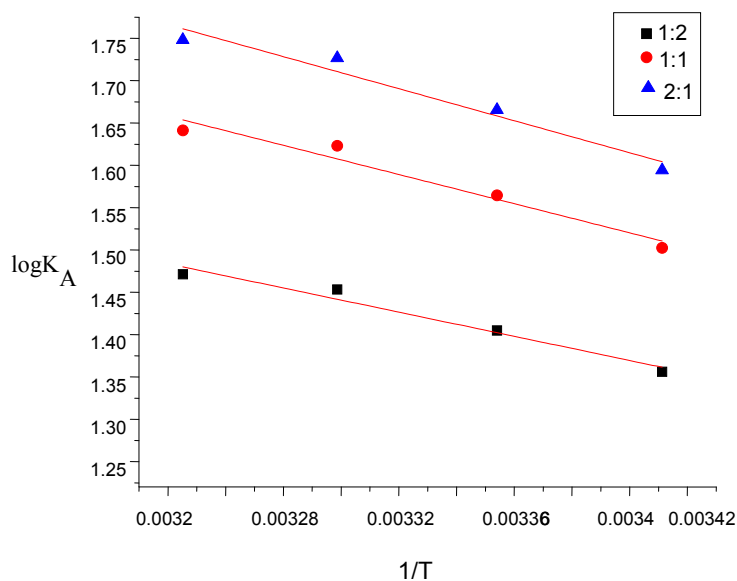
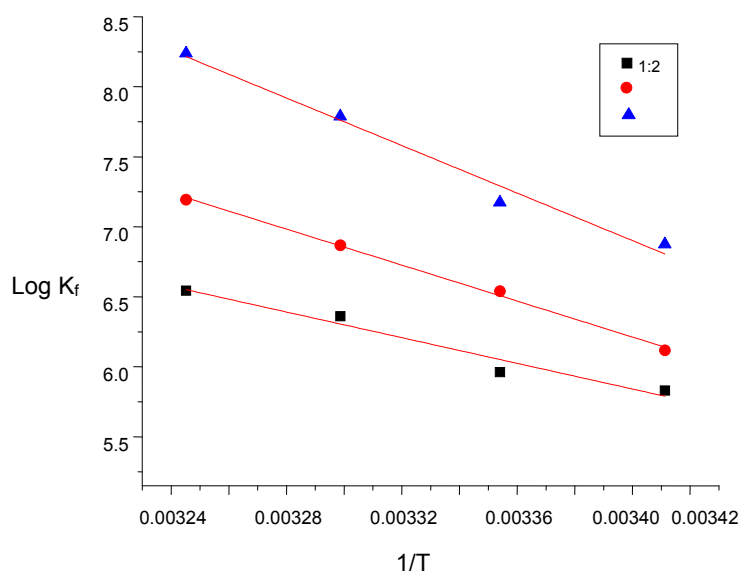


Figure 7. The relation between ($\log K_A$) and ($1/T$)

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)

ΔH_A (KJ/mol) and ΔS_A (KJ/mol.K)				
1 : 2 (M/L)				
Temp	293.15 K	298.15 K	303.15 K	308.15 K
ΔH_A	13.8326	13.8326	13.8326	13.8326
ΔS_A	0.07316	0.07329	0.07347	0.07305
1 : 1 (M/L)				
Temp	293.15 K	298.15 K	303.15 K	308.15 K
ΔH_A	16.5043	16.5043	16.5043	16.5043
ΔS_A	0.08505	0.08530	0.08551	0.08497
2 : 1 (M/L)				
Temp	293.15 K	298.15 K	303.15 K	308.15 K
ΔH_A	18.1299	18.1299	18.1299	18.1299
ΔS_A	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)

ΔH_f (KJ/mol) and ΔS_f (KJ/mol.K)				
1 : 2 (M/L)				
Temp	293.15K	298.15 K	303.15 K	308.15 K
ΔH_f	87.7317	87.7317	87.7317	87.7317
ΔS_f	0.4109	0.4083	0.4112	0.4099
1 : 1 (M/L)				
Temp	293.15 K	298.15 K	303.15 K	308.15 K
ΔH_f	123.0207	123.0207	123.0207	123.0207
ΔS_f	0.5399	0.5360	0.5367	0.0536
2 : 1 (M/L)				
Temp	293.15 K	298.15 K	303.15 K	308.15 K
ΔH_f	162.4927	162.4927	162.4927	162.4927
ΔS_f	0.6859	0.6823	0.6789	0.6850

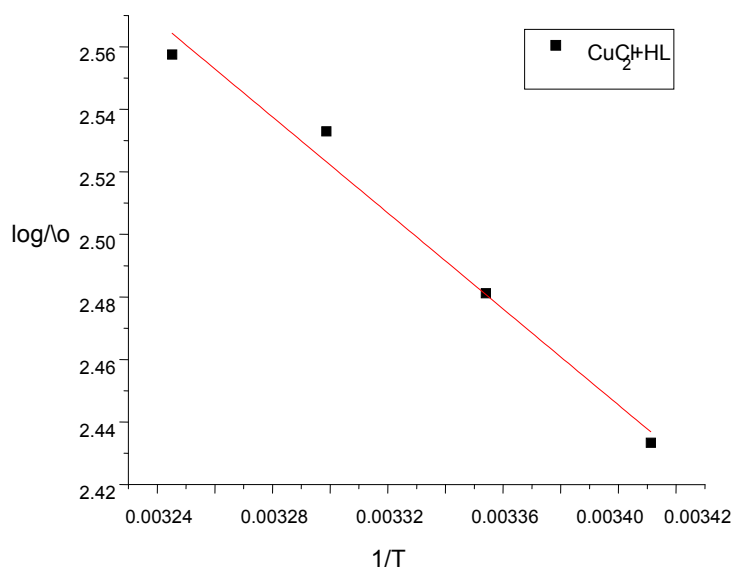


Figure 9. The relation of ($\log \Lambda_0$) and $1/T$

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	(S) of HL			
	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

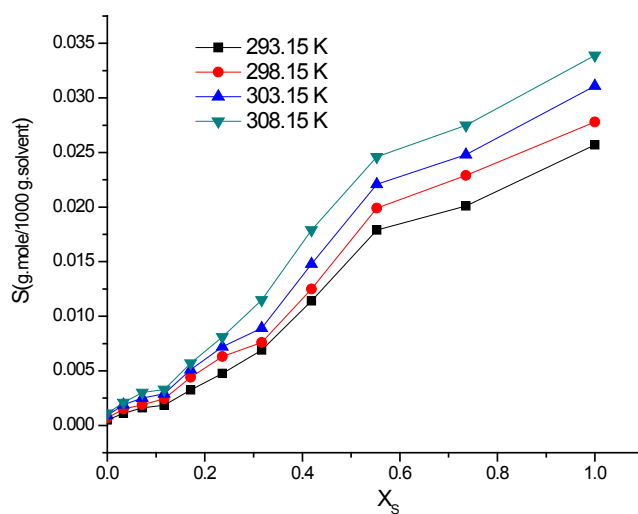


Figure 10. Variation of the molal solubility (S) of HL with the mole fraction (X_s) of EtOH at different temperatures

Table 8. The solvation free energies (ΔG) S of HL in EtOH-H₂O mixture at different temperatures (293.15 K, 298.15 K, 303.15K and 308.15 K)

Vol. % of EtOH	$(\Delta G)_s$ (KJ/mol)				$(\Delta H)_s$ (KJ/mol)
	293.15 K	298.15K	303.15K	308.15K	
0	18.5286	18.0104	17.6789	17.7005	35.1255
10	16.6066	16.1209	15.7953	15.7994	32.7945
20	15.6932	15.5348	15.1035	14.8854	32.4435
30	15.3393	14.9045	14.7294	14.6412	28.6884
40	13.9657	13.4528	13.3063	13.2407	27.6306
50	13.0406	12.5629	12.4370	12.3403	26.1393
60	12.1305	12.0978	11.9026	11.4422	25.3114
70	10.9065	10.8642	10.6206	10.3085	22.8197
80	9.8067	9.7113	9.6099	9.4937	15.9020
90	9.5241	9.3632	9.3193	9.2082	15.3366
100	8.9250	8.8825	8.7487	8.6721	14.1599

4.10. Thermodynamics of Solvation

The solvation free energies ΔG_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):

$$(\Delta G)_s = -2.303 RT \log K_{sp} \quad (10)$$

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 (ΔH_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):

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

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 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 $\Delta G_f(2:1) > \Delta G_f(1:1) > \Delta G_f(1:2)$ for (M:L)

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