AASCIT Communications
Volume 3, Issue 4
ISSN: 2375-3803

AASCIT American Association for Science and Technology

The Association and Complex Formation Constants for $CuSO_4$, $NiSO_4$ Stiochiometric Complexes with (E)-N'-(2-hydroxy-3H-indol-3-ylidene)-3-oxo-3-(Thiazol-2-Ylamino) Propanehydrazide in Ethanol Solutions at 294.15K

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Received: April 3, 2016; **Accepted**: April 11, 2016; **Published**: June 21, 2016

Keywords

Association, Complex Formation, Copper Sulfate, Nickel Sulfate, Propanehydrazide, Ethanol

The association constants and Gibbs free energies of association are calculated from the conductometric titration curve of $CuSO_4$, $NiSO_4$ with ligand H_2IH, (E)-3-(2-benzylidene hydrazinyl)-3-oxo-N-(thiazol-2-yl) propanehydrazide in ethanol solutions at 294.15K. The conductometric titration of $CuSO_4$ and $NiSO_4$ as titrant against the ligand (*N'*-(2-hydroxy-3H-indol-3-ylidene)-3-oxo-3-(thiazol-2-ylamino) propanehydrazide) in absolute ethanol as solvent at 294.15 K was constructed to evaluate the Gibbs free energies involving the different association constants. From the relation between molar conductivity and the molar ratio [L]/[M], various straight lines are gained detecting that the production of metal complexes with two stiochiometric which are 2:1 and 1:1 [L]/[M]. Gibbs free energies involving the formation constants for each stiochiometric type of complexes were calculated and their values were discussed. Preparation of new ligand is necessary for estimation and physicochemical studies of some transition metal ions like copper and nickel ions in absolute ethanol solutions. Many biological applications for copper and nickel salts are needed; therefore their estimation and conductometric studies were selected.

Introduction

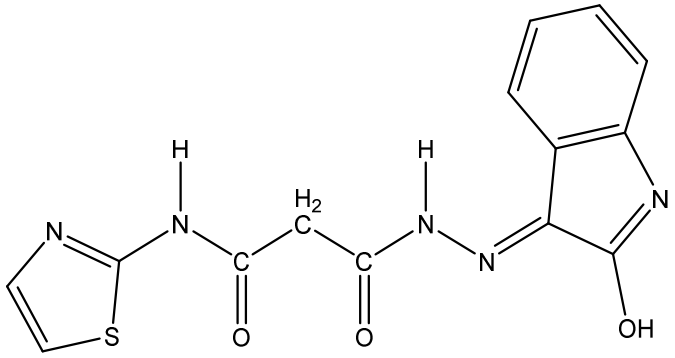
Recently, there are many interest articles concerned with the development of ligands that are able to selective to bind metal ions through multiple non-covalent interactions [1]. Copper (II) and Nickel (II) ions are involved in metalloproteinase. For example, metallo-enzymes belong to metalloproteinase which performed a specific catalytic function. There are three known classes of dioxygen transport proteins involved in respiration which are the haemoglobin-myoglobin family, haemocyanines and hemerythrins. These metal ions may differ from one organism to another. The concentrations of metal ions are very important for the normal function of biological systems. An excess of Cu(II) and Ni(II) may include thalaseamia disease [2, 3].

The aim of this work is the evaluation of non-covalent behavior of $CuSO_4$ and $NiSO_4$ against the ligand (H_2IH) in absolute ethanol solvent at 294.15 K. These non-covalent behavior can provide us with information about the analysis of metal salts in the biological systems.

Experimental

Prepartion of the Ligand

The ligand was prepared by mixing equimolar amounts of 3-hydrazinyl-oxo-*N*-(thiazole-2-) propanamide (0.01 mol; 2.00 g) in 40 ml absolute ethanol (Structure 1). This reaction mixture was kept on reflux for three hours. The mixture was concentrated to its half-volume and allowed to cool. The yields were isolated by filtration, recrystallization and drying over anhydrous $CaCl_2$ in a vacuum desiccator. (M.p.: 235°C) and (yield 75%) respectively. The purity of these compounds was checked by TLC.



N'-(2-hydroxy-3*H*-indol-3-ylidene)-3-oxo-3-(thiazol-2-ylamino)propanehydrazid

Structure 1. *(H_2IH).*

Conductometric Titrations

The conductance of the solid complexes are detected by the preparation of 10^{-3} mol L^{-1} solutions in DMSO and measured on a (HANNA, H1 8819 N) conductivity bridge. Also, the conductometric titrations are done using ($1x10^{-3}$) mole/l of metal sulphate solutions ($CuSO_4$ and $NiSO_4$) and ($1x10^{-4}$) mole/l of the ligand (H_2IH). 20 ml of ligand is taken and titrated against 0.5 ml interval additions from the metal sulphate salts solutions. Both the solutions of ligand and metal salts are prepared in hot ethanol.

Results and Discussion

The molar conductivity ($/\backslash_m$) of various concentrations of MSO_4 solutions in presence or absence of the ligand (H_2IH) were evaluated [4, 5] according to this equation (1):

$$/\backslash_m = [(K_s - K_{solv}) \times K_{cell} \times 1000] / C \quad (1)$$

Where (K_s) is the solution's specific conductance,

(K_{solv}) is the solvent's specific conductance,

(K_{cell}) is the cell constant which equals to unity,

(C) is the MSO_4 solutions' concentration expressed in molarity.

The ($/\backslash_m$) of different MSO_4 concentrations in the absence of ligand were studied by plotting ($/\backslash_m$) versus ($\sqrt{C}$) (Figure 1) where it is noticed that the linear decreasing of the molar conductance values ($/\backslash_m$) by increasing the metal concentration. In the same way, the molar conductance ($/\backslash_m$) of different MSO_4 concentrations in the presence of the ligand were constructed by plotting ($/\backslash_m$) versus ($\sqrt{C}$). In this case, straight lines were obtained (Figure 2). Also the limiting molar conductance ($/\backslash_o$) at infinite dilutions are estimated for MSO_4 in absence and presence of the ligand by extrapolating the relation between ($/\backslash_m$) and ($\sqrt{C}$) to zero concentration for each line. Moreover, the molar conductance ($/\backslash_m$) was drawn against the molar ratio ([L]/[M]) in the presence of ligand (Figure 3). Where [L] is the ligand concentration and [M] is the metal concentration. Different curves were gained with sharp breaks corresponding to different stoichiometric ratios.

The association constants of MSO_4 in the presence of ligand could be calculated in tables (1 and 4) using equation (2) [6].

$$K_A = \Lambda_o^2 (\Lambda_o - \Lambda_m) / (4C_m^2 + \Lambda_m^3 S_{(Z)}) \quad (2)$$

Where ($/\backslash_o$) are the limiting molar conductance of MSO_4. C_m is MSO_4 concentration. $S_{(Z)}$ is Fuoss-Shedlovsky factor and equal to unity for strong electrolytes [7]. The Gibbs free energies of association (ΔG_A) [8, 9] were calculated from the association constant values by equation (3).

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

Where R is the gas constant and T is the absolute temperature.

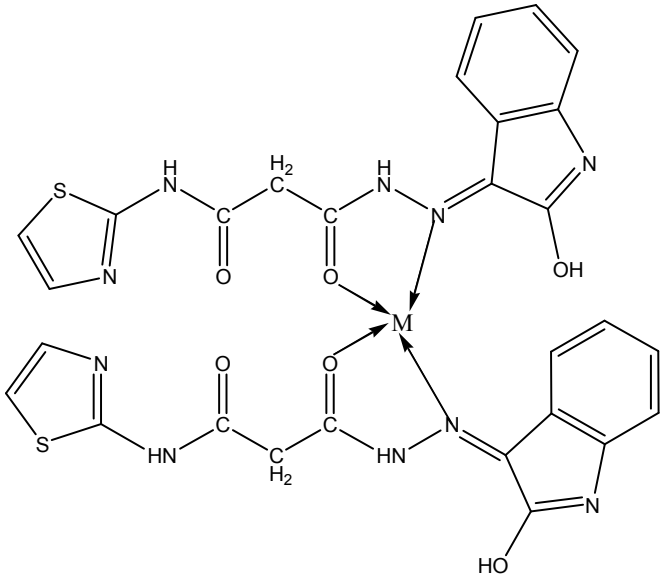
The formation constants (K_f) for MSO_4 – ligand complexes can be calculated for each line in ([L]/[M]) relation against ($/\backslash_m$). Equation (4) is used for calculating the formation constants for the complexes [10-20].

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

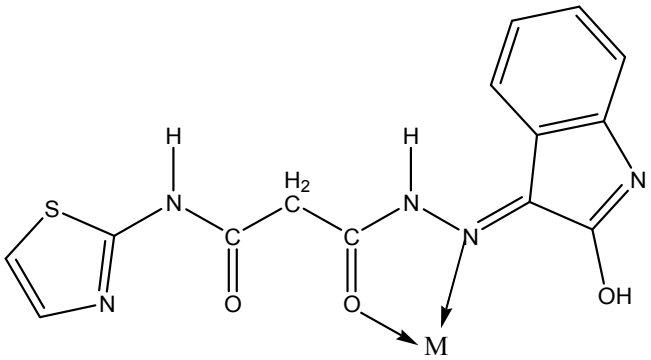
Where ($/\backslash_m$)is the molar conductivity of the metal sulphate before addition of the ligand, ($/\backslash_{obs}$)is the molar conductance of solution during titration and ($/\backslash_{ML}$) is the molar conductance of the complexed ion. Also, the Gibbs free energies of formation [21-30] for each MSO_4 complexes with ligand were calculated in Tables (2, 3, 5, 6) using equation (5).

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

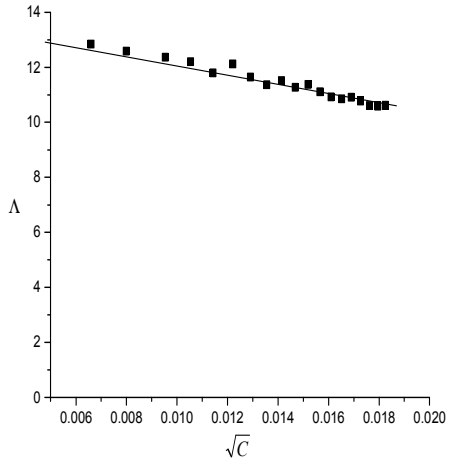
The formation constants and Gibbs free energies of formation follow the following order K_f (2:1) › K_f (1:1) and ΔG_f (2:1) › ΔG_f (1:1) for ([L]/[M]) in the stoichiometric complexes formed by the interaction of MSO_4 with (H_2IH) ligand (Structure 2, 3). The association free energies evaluated are small and spontaneous improving that the presence of electrostatic attraction force in the solution.



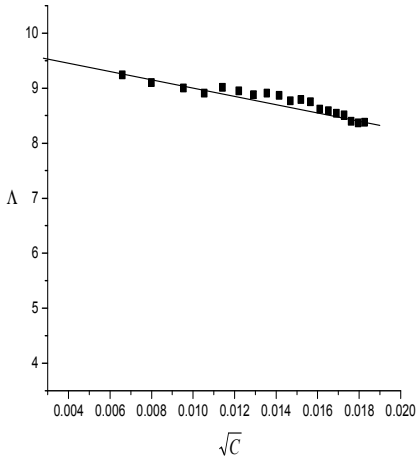
Structure 2. *2:1 (H_2IH: M) stiochiometric complex may exist as the above structure.*



Structure 3. *1:1 (H_2IH: M) stiochiometric complex may exist as the above structure.*

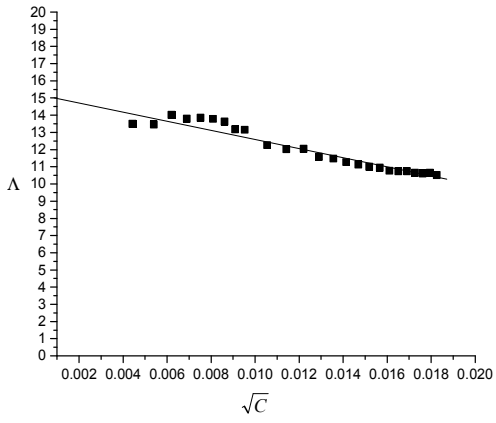


(A)

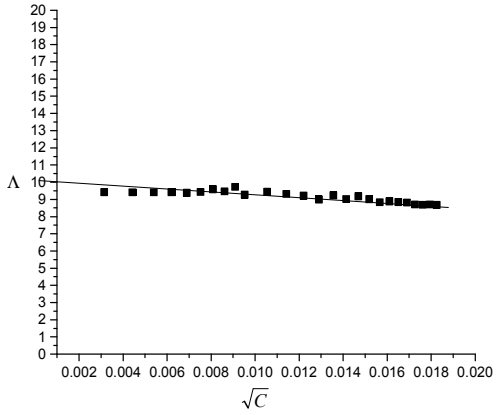


(B)

Figure 1. *The relation between molar conductance and (√C) of (A) $CuSO_4$ alone and (B) $NiSO_4$ alone in ethanol at 294.15 K.*

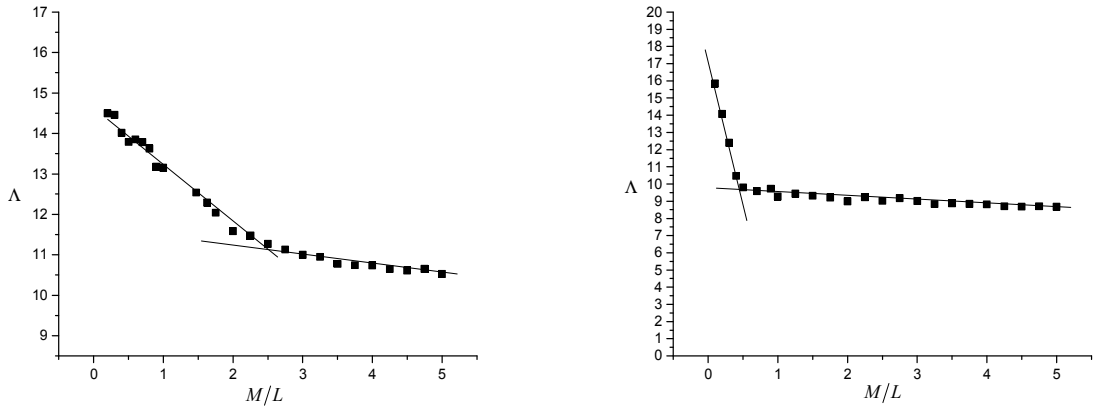


(A)



(B)

Figure 2. *The relation between molar conductance and (√C) of (A) $CuSO_4$ and (B) $NiSO_4$ in the presence of (H_2IH) in ethanol at 294.15 K*



(A) (B)

Figure 3. *The relation between molar conductance and (√C) of (A) $CuSO_4$ and (B) $NiSO_4$ in the presence of (H_2IH) in ethanol at 294.15 K.*

Table 1. *Association constants and Gibbs free energies of association for $CuSO_4$ with (H_2IH) in ethanol at 294.15K.*

Λ_m($cm^2.Ohm^{-1}$)	C_m($mol.L^{-1}$)	K_A	ΔG_A(kJ/mol)
11.47	1.84E-04	1.058	-137.57
11.27	2.00E-04	1.1562	-355.102
11.13	2.16E-04	1.2287	-503.809
10.99	2.31E-04	1.3027	-646.864
10.94	2.45E-04	1.3326	-702.215
10.77	2.59E-04	1.4386	-889.475
10.74	2.73E-04	1.457	-920.546

Λ_o = 15 $cm^2.ohm^{-1}$

Table 2. *Formation constants and Gibbs free energies of formation for 2:1 (M/L) $CuSO_4$-(H_2IH) complexes in ethanol at 294.15K.*

Λ_{obs} ($cm^2.Ohm^{-1}$)	[L]	K_f	ΔG_f (kJ/mol)
11.27	8.00E-05	8.33E-05	22971.55
11.13	7.84E-05	7.56E-05	23207.93
10.99	7.69E-05	6.92E-05	23.423.78
10.94	7.55E-05	6.62E-05	23532.56
10.77	7.41E-05	5.99E-05	23777.77

Λ_M = 13 $cm^2.ohm^{-1}$, Λ_{ML} = 11.2 $cm^2.ohm^{-1}$

Table 3. *Formation constants and Gibbs free energies of formation for 1:1 (M/L) CuSO4-(H2AH) complexes in ethanol at 294.15K.*

Λ_{obs} ($cm^2.Ohm^{-1}$)	[L]	K_f	ΔG_f (kJ/mol)
10.73	7.14E-05	7.89E-05	23103.76
10.64	7.02E-05	7.46E-05	23242.06
10.61	6.90E-05	7.22E-05	23321.41
10.55	6.78E-05	7.22E-05	23321.86
10.52	6.67E-05	6.74E-05	23490.22

Λ_M = 13 $cm^2.ohm^{-1}$, Λ_{ML} = 10.5 $cm^2.ohm^{-1}$

Table 4. *Association constants and Gibbs free energies of association for $NiSO_4$ with (H_2IH) in ethanol at 294.15K.*

Λ_m($cm^2.Ohm^{-1}$)	C_m($mol.L^{-1}$)	K_A	ΔG_A(kJ/mol)
19.6	1.84E-04	1.188	-421.387
20.69	2.00E-04	1.2217	-489.84
22.46	2.16E-04	1.3322	-701.521
22.47	2.31E-04	1.3415	-718.566
23.46	2.45E-04	1.3713	-874.978
25.74	2.59E-04	1.4301	-931.571
26.82	2.73E-04	1.4636	-944.351

Λ_o = 10 $cm^2.ohm^{-1}$

Table 5. *Formation constants and Gibbs free energies of formation for 2:1 (M/L) NiSO4-(H2IH) complexes in ethanol at 294.15K.*

Λ_{obs} ($cm^2.Ohm^{-1}$)	[L]	K_f	ΔG_f (kJ/mol)
9.17	8.00E-05	6.46E-05	23592.74
9.02	7.84E-05	6.05E-05	23752.95
9	7.69E-05	5.78E-05	23864.93
8.88	7.55E-05	5.25E-05	24099.93
8.83	7.41E-05	5.78E-05	24114.84

Λ_M = 11 $cm^2.ohm^{-1}$, Λ_{ML} = 9.5 $cm^2.ohm^{-1}$

Table 6. *Formation constants and Gibbs free energies of formation for 1:1 (M/L) NiSO4-(H2IH) complexes in ethanol at 294.15K.*

Λ_{obs} ($cm^2.Ohm^{-1}$)	[L]	K_f	ΔG_f (kJ/mol)
8.86	7.14E-05	8.18E-05	23016.6
8.81	7.02E-05	7.66E-05	23177.6
8.72	6.90E-05	7.45E-05	23245.7
8.7	6.78E-05	7.38E-05	23266.4
8.67	6.67E-05	7.17E-05	23339.6

Λ_M = 11 $cm^2.ohm^{-1}$, Λ_{ML} = 8.5 $cm^2.ohm^{-1}$

Conclusion

The thermodynamic parameters for the interaction of some transition metals like $CuSO_4$ and $NiSO_4$ are necessary to do which facilitate their physicochemical and analytical estimation in ethanol by simple conductance measurements. Non-covalent behavior of ($CuSO_4$ and $NiSO_4$) with new ligand (H_2IH) in ethanol solutions at 294.15 K was carefully discussed. These non-covalent interactions can provide us informations about the analysis of metal salts nature. ■

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References

[1] Zhibo Yang, Ph.D. thesis, Wayne State University, Detroit, Michigan, U.S.A. (2005).

[2] M. Di Donato, J. Zhang, Jr Que.., Sarka, B. J., Biol. Chem, 277, (2002) 13409.

[3] J. Anastassopoulou, Anifantakis, B., Anifantakis, Z-A; Dovas, A., Theophanides, T. Bioinorg. Chem., 79, (2000) 327.

[4] W. Grzybkowski and R. Pastewski; Electrochimica Acta., 25, 279 (1980).

[5] N. A. El-Shishtawi, M. A. Hamada and E. A. Gomaa, J. Chem. Eng. Data, (2010).

[6] Manny A. Hamada, Nagah El-Shishtawi and Esam Gomaa, South. Braz. J. Chem, vol. 17, (2009) 33.

[7] J. J. Christensen, J. O. Hill and R. M. Izatt; Science, 174, (1971) 459.

[8] A. K. Covington and T. Dickinson, "Physical Chemistry of Organic Solvent System", Plenum Press, London (1973).

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

[10] Y. Tekeda, Bull. Chem. Soc. Jpn, 56, (1983) 3600.

[11] M. Rahmi-Nasrabadi, F. Ahmedi, S. M. Pourmor-tazavi, M. R., Ganjali, K. Alizadeh, J. Molecular Liquids, 144, (2009) 97.

[12] Esam A. Gomaa, Physics and Chemistry of Liquids, 50 (2012) 279-283.

[13] Esam A. Gomaa, International Journal of Materials and Chemistry, 2 (1), (2012) 16–18.

[14] Esam A. Gomaa, American Journal of Environmental Engineering 2 (3), (2012) 54-57.

[15] Esam A. Gomaa, American Journalist of Polymer Science 2 (3), (2012) 35–47.

[16] Esam A. Gomaa, Eur. Chem. Bull, 1 (2013) 259-261.

[17] Esam A. Gomaa, Elsayed M. Abou Elleef and E. A. Mahmoud, Eur, Chem. Bull, 2 (2013) 732-735.

[18] Esam A. Gomaa, Elsayed M. Abou Elleef, American Chemical Science Journal, 3 (2013), 489-499

[19] Esam A. Gomaa, Elsayed M. Abou Elleef, Science and Technology, 3 (2013) 118-122

[20] Esam A. Gomaa, International Journal of Theoretical and Mathematical Physics, 3 (2012) 151-154.

[21] Esam A. Gomaa, and B. A. Al- Jahdali, Education, 2 (3), (2012), 25-28.

[22] Esam A Gomaa, Orient. J. Chem., 6 (1990) 12-16 and E. A. Gomaa, Indian J. of Tech, 24 (1986) 725.

[23] E. A. Gomaa and G. Begheit, Asian J. of Chem., 2 (1990) 444 and E. A. Gomaa, A. H. El-Askalany and M. N. H. Moussa. Asian J. Chem, 4 (1992) 553.

[24] Esam A. Gomaa, and, Elsayed M. Abou-Elleef, Thermal and Power Engineering, 3 (2014) 47-55.

[25] Esam A. Gomaa, Research and Reviews: Journal of Chemistry 3 (2014) 28-37.

[26] Esam A. Gomaa, A. H. El-Askalany and M, N, H, Moussa, Rev Roum. Chim, 3 (1987) 243.

[27] Esam A Gomaa, Theromochimica Acta, 128 (1988) 99.

[28] Esam A Gomaa, Indian J. of Tech., 24 (1986) 725 and E. A. Gomaa. Thermochim. Acta, 80 (1984) 355.

[29] Esam A Gomaa, Croatica Chimica Acta, 62 (1989) 475.

[30] E. A. Gomaa, A. M. Shallapy and M. N. H. Moussa. Asian J. of Chem., 4, (1992) 518.