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SPECTROSCOPIC STUDY OF COPPER-GLUTAMIC ACID INTERACTION AND DETERMINATION OF STABILITY CONSTANT

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ABSTRACT

The interactions of copper(II)-glutamic acid have been studied by UV-visible spectroscopic technique. The metal to ligand ratio in the complex was determined using mole ratio, continuous variation and slope ratio methods in aqueous medium. The ratio of metal to ligand was found almost 1:1 for the system. The formation constants of the systems were determined at different temperature using Benesi-Hildebrand equation. The value of formation constants varies inversily with temperature. Moreover, thermodynamic paramerers such as ΔG, ΔS and ΔH were calcualted which reveals the complex formation is exothermic and spontaneous.

Keywords: *Spectrocopic, interaction, Benesi-Hildebrand equation, stability constant.*

1. INTRODUCTION

Metals play a vital role in all living systems. Transition metal ions are responsible for proper functioning of different enzymes. Metal ions are essential component of different organs of animals such as blood, bones, teeth, nerves, some proteins and enzymes. Any malfunctioning of these metals can initiate a number of physiological abnormalities and symptoms of clinical disorders. The main function of the essential trace elements is to act as cofactors in various enzyme systems i.e. as metallo-enzymes or as enzymatic activators. Copper is widely distributed in nature as sulfides, arsenides, chlorides, carbonates and so on (Cotton, 1988). It is one of the trace elements essential to the healthy life of humans and animals (Wolfgang, 2006; Tirmizi, 2009). Furthermore Cu as a metal ion plays an important role in human physiology (Subudhi, 2009).

Amino acids perform crucial functions in all biological processes. They function as catalyst, transport and store other molecules such as oxygen. They also provide mechanical support and immune protection. They generate movement; transmit nerve impulses, control growth and differentiation (Berg, 2001).

Glutamic acid is a multifunctional amino acid involved in taste perception, excitatory neurotransmission and intermediary metabolism (Kondoh, 2009). It plays an important role in gastric phase digestion with multiplicity effects in the gastrointestinal tract when consumed with nutrients by enhancing gastric exocrine secretion (Berg, 2001). Glutamic acid is a specific precursor for other amino acids i.e., arginine and proline as well as for bioactive molecules such as γ-amino butyric acid (GABA) and glutathione. GABA possesses several well-known physiological functions i.e., anti-hypertension (Inoue, 2003) and anti-diabetic (Hagiwara, 2004) and glutathione plays a key role in the protection of the mucosa from peroxide damage and from dietary toxins (Beyreuther, 2006). Furthermore, a number of studies have shown the possible usefulness of glutamic acid in enhancing nourishment in the elderly and in patients with poor nutrition (Tomoe, 2009; Yamamoto, 2009).

Stability constants can be key parameters for the investigation of equilibria in solution. They are very important in many fields such as industrial chemistry (Tewari, 1995), environmental studies (Pandey, 2000), and medicinal (Ibrahim, 2000) and analytical chemistry (Pakhomova, 2001). Therefore, complexation reactions of metal ions with different ligands have been widely studied (Hulanicki, 1983; Zhou, 1996; Colston, 1997). In this paper we report the determination of metal to ligand ratio of the complex of copper(II)-glutamic acid system in aqueous medium, formation constant and thermodynamic parameters of the complexes using UV-visible spectrophotometry.

2. EXPERIMENTAL

2.1 Chemicals

The chemicals used in the present study were, (i) copper nitrate (MERCK, Germany), (ii) ferrous ammonium sulphate hexahydrate (MERCK, Germany) (iii) glutamic acid Na salt (MERCK, Germany), (iv) potassium chloride (BDH). (v) pyridine-2,2-dicarbonsaur (MERCK, Germany), (vi) bipyridine (MERCK, Germany). The buffer solution were prepared by using sodium acetate (MERCK, Germany) and acetic acid (Sigma-Aldrich). For cleaning and all other purposes deionized water was used.

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2.2 Equipments

Spectroscopic analysis measurements were done using a UV-visible spectrophotometer (UV-Prove-1800PC) from Shimadzu Corporation, Japan. Preparation of the solutions was done using volumetric flasks and graduated pipettes. A pH meter, ORION 2 STAR, made by Thermo Electron Corporation was used to mesure the pH of the solutions.

3. RESULTS AND DISCUSSION

The composition of the metal glutamic acid complex in solution was determined spectrophotometrically and formation constant of the complex was determined by using
Benesi-Hildebrand equation.

3.1 Determination of metal to ligand ratio in the aqueous medium

The copper-ligand interaction in aqueous solution was studied by visible spectrophotometry. The ligand to metal ratio in aqueous medium was determined using three different methods such as mole ratio method, continuous variation method and slope ratio method.

Mole ratio method: The copper-ligand interaction was studied spectroscopically by this method. Various mixtures of Cu(II) and glutamic acid solutions of same concentration were made using fixed volume of (4 mL) Cu(II) solution and various volume (4, 6, 8, 10, 12, 16, 18, 20, 22 and 24 mL) of ligand (glutamic acid). The absorbances of all mixtures were measured at room temperature at 730 nm wavelegth. A plot of absorbance against mole ratio of ligand is shown in Figure 1.

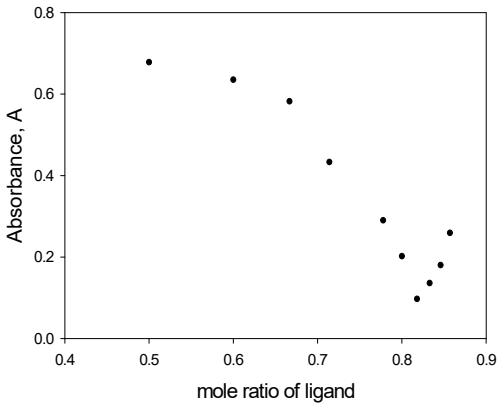

Figure 1: The variation of absorbance with the different mole ratio of ligand

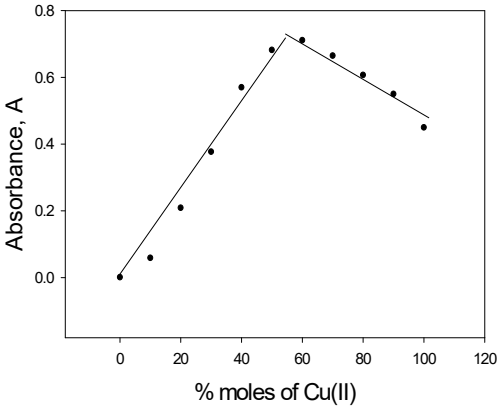

Figure 2: Variation of absorbance with the % moles of Cu(II)

Figureure 1 shows that the absorbance is maximum at metal-ligand mole ratio 1:1 and decreases with increase of mole ratio. This indicates that maximum interaction occurs at ratio 1:1.

Continuous variation method: In this method equimolar solutions of Cu(II) and glutamic acid were mixed with different ratio of volume and values of absorbance were recorded. A plot of absorbance against % mole of Cu(II) is shown in Figure 2.

The Figureure reveals that the absorbance increases with the increase of % moles of metal and absorbance is highest at 55 % moles of Cu(II) and then decreases. If we draw two straight lines through the points, they intersect at 45:55 ratio so the ratio of moles of Cu(II) and ligand was obtained almost 1:1.

Slope ratio method: In slope ratio method, two series of solutions were prepared in which varying amount of one component in the complex were added to a very large excess compared to the other component. The absorbance of Cu(II) with constant concentration of glutamic acid after interaction was measured. Again constant concentration of Cu(II) and variable concentration of glutamic acid was also measured by spectrophotometer at 730 nm wavelength. A plot of absorbance against concentration of ligand and Cu(II) are is shown in Figure 3.

Figure 3 demonstrates that, absorbance increases with the increase of concentration of ligand and Cu (II). Upper line is for different concentration of ligand and lower line is for the different concentration of metal. The slope ratio is found almost 1.5 which indicates that mole ratio of ligand to metal is almost one. So the maximum interaction may occur at 1:1 ratio of ligand to metal.

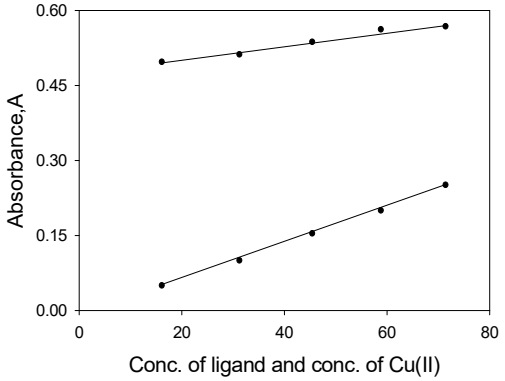

Figure 3: Variation of absorbance with concentration of ligand and metal

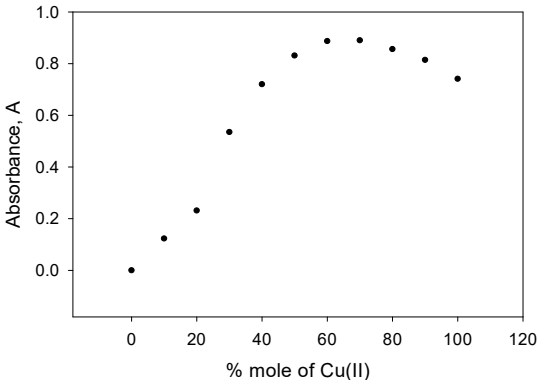

Figure 4: Plot of absorbance of Cu(II)–glutamic acid complex against % moles of Cu (II) in acetate buffer of pH 4.69

3.2 Determination of metal to ligand ratio in acetate buffer of different pH

Cu(II) and glutamic acid solution having same concentration were mixed with continuous variation of their volume. Both the solution were prepared in acetate buffer of particular pH. The absorbance was taken 2 hours after starting the reaction at room temperature (303 K).

Continuous variation method at pH 4.69: This process was done at room temperature in acetate buffer of pH 4.69. A plot of absorbance against % mole of Cu(II) is shown in Figure 4. It is found that the absorbance of complexes firstly increased with increase of % moles of Cu(II) and then decreased with increasing % moles of Cu(II) and the maximum absorbance was at approximately 1:1 ratio (i.e. 55:45 of % of Cu(II) and ligand). So the Cu(II) and glutamic acid interacts at 1:1 ratio at pH 4.69. Similar result was found in acetate bufferat of pH 5.51.

3.3 Determination of formation constant, K_f by using Benesi-Hildebrand equation

The formation constant of metal-ligand complex, K_f can be obtained by using UV-Visible spectroscopy with the help of Benesi-Hildebrand equation, $[D]/A = 1/(KC\epsilon) + 1/\epsilon$. Here, [D] and [C] are the initial concentration of ligand and metal respectively in mole/liter, ϵ is the molar absorption coefficient of the metal-ligand complex at its given particular wave length and K_f is the formation constant given in liter/mole. A plot of [D]/A versus 1/[C] gives a straight line with a slope of $1/(K\epsilon)$ and an intercept of $1/\epsilon$.

The slope of the plot obtained from Benesi-Hildebrand equation is reciprocal of the formation constant (K_f) multiplied by molar absorption coefficient of complexation (ϵ). Thus, 1/(slope x molar absorption coefficient) gives formation constant (K_f) (Otto, 1997; Chao, 2000; Anslyn, 2006).

Cu(II) solution and glutamic acid solution of same volume but different concentration were prepared in acetate buffer of particular pH. The concentration of ligand solution were kept constant and Cu(II) solution concentration were varied.

3.4 Determination of formation constant of Cu(II)- glutamic acid complex at pH 4.40

This process was done at room temperature (303 K) in acetate buffer of pH 4.40. The data of absorbance of Cu(II)-ligand solutions for different concentration of Cu(II) as well as the calculated values of (1/C) and (D/A) are shown in Table 1. Volume of metal and ligand solutions was same (10 mL). Concentration of ligand was 2.00×10^{-4} mol/L and concentration of Cu(II) solution was varying. A plot of D/A against (1/C) is plotted in Figure 5.

Similar data and plot were obtained for Cu(II)-glutamic acid solutions for different concentrations of Cu(II) in acetate buffer of pH 4.94, and 5.47 at room temperature. From the values of intercept and slope of the graph of 1/C vs. D/A, the values of formation constant, K_f were calculated for the Cu(II)-glutamic acid complex at room temperature in different pH.

The values of K_f were found as 7.5, 6.2 and 4.0 litter/mole at pH 4.40, 4.94 and 5.57 respectively. The variation of formation constant (K_f) values with pH are shown in Figure. 7. It is observed that the value of formation constant is greater at lower pH and decrease with increase of pH.

Table 1: Absorbance data of Cu(II)-glutamic acid solution at 303 K at pH 4.4

Conc. of metal, C (mol/L)	Absorbance (A)	1/(C)	(D/A) x 10^{-4}
0.005	0.046	200.0	21.74
0.010	0.087	100.0	11.5
0.020	0.156	50.0	6.41
0.030	0.220	33.3	4.55
0.040	0.280	25.0	3.57
0.050	0.332	20.0	3.01
0.100	0.580	10.0	1.72

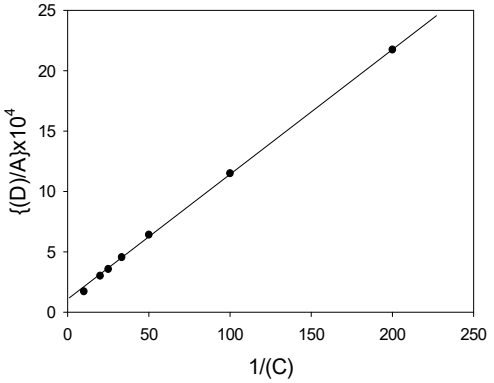

Figure 5: Plot of absorbance of Cu(II)-glutamic acid complex in acetate buffer of pH 4.4 at 303 K

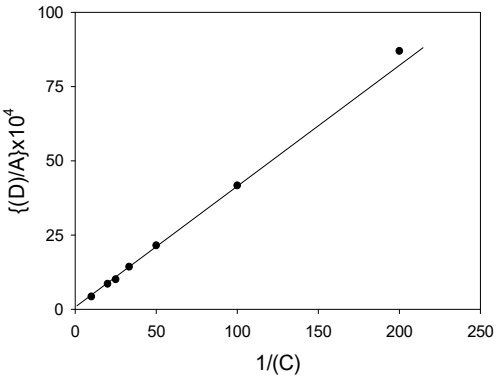

Figure 6: Plot of absorbance of Cu(II)-glutamic acid complex in water at 303 K

3.5 Effect of temperature on formation constant

To understand the effect of temperature on formation constant, the value of K_f for the interaction between Cu(II) and glutamic acid at temperatures 303, 313 and 322 K were determined using same method.

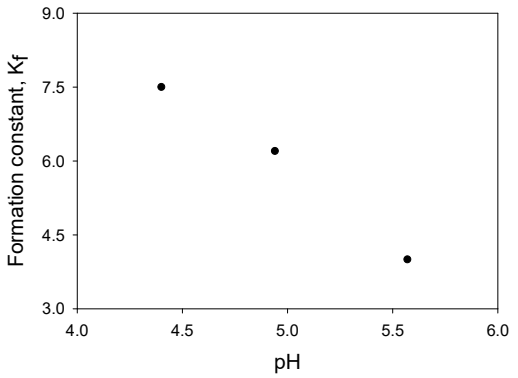

Figure 7: Variation of formatin constant (K_f) with pH

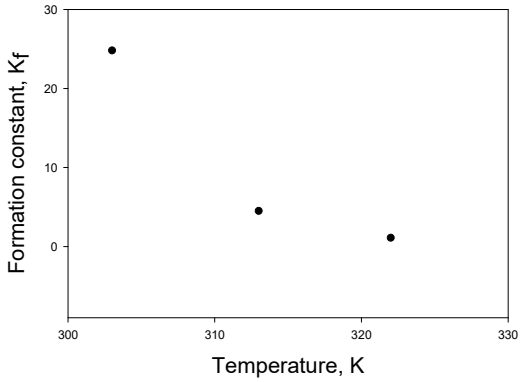

Figure 8: Variation of formatin constant (K_f) with temperature

K_f **at room temperature (303 K):** The data of absorbance of Cu(II)-glutamic acid solutions for different concentration of Cu(II) was recorded and the values of (1/C) and (D/A) were calculated. Volume of metal and ligand solutions was same (10 mL). Concentration of ligand was 2.00 x 10^{-4} mol/L and concentration of Cu(II) solution was varying. A plot of D/A against 1/C is shown in Figure 6. From the values of intercept and slope of the graph of 1/C vs. D/A, the values of formation constant, K_f were calculated at different temperatures.

Similar data and plot were obtained for Cu(II)-ligand solutions for different concentration of Cu(II) in water at temperature 313 K and 322 K. The values of K_f in water medium were found as 24.8, 4.5 and 1.1 L/mol at 303, 313 and 322 K respectively. The variation of formation constant with temperature is given in Figure 8. This demonstrates that the values of formation constant of Cu(II)-glutamic acid complex decreases with the increase of

temperature. This trend divulges exothermic nature of the reactions (Singh, 2011). Thermodynamic paramerers such as ΔG, ΔS and were calcualted at room temperature and were found as ΔG = -8.1 kJ/mole, ΔS = +149.4 JK^{-1} $mole^{-1}$ and ΔH = -52.9 kJ/mole which reveals the complex formation is exothermic.

4. CONCLUSIONS

The ratio of Glutamic acid to Cu(II) was found almost as 1:1 both in aqueous medium as well as in acetate buffer of different pH. The values of formation constant, K_f of Cu(II)-glutamic acid complex in acetate buffer of different pH were found as 7.5, 6.2 and 4.0 litter/mole at pH 4.40, 4.94 and 5.57 respectively. The values of formation constant decrease with increase of pH. The values of formation constant of Cu(II)-glutamic acid complex in aqueous medium were also determined at different temperature using Benesi-Hildebrand equation and were found as 24.8, 4.5 and 1.1 L/mol at 303, 313 and 322 K respectively. The values of formation constant of Cu(II)-glutamic acid complex decreases with the increase of temperature. In addition, values of thermodynamic parameters such as ΔG, ΔS and ΔH were calcualted and found as ΔG = -8.1 kJ/mole, ΔS = +149.4 JK^{-1} $mole^{-1}$ and ΔH = -52.9 kJ/mole which reveals the complex formation is exothermic.

REFERENCES

Anslyn, E.: Modern Physical Organic Chemistry, Uiversity Science Books, California, 221, 2006.

Berg, J. M., Tymoczko, J. L. and Stryer, L.: Biochemistry, W. H. Freeman and Company, New York 41, 2001.

Chao, Y., Lei, L., Wei, M. T. and Xiang, G. Q.: Analytical Sciences, Vol. 16, 537-539, 2000.

Colston, B. J. and Robinson, V. J.: Analyst, Vol. 122, 1451–1456, 1997.

Cotton, F. A., Wilkinson, G., Murillo, C. A. and Bochmann, M.: Advanced Inorganic Chemistry, John Wiley & Sons, New York, 854, 1988.

Hagiwara, H., Seki, T., and Ariga, T.: Biosci. Biotechnol. Biochem., Vol. 68, 444–447, 2004.

Hulanicki, S., Glab, A. and Ackermann, G.: Pure Appl. Chem.: Vol. 55, 1137–1230, 1983.

Ibrahim, G., Bouet, G. M., Hall, I. H. and Khan, M. A.: Inorg. Biochem.: Vol. 81, 29–34, 2000.

Inoue, K., Shirai, T., Ochiai, H., Kasao, M., Hayakawa, K., Kimura, M. and Sansawa, H.: Eur. J. Clin. Nutr., Vol. 27, 490–495, 2003.

K., Biesalski, H., Fernstrom, J., Grimm, P., Hammes, W., Heinemann, U., Kempski, O., Stehle, P., Steinhart, H. and Walker, R. Eur. J. Clin. Nutr., Vol. 61, 304–313, 2006.

Kondoh, T., Mallic, H. N., and Torii, K.: Am. J. Clin. Nutr., Vol. 90, 832–837, 2009.

Otto, E.: Chemometrics and intelligent laboratory systems, Vol. 39, 85-88, 1997.

Pakhomova, S. V., Proskurnin, M. A., Chernysh, V. V., Kononets, M. Y. and Ivanova, E. K.: J. Anal. Chem.: Vol. 56, 910–917, 2001.

Pandey, A. K., Pandey, S. D. and Misra, V.: Ecotoxicol. EnViron. Saf.: Vol. 47, 195–200, 2000.

Singh, L. J. and Singh, A. M.: J. Chem. Pharm. Res., Vol. 3(6), 1022-1027, 2011.

Subudhi, B. B., Pandaa, P. K., Bhattaa, D. and Jenab, A.: Iranian Journal of Pharmaceutical Sciences, Vol. 5(2), 83-88, 2009.

Tewari, B. B.: J. Chromatogr. A, Vol. 718, 454–458, 1995.

Tirmizi, A., Wattoo, F. H., Wattoo, M. H. S., Sarwar, S., Anwar, W., Memon, A. N. and Iqbal, J.: The Arabian Journal for Science and Engineering, Vol. 34, 43-48, 2009.

Tomoe, M., Inoue, Y., Sanbe, A., Toyama, K., Yamamoto, S. and Komatsu, T.: Ann. N. Y. Acad. Sci., Vol. 1170, 82–86, 2009.

Wolfgang, K.., and Brigitte, S.: Bioinorganic Chemistry, Inorganic Elements in the Chemistry of Life, John Wiley & Sons, New York, 187–214, 2006.

Yamamoto, S., Tomoe, M., Toyama, K., Kawai, M. and Uneyama, H.: Am. J. Clin. Nutr.: Vol. 90, 844–849, 2009.

Zhou, J., Vin, Z. H., Qu, J. X. and Shum, H. Y.: Talanta, Vol. 43, 1863–1867, 1996.