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# SPECTROSCOPIC INVESTIGATION OF INTERACTION OF Fe(II) WITH DIFFERENT LIGANDS AND DETERMINATION OF STABILITY CONSTANTS

**Omar Faruq[1], Md. Elius Hossain[2] Md. Mahmudul Hasan[1], Md Uzzal Hossain[1] and M. Q. Ehsan[1*]**

[1]*Department of Chemistry, University of Dhaka, Dhaka-1000, Bangladesh*
[2]*Department of Chemistry, BUET, Dhaka-1000, Bangladesh*

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**ABSTRACT**

*The interactions of Fe(II) with pyridine-2,4-dicarbonsaur and 2,2-bi-pyridine have been studied by UV-visible spectroscopic method. The metal to ligand ratio in the complexes was determined using three different methods namely, mole ratio, continuous variation and slope ratio method in aqueous medium. The ratio was found 1:2 for Fe(II)-pyridine-2,4-dicarbonsaur and 1:3 for Fe(II)- bi-pyridine. The stability constants of Fe(II)-ligand complexes in acetate buffer of pH 4.15 were determined at different temperatures using Benesi-Hildebrand equation. The value of stability constants varies inversily with temperature. Moreover, thermodynamic parameters such as ΔG, ΔS and ΔH were calcualted which reveals the complex formation is exothermic and spontaneous.*

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

## 1. INTRODUCTION

Stability constant can be the key for the investigation of equilibrium in solution. It is very important in many fields such as industrial chemistry (Tewari, 1995), environmental studies (Pandey *et al.*, 2000), medicinal chemistry (Ibrahim *et al.*, 2000) and analytical chemistry (Pakhomova *et al.*, 2001). However, stability of a complex compound in a particular environment may be reffered in terms of thermodynamic stability and kinetic stability. The thermodynamic stability of a complex is generally expressed in terms of stability constant or formation constant. The stability constants of a complex is obviously related to the energies of the metal-ligand bond which is measured by some thermodynamic s such as ΔG, ΔS and ΔH (Haider, 2002). Thus the study of stability constant and some thermodynamic s such as ΔG, ΔS and ΔH are also very important to understand metal-ligand complex formation.

Fe(II) is a transition metal ion with vacant *d* orbitals. It can form coordination compounds with different ligands. But isolation of Fe(II) complexes in the solid state is very much difficult since Fe(II) oxidises readily in the aqueous medium. So the study of interaction of Fe(II) with different ligands in solution is important in coordination chemistry. Several studies on the determination of stability constant and thermodynamic s of metal-ligand complex have been done potentiometrically (Mahmooda and Farida, 1997; Rafiquzzaman *et al.*, 1990; Farida *et al.*, 1990; Enamullah *et al.*, 1991; Saha *et al.*, 1993).

UV-visible spectroscopic method is simple and straightforward experimental technique. We reported the stability constant of copper-glutamic acid complex in our previous work. In this paper we report the determination of metal to ligand ratio of Fe(II)- pyridine-2,4-dicarbonsaur and Fe(II) -bi-pyridine complexes in aqueous medium, stability constants and thermodynamics of the complexes using UV-visible spectrophotometry. The metal to ligand ratio in the complex was determined using three different methods namely, mole ratio, continuous variation and slope ratio method in aqueous medium.

## 2. EXPERIMENTAL

### 2.1 Chemicals

The chemicals used in the present study were, (i) Ferrous ammonium sulphate hexahydrate (MERCK, Germany), (ii) pyridine-2,4-dicarbonsaur (MERCK, Germany), (iii) bi-pyridine (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.

### 2.2 Equipments

Spectroscopic analysis was done using a UV-visible spectrophotometer (UV-Prove-1800PC) from SHIMADZU CORPORATION, JAPAN. Preparation of the solutions was done using volumetric flasks (50 mL, 100 mL, 250 mL and 1000 mL) and pipettes (graduated 10 mL and 25 mL). A pH meter, ORION 2 STAR, made by Thermo Electron Corporation was used to mesure the pH of the solutions.

* Corresponding Author: mqehsan@yahoo.com

## 3. RESULTS AND DISCUSSION

The metal to ligand ratio in in the complexes was determined using three different methods namely mole ratio, continuous variation and slope ratio method. The stability constant of metal-ligand complex, $K_f$ was determined by using UV-Visible spectroscopy with the help of Benesi-Hildebrand equation.

### 3.1 Determination of metal to ligand ratio in aqueous medium using UV-visible Spectrophotometer

#### 3.1.1 Fe(II)- pyridine-2,4-dicarbonsaur system

**Continuous variation method**

In this method mole concentration of Fe(II) and ligand is kept constant while their ratio of volume is continuously varied by small amount and values of absorbance were recorded. A plot of absorbance against % mole of Fe(II) is shown in Figure 1.

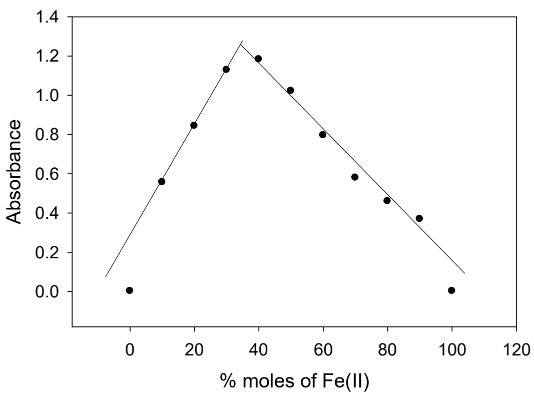


**Figure 1:** Variation of absorbance with the % moles of Fe(II)

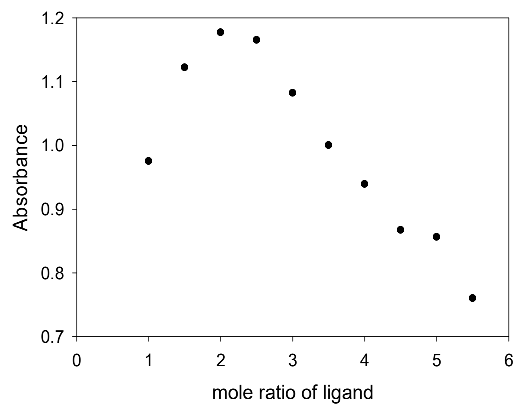


**Figure 2:** The variation of absorbance with the different mole ratio of ligand

Figure 1 reveals that the absorbance increases with the increase of % moles of metal and absorbance is highest at 40% moles of Fe(II) and then decreases. If we plot two straight lines through the points, they intersect at 34:66 ratio. So the ratio of moles of Fe(II) and ligand was obtained almost 1:2.

**Mole ratio method**

In this method the absorbance of 2 mL 5 x $10^{-4}$ M Fe(II) solution and various volume (4, 8, 10, 12, 14, 16, 18, 20, and 22 mL) of the ligand was measured at room temperature at 442 nm wavelegth ($\lambda_{max}$). The concentration of ligand was taken same as Fe(II) solution. A plot of absorbance against mole ratio of ligand is shown in Figure 2. From the plot it was found that the absorbance is maximum in ratio 2 and then decreases with increase of mole ratio. This indicates that maximum interaction occurs at metal-ligand ratio of 1:2.

**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 Fe(II) solution with solution of constant concentration of ligand was measured (after interaction). Again absorbance of mixture of Fe(II) solution (constant concentration) and variable concentration of ligand was also measured by spectrophotometer at 442 nm wavelength. A plot of absorbance against concentration of ligand and Fe(II) solution is shown in Figure 3.

Figure 3 demonstrates that, absorbance increases with the increase of concentration of ligand and Fe (II) solution. The slope ratio is found almost 2.3 (≈2) which indicates that the mole ratio of metal to ligand is almost two. So the maximum interaction may occur at 1:2 ratio of metal to ligand.

#### 3.1.2 Fe(II) and bi-pyridine system

The metal to ligand ratio of the Fe(II) and bi-pyridine system in aqueous medium was also determined using three different methods. Exactly same procedure was adopted here as before.

**Continuous variation method**

The plot of absorbance against % mole of Fe(II) is shown in Figure 4. The figure reveals that the absorbance increases with the increase of % moles of Fe(II) and absorbance is highest at 30% moles of Fe(II) and then decreases. If we plot two straight lines to the points, they intersect at 24:76 ratio. So the ratio of moles of Fe(II) and ligand was obtained almost 1:3.

**Mole ratio method**

The interaction of Fe(II) and bi-pyridine solution was studied spectroscopically by the mole ratio method by using same concentration of metal and ligand solution as in the previous experiment.

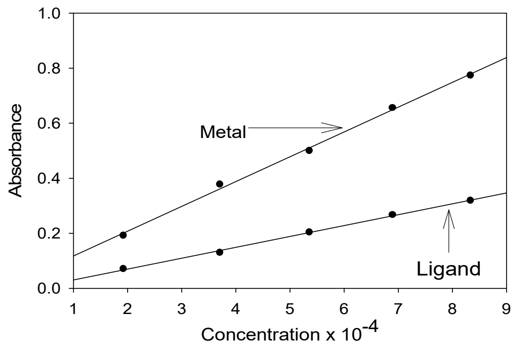


**Figure 3:** Variation of absorbance with concentration of ligand and metal

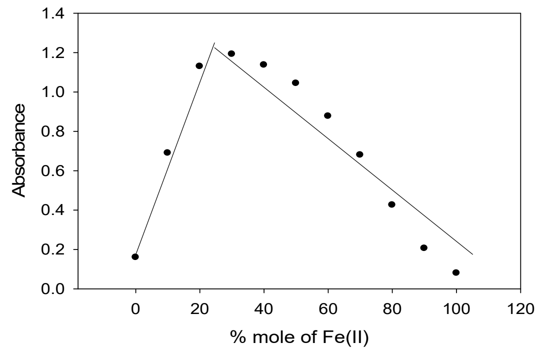


**Figure 4:** Variation of absorbance with the % moles of Fe(II)

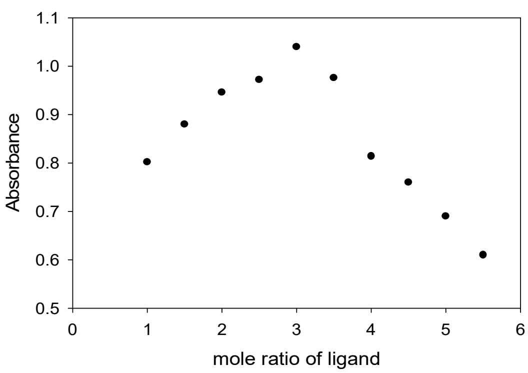


**Figure 5:** The variation of absorbance with the different mole ratio of ligand

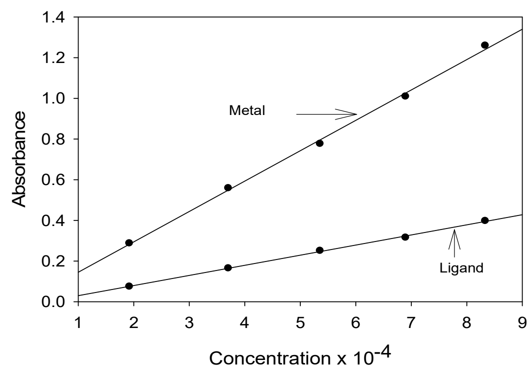


**Figure 6:** Variation of absorbance with concentration of ligand and metal

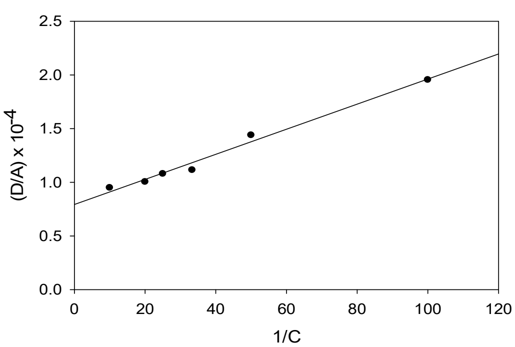


**Figure 7:** A plot of [D]/A vs 1/C for Fe(II)- pyridine 2,4 dicarbonsaur at 305 K

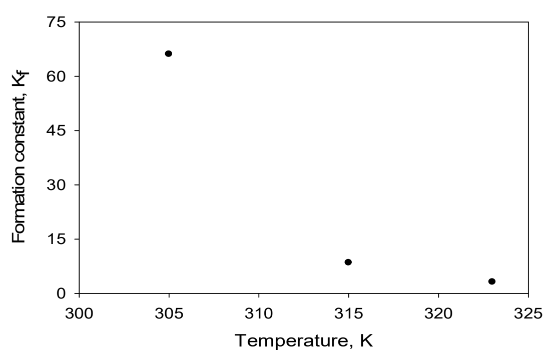


**Figure 8:** Variation of formatin constant ($K_f$) with temperature

A plot of absorbance against mole ratio of ligand is shown in Figure 5. From the figure it is found that the absorbance is maximum at ratio 3 and then decreases with increase of mole ratio. This indicates that maximum interaction occurs at ratio 1:3.

**Slope ratio method**

A plot of absorbance against concentration of ligand and Fe(II) solution is shown in Figure 6. The figure demonstrates that, absorbance increases with the increase of concentration of ligand and Fe (II). The slope ratio was found at 3.1 (≈3) which indicates that mole ratio of metal to ligand is almost three. So the maximum interaction may occur at 1:3 ratio of metal to ligand.

## 3.2 Determination of stability constant of the complex by Benesi-Hildebrand equation

### 3.2.1 Fe(II)- pyridine-2,4-dicarbonsaur system

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

(€). Thus, 1/(slope x €) gives stability constant ($K_f$). (Otto, 1997; Chao *et al.*, 2000; Anslyn, 2006). The free energy change for the complex formation reaction is calculated using equation $\Delta G = -2.303\ RT \log K_f$ (Marun, 1972).

Other thermodynamic paramerers such as ΔH and ΔS were also calcualted at 305 K.

In doing the experiment, same volume of metal and ligand solution were mixed and the absorbance of the mixtures were recorded. The concentration of ligand solution were kept constant and that of Fe(II) solution were varied. The process was carried out in acetate buffer of pH 4.15 and at temperatures 305 K. A plot of $[D]/A$ against ($1/C$) at 305 K is displayed in Figure 7.

Same experiments were done at 315 K and 323 K and similar plots were obtained for the system at 315 K and 323 K (Not shown here). From the values of intercept and slop of the graph of $[D]/A$ vs $1/C$ plot, the values of stability constant $K_f$ were calculated. The values of $K_f$ were found as 66.10 L/mole, 8.48 L/mole and 3.17 L/mole at 305 K, 315 K and 323 K respectively. The variation of formation constant values with temperature is given in Figure 8. This demonstrates that the values of formation constant of Fe(II)- pyridine 2,4 dicarbonsaur complex decreases with the increase of temperature. This trend divulges exothermic nature of the reactions (Singh and Singh, 2011).

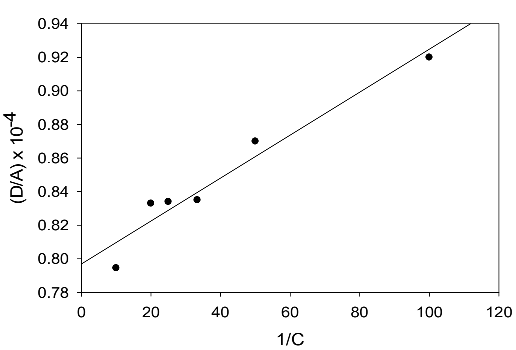


**Figure 9:** A plot of [D]/A vs 1/C for Fe(II)- bi-pyridine at 305 K

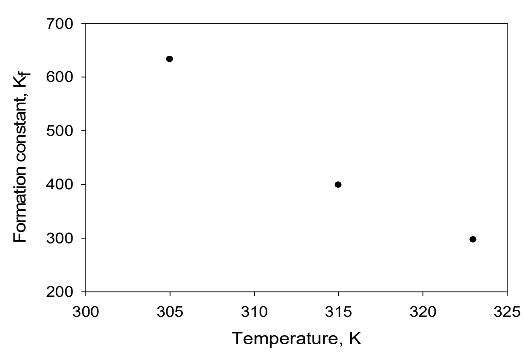


**Figure 10:** Variation of formatin constant ($K_f$) with temperature

Thermodynamic paramerers such as ΔG, ΔS and ΔH were calcualted at 305 K and were found as ΔG = -10.63 kJ/mole, ΔS = +14.14 $JK^{-1}mole^{-1}$ and ΔH = -94.61 kJ/mole. The negative values of free energy and enthalpy change indicates that the metal-ligand formation reactions are exothermic and the reactions are favourable at lower temperature which is also indicated by the greater value of stability constant at lower temperature. The negative values of ΔG and the positive value of ΔS suggest that the reactions are spontaneous (Haider, 2002; Peter, 2001). The relatively large ΔH value compared with the small value of ΔS indicate that enthalpy change is the principal driving force for the reaction. The comparatively large ΔH value suggests strong metal-ligand bond formation (Mahmooda and Farida, 1997).

### 3.2.2 Fe(II) and bi-pyridine system

Exactly same experiments were done to estimate the formation constants of Fe(II) and bi-pyridine system. The process was carried out in buffer solution of pH 4.15 at different temperatures (305 K, 315 K and 323 K). A plot of *[D]/A* against (*1/C*) at 305 K is shown in Figure 9. Similar plots were obtained for the Fe(II) – bi-pyridine compex at 315 K and 323 K (Not shown here). From the values of intercept and slop of the graph of *D/A* vs *1/C*, the values of stability constant $K_f$ were calculated. The values of $K_f$ were found as 632.65 L/mole, 398.60 L/mole and 296.68 L/mole at 305 K, 315 K and 323 K respectively. The variation of formation constant values with temperature is given in Figure 10. The decreasing values of formation constant of Fe(II)- bi-pyridine complex with temperature discloses exothermic nature of the reactions (Singh and Singh, 2011).

Thermodynamic paramerers such as ΔG, ΔS and ΔH were calcualted at 305 K and were found as ΔG = -16.35 kJ/mole, ΔS = +46.89 $JK^{-1}mole^{-1}$ and ΔH = -35.62 kJ/mole. In this system also thethermodynamic s shows similar trends. The negative value of ΔG and the positive value of ΔS suggest that the reactions are spontaneous (Haider, 2002; Peter, 2001). The relatively small ΔH value compared with the large value of ΔS indicate that entropy is the principal driving force for the reaction (Rafiquzzaman *et al.*, 1990).

## 4. CONCLUSION

In conclusion it may be concluded that the ratio of metal to ligand was found almost 1:2 for Fe(II) -pyridine-2,4-dicarbonsaur and 1:3 for Fe(II)-bi-pyridine in aqueous medium. The values of stability constant varies inversily with temperature for both complexes. Moreover, thermodynamic paramerers such as ΔG, ΔS and ΔH reveal that the complex formation is exothermic and spontaneous.

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