▼ Journal of Research (Science), Bahauddin Zakariya University, Multan, Pakistan.
Vol. 18, No. 4, October 2007, pp. 219-235 ISSN 1021-1012

Article presented in 6th International and 16th National Chemistry Conference
"Quality of Life and Chemical Sciences" (April 6-8, 2006)

# ADDITION PRODUCT OF IRON(II) COMPLEX OF AROMATIC DIIMINE WITH SULPHURIC ACID

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## Abstract

Tris(2,2′-bipyridine) iron(II) cation was identified by the methods like Job's continuous variation, slope ratio and mole ratio. Stability constant of the complex ion was established with the help of Job's continuous variation method. Sulphate salt of the complex ion in the form of addition product with sulphuric acid of the type $[Fe(bipy)_3]SO_4.4H_2O.H_2SO_4$ was crystallized out and characterized by different techniques like elemental analysis, IR-spectroscopy, pH-metry and UV-Visible absorption spectrophotometry. The data suggests a 1:1 ($[Fe(bipy)_3]SO_4.4H_2O$ : $H_2SO_4$) stoichiometry for the addition product. It was also found that aqueous solution of the addition product shows acidic behavior due to the presence of $H_2SO_4$. Other characteristics like wavelength maximum, molar extinction coefficient and stability of $[Fe(bipy)_3]SO_4.4H_2O.H_2SO_4$ were spectrophotometrically established.

**Keywords:** Addition product, IR Spectroscopy, pH-metry, UV-Visible absorption spectrophotometry.

## INTRODUCTION

A most important part of chemistry has always been the synthesis of complex compounds. Certainly research in the chemical industry is largely oriented towards the synthesis of new and useful complexes and that is an excellent way of facilitating our lives through chemistry. 2, 2′-bipyridine is a polypyridyl ligand and relatively weak base. In the field of biology, it is a useful anthelmintic and has some but not pronounced bactericidal value. It functions as a typical bidentate chelate molecule through the nitrogen atoms with the formation of five-membered ring. The good σ-donor and π-acceptor property of this α, α′-diimine chelate ligand makes it high field donor of comparable strength to that of cyanide ion. Yet it chelates with a wide variety of metal ions. Bipyridine is well known for determination of iron in samples of soil, biological materials and miscellaneous materials and thus it has wide ranging applications. The tris-chelate complex ion of 2,2′-bipyridine with the ferrous ion is a low spin complex with an intense red color, high value of molar absorptivity (8800 $M^{-1}$ $cm^{-1}$) and a large value of formation constant $6.4\times10^{18}$. The large cationic iron(II) complex with bipyridine is useful in the specific precipitation of anions in gravimetric procedures and also employed for microscopic identification of anions. For the spectrophotometric and colorimetric determination of iron by the analytical chemists, bipyridine ligand has attained international usage.

In this paper we report on the synthesis, isolation and characterization of the addition product of iron(II) complex of aromatic diimine with sulphuric acid.

## MATERIALS AND METHODS

All the chemicals including diammoniumiron(II) sulphate-6-hydrate, 2,2′-bipyridine, sodium sulphate, sodium oxalate, potassium permanganate, oxalic acid, sodium hydroxide, sulphuric acid and ethanol were of AnalaR grade. Deionized water was employed for preparation of the solutions.

### IDENTIFICATION OF THE TRIS(2,2′-BIPYRIDINE) IRON(II) ION

The tris(2,2′-bipyridine)iron(II) ion was spectrophotometrically identified by the method of Job's continuous variation. A series of solutions containing portions of ferrous ions and 2, 2′-bipyridine, were prepared. Ferrous solutions of required concentrations were prepared by dilution of the stock solution which was prepared by dissolving appropriate amount of the diammmoniumiron (II) sulphate-6-hydrate in the deionized water and making up to the required volume by the same solvent. Whereas dilutions of required concentrations of 2,2′-bipyridine were prepared from the stock solution of the ligand which was prepared by dissolving necessary amount of the ligand in ethanol and making up to the required volume by deionized water. Subsequently dilutions of the metal ion and the ligand were made in deionized water. Further to that optical density measurements at the wavelength of maximum absorption ($\lambda_{max}$); 522 nm, of the complex ion, were carried out and with the help of following calculations, metal to ligand ratio of the complex ion was established.

Formation of a complex ion can be shown by the following equilibrium:

$$M^{z+} \;+\; nL \;\xleftrightarrow{\beta_x}\; [ML_n]^{z+}$$

| | | | |
|---|---|---|---|
| *Initial concentration* | $(1-\alpha)C$ | $\alpha C$ | 0 |
| *Final concentration* | $(1-\alpha-\gamma)C$ | $(\alpha-n\gamma)C$ | $\gamma C$ |

where sum of the total molar concentrations (mol dm$^{-3}$ or M); $[\;]_t$, of the metal ion and the ligand $[M^{z+}]_t + [L]_t$ is set equal to $C$ because in this method sum of the concentration fractions of the metal ion and the ligand; $[M^{z+}]_t + [L]_t$ is held constant for all sets of solutions that are examined. However, each solution may have different value for $[M^{z+}]_t$ and $[L]_t$. $\alpha C$ is the initial concentration of ligand and $\gamma C$ is the final concentration of the complex species $[ML_n]^{z+}$. However, for the above given reaction:

$$\beta_x = \frac{[ML_n{}^{z+}]}{[M^{z+}][L]^n}$$

and that here in the concentrations are those of the final solution that has attained the equilibrium.

When the reaction completes or equilibrium is attained, concentration of the complex will be maximum at this point and thus value of the $\gamma$ will be maximum whereas concentrations of the metal ion and the ligand will be very small and can assumed to be, $[M^{z+}]$ and $[L] \approx 0$

$$[M^{z+}] = (1-\alpha_{max} - \gamma_{max})C = 0$$

$$[L] = (\alpha_{max} - n\gamma_{max})C = 0$$

$$1-\alpha_{max} - \gamma_{max} = 0 \qquad (1)$$

$$\alpha_{max} - n\gamma_{max} = 0 \qquad (2)$$

On combining equations (1) and (2), we get equation (3)

$$(n-1)\gamma_{max} - 2\alpha_{max} + 1 = 0 \qquad (3)$$

From equation (1) value of the $\gamma_{max}$ is derived and put in equation (3)

$$\gamma_{max} = (1-\alpha_{max})$$

$$\alpha_{max} = \frac{n}{n+1} \qquad (4)$$

Optical density is plotted as a function of composition of the reaction mixture, that's against the ratio:

$$\frac{[M^{z+}]_t}{[M^{z+}]_t + [L]_t} = \frac{[M^{z+}]_t}{C}$$

and absorption measurements are carried out at the wavelength of maximum absorption ($\lambda_{max}$) of the colored complex ion, $[ML_n]^{z+}$. Therefore, position of the maximum absorption at the plot can be represented by the following equation:

$$\frac{[M^{z+}]_t}{[M^{z+}]_t + [L]_t} = \frac{(1-\alpha_{max})C}{(1-\alpha_{max})C + \alpha_{max}C} = \frac{1-\alpha_{max}}{1} \qquad (5)$$

By putting value of the $\alpha_{max}$ from equation (4) in equation (5), we get

$$\frac{[M^{z+}]_t}{[M^{z+}]_t + [L]_t} = \frac{1}{n+1} \qquad (6)$$

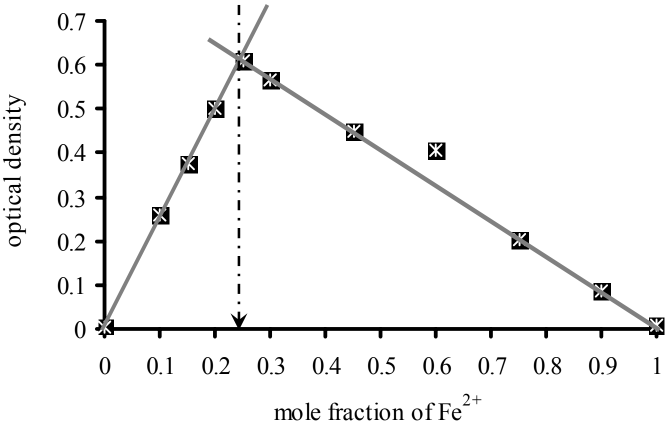

**Fig. 1:** The Job's Plot obtained when $[Fe(bipy)_3]^{2+}$ Complex Species is formed.

So "$\alpha_{max}$" and thus "n" was determined in a systematic way, from position of the maximum absorption at the plot of optical density versus $[Fe^{2+}]_t/([Fe^{2+}]_t+[bipy]_t)$, and found as ¾ and 3 respectively. Thus chemical formula of the complex ion is established as $[Fe(bipy)_3]^{2+}$. The results are reported in the Table 1 and Fig. 1.

**Table 1:** Determination of Metal to Ligand Ratio in the Iron(II)Bipyridine Complex Ion by the Job's Method of Continuous Variation.
Diammoniumiron(II) sulphate-6-hydrate = $2.8\times10^{-4}$ M, 2,2′-Bipyridine = $2.8\times10^{-4}$ M,
$\lambda_{max}$ = 522 nm, Temperature = 30 °C

| S. No. | Composition of the reaction mixture | | Optical density |
|---|---|---|---|
| | $\frac{[Fe^{2+}]_t}{([Fe^{2+}]_t+[bipy]_t)}$ | $\frac{[bipy]_t}{([Fe^{2+}]_t+[bipy]_t)}$ | |
| 1. | 0.00 | 1.00 | 0.003 |
| 2. | 0.10 | 0.90 | 0.258 |
| 3. | 0.15 | 0.85 | 0.378 |
| 4. | 0.20 | 0.80 | 0.502 |
| 5. | 0.25 | 0.75 | 0.609 |
| 6. | 0.30 | 0.70 | 0.565 |
| 7. | 0.45 | 0.55 | 0.450 |
| 8. | 0.60 | 0.40 | 0.408 |
| 9. | 0.75 | 0.25 | 0.203 |
| 10. | 0.90 | 0.10 | 0.086 |
| 11. | 1.00 | 0.00 | 0.010 |

Empirical formula of the tris(2,2′-bipyridine) iron(II) ion was also established spectrophotometrically with the help of other methods like mole ratio and slope ratio (Tables 2-4 and Figs. 2-3).

**Table 2:** Determination of the Empirical Formula of the Iron(II)Bipyridine Complex Ion by Mole Ratio Method. Diammoniumiron (II) Sulphate-6-hydrate = $1.75\times10^{-3}$ M, 2,2′-Bipyridine = $1.75\times10^{-3}$M,
$\lambda_{max}$ = 522 nm, Medium = deionized water, Temperature = 30 °C

| S. No. | Composition of the reaction mixture in 25 cm$^3$ | | | $10^5[Fe^{2+}]_t$ (M) | $10^5[bipy]_t$ (M) | $\frac{[bipy]_t}{[Fe^{2+}]_t}$ | Optical density |
|---|---|---|---|---|---|---|---|
| | $Fe^{2+}$ (cm$^3$) | bipy (cm$^3$) | $H_2O$ (cm$^3$) | | | | |
| 1. | 1 | 0 | 24 | 7 | 0 | 0 | 0.002 |
| 2. | 1 | 1 | 23 | 7 | 7 | 1 | 0.200 |
| 3. | 1 | 2 | 22 | 7 | 14 | 2 | 0.413 |
| 4. | 1 | 3 | 21 | 7 | 21 | 3 | 0.615 |
| 5. | 1 | 4 | 20 | 7 | 28 | 4 | 0.620 |
| 6. | 1 | 5 | 19 | 7 | 35 | 5 | 0.625 |
| 7. | 1 | 6 | 18 | 7 | 42 | 6 | 0.625 |
| 8. | 1 | 7 | 17 | 7 | 49 | 7 | 0.625 |
| Empirical formula found, for the complex ion | | | | | | $[F(bipy)_3]^{2+}$ | |

For applying these methods a series of the solutions containing varying concentrations of the metal ion and the ligand was prepared. Later on optical density measurements at the wavelength of maximum absorption of the tris(2,2′-bipyridine) iron(II) ion ($\lambda_{max}$); 522 nm, were recorded. Solutions of the ferrous ions and the ligand were prepared using the same solvents as the ones in Job's method.

**Table 3:** Determination of Composition of the Iron(II)Bipyridine Complex Ion by the Slope Ratio Method. Diammoniumiron (II) Sulphate-6-hydrate = 4.0 × $10^{-4}$ M, 2,2′-Bipyridine = 1.99 × $10^{-2}$ M, $\lambda_{max}$ = 522 nm, Medium = deionized water, Temperature = 30 °C

| S. No. | Composition of the reaction mixture in 25 $cm^3$ | | | $10^5\,[Fe^{2+}]_t$ (M) | $10^4\,[bipy]_t$ (M) | Optical density | Slope $= \frac{\varepsilon b}{m}$ ($M^{-1}$) |
|---|---|---|---|---|---|---|---|
| | $Fe^{2+}$ ($cm^3$) | bipy ($cm^3$) | $H_2O$ ($cm^3$) | | | | |
| 1. | 1 | 0 | 24 | 1.6 | 00.00 | 0.002 | 8740 |
| 2. | 2 | 6 | 17 | 3.2 | 47.76 | 0.285 | |
| 3. | 3 | 6 | 16 | 4.8 | 47.76 | 0.422 | |
| 4. | 4 | 6 | 15 | 6.4 | 47.76 | 0.561 | |
| 5. | 5 | 6 | 14 | 8.0 | 47.76 | 0.692 | |
| 6. | 6 | 6 | 13 | 9.6 | 47.76 | 0.842 | |
| 7. | 7 | 6 | 12 | 11.2 | 47.76 | 0.979 | |

**Table 4:** Determination of Composition of the Iron(II)Bipyridine Complex Ion by the Slope Ratio Method. Diammoniumiron (II) Sulphate-6-hydrate = 1.99 × $10^{-2}$ M, 2,2′-Bipyridine = 1.2 × $10^{-3}$ M, $\lambda_{max}$ = 522 nm, Medium = deionized water, Temperature = 28 °C

| S. No. | Composition of the reaction mixture in 25 $cm^3$ | | | $10^4\,[Fe^{2+}]_t$ (M) | $10^5\,[bipy]_t$ (M) | Optical density | Optical density after approx. 20 mins | Slope $= \frac{\varepsilon b}{n}$ ($M^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| | $Fe^{2+}$ ($cm^3$) | bipy ($cm^3$) | $H_2O$ ($cm^3$) | | | | | |
| 1. | 6 | 0 | 19 | 47.76 | 0.0 | 0.007 | 0.007 | 2780 & 2610 |
| 2. | 6 | 2 | 17 | 47.76 | 9.6 | 0.222 | 0.219 | |
| 3. | 6 | 3 | 16 | 47.76 | 14.4 | 0.406 | 0.360 | |
| 4. | 6 | 4 | 15 | 47.76 | 19.2 | 0.554 | 0.492 | |
| 5. | 6 | 5 | 14 | 47.76 | 24.0 | 0.655 | 0.607 | |
| 6. | 6 | 6 | 13 | 47.76 | 28.8 | 0.788 | 0.774 | |
| 7. | 6 | 7 | 12 | 47.76 | 33.6 | 0.951 | 0.895 | |

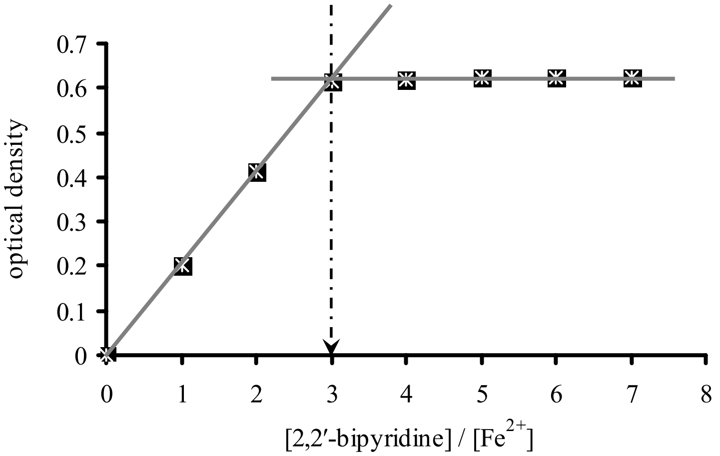

**Fig. 2:** Determination of Formula of $[Fe(bipy)_3]^{2+}$ Complex Species by the Mole Ratio Method.

Following calculations were used to establish a metal to ligand ratio in the complex cation when applying slope ratio method.

In the reaction,

$$mM^{z+} + nL \xleftrightarrow{\beta_x} [M_mL_n]^{z+}$$

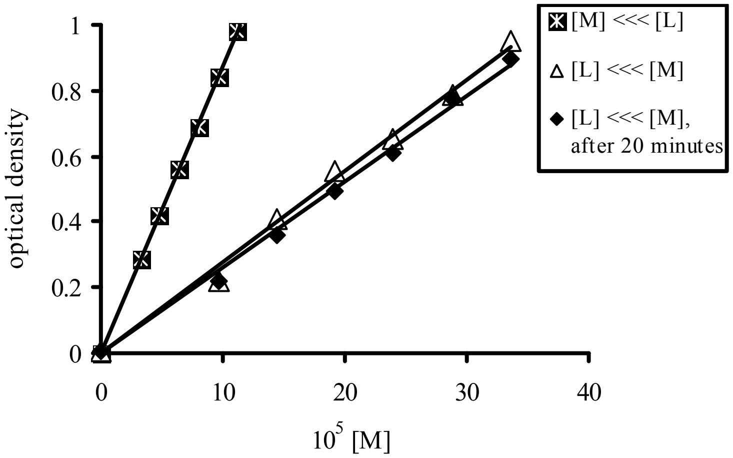

**Fig. 3:** Determination of the Composition of $[Fe(bipy)_3]^{2+}$ Complex Species by the Slope Ratio Method.

where $M^{z+}$ = metal ion, L = ligand, and $[M_mL_n]^{z+}$ = complex compound If $[M^{z+}]_t$ <<< $[L]_t$ then, concentration of the ligand will be in sufficient excess to ensure negligible reverse reaction. Equilibrium concentration of the complex compound $[M_mL_n]^{z+}$ will be essentially proportional to the analytical concentration of the metal ion added to the reaction,

$$[M^{z+}]_t = [M^{z+}]_R + m\left[M_mL_n{}^{z+}\right] \tag{7}$$

$$\therefore [M^{z+}]_R \langle\langle\langle\, m\left[M_mL_n{}^{z+}\right]$$

$$[M^{z+}]_t = m\left[M_mL_n{}^{z+}\right] \tag{8}$$

$$\therefore [M^{z+}]_t = C_M,\ \left[M_mL_n{}^{z+}\right] = C$$

$$\left[M_mL_n{}^{z+}\right] = C = \frac{C_M}{m} \tag{9}$$

[ ] = molar concentration (M) of the reacting species,
$[\ ]_t$ = total molar concentration of the reacting species,
$[\ ]_R$ = remaining molar concentration of the reacting species,
*C* = analytical concentration of the reacting species.

Optical density (absorbance) measurements are carried out at the wavelength of maximum absorption ($\lambda_{max}$) of the complex compound, $[M_mL_n]^{z+}$. Hence by applying Beer-Lambert's law on Eq. (9), we get

$$A = \varepsilon bc = \varepsilon b\left[M_mL_n{}^{z+}\right] = \varepsilon bC = \varepsilon b\frac{C_M}{m} \tag{10}$$

If a plot is made between optical density (A) of the system and the total molar concentration of the reacting species, $C_M$, then slope of the plot will be εb/m.

In the same way if, $[L]_t <<< [M^{z+}]_t$, then

$$\left[M_m L_n^{z+}\right] = C = \frac{C_L}{n} \tag{11}$$

$$A = \varepsilon bc = \varepsilon b\left[M_m L_n^{z+}\right] = \varepsilon bC = \varepsilon b\frac{C_L}{n} \tag{12}$$

and slope of the plot will be εb/n, if a plot is made between optical density of the system and total molar concentration of the reacting species, $C_L$.

Empirical formula of the complex compound was thus evaluated from the ratio between slopes of the plots:

$$\frac{\text{slope 1}}{\text{slope 2}} = \frac{\frac{\varepsilon b}{m}}{\frac{\varepsilon b}{n}} = \frac{n}{m} \tag{13}$$

## FORMATION CONSTANT (STABILITY CONSTANT) OF THE COMPLEX COMPOUND

For the formation of a complex compound the equilibrium may be expressed as,

$$M^{z+}{}_{(aq)} \quad + \quad nL_{(aq)} \quad \xleftrightarrow{\beta_x} \quad \left[ML_n\right]^{z+}{}_{(aq)}$$

Expression of the equilibrium constant (formation constant) for the system will thus be

$$\beta_x = \frac{\left[ML_n^{z+}\right]}{[M^{z+}][L]^n} \tag{14}$$

It is apparent from Eq (14) that knowledge of composition or empirical formula of the complex compound, molar concentrations (M or mol dm$^{-3}$); [ ], of the metal ion, ligand and the complex formed, at the state of equilibrium, is required to establish the formation constant ($\beta_x$) of the complex under the conditions employed during the experiment. Composition of the complex compound was established by using different spectrophotometric methods like Job's method. Aqueous solutions of the metal ion and the ligand of known strengths were mixed and left for sufficient time so that the resulting solution attained equilibrium. Then molar concentration of the only one species i.e. $[ML_n]^{z+}$ was required for determining equilibrium concentrations of the other specie, as shown:

$$[M^{z+}] = [M^{z+}]_o - \left[ML_n^{z+}\right] \tag{15}$$

$$[L] = [L]_o - n\left[ML_n^{z+}\right] \tag{16}$$

[ ] = molar concentration of the reacting species at equilibrium,

$[\ ]_o$ = initial molar concentration of the reacting species.

Molar concentration of the complex at equilibrium was determined by applying Beer-Lambert's law, through measuring optical density of the system at a wavelength of maximum absorption ($\lambda_{max}$) of the complex compound.

Value of formation or stability constant of the complex ion is thus evaluated with the help of expression (14) and found to have log $\beta_x$ as 18.8062.

## SYNTHESIS AND ISOLATION OF THE ADDITION PRODUCT OF TRIS(2,2′-BIPYRIDINE)IRON(II) SULPHATE TETRAHYDRATE WITH SULPHURIC ACID

The intense red colored small crystalline addition product of the tris(2,2′-bipyridine)iron(II) sulphate tetrahydrate with the sulphuric acid of the chemical formula $[Fe(bipy)_3]SO_4.4H_2O.H_2SO_4$ was synthesized and isolated by applying following procedure.

To a 40 $cm^3$ (0.02 mole) of the standard solution of diammoniumiron (II) sulphate-6-hydrate in 0.5 M aqueous sulphuric acid (the solution was standardized against the standard solution of potassium permanganate), a 100 $cm^3$ (0.06 mole) solution of the ligand 2,2′-bipyridine in ethanol, was added with vigorous and constant stirring. It was established earlier (Tables 1-4 and Figs. 1-3) by the method of Job's continuous variation etc., that when metal and ligand are mixed in the concentration ratio of 1:3 respectively, a dark red colored solution of the tris(2,2′-bipyridine)iron(II) cation is obtained. To the resulting solution a 21 $cm^3$ (0.0168 mole) solution of sodium sulphate in water was added slowly and with stirring, followed by 100 $cm^3$ of ethanol. The solution was then heated (not boiled) on a hot plate (in the hood) until a highly saturated solution was obtained which was then left to cool at room temperature. Small dark red crystals slowly developed. The intense red colored small crystalline product thus obtained was first dried with 30 $cm^3$ of petroleum ether and then in the desiccators over the desiccant silica gel blue at room temperature. Ethanol was used to recrystallize the product. For this purpose a saturated solution was obtained by using a suitable volume of ethanol to dissolve the substance completely at high temperature. After cooling the solution, impurities were separated out by the process of filtration. Double filter papers (Whatman 540) were used for almost complete filtration. The filtrate was heated (not boiled) in hood to evaporate ethanol from the mixture until a little volume remained. After cooling to room temperature the pure product was slowly crystallized out, and dried in oven at 80°C for approximately 10−15 minutes and then cooled, and kept in a desiccator over silica gel blue (freshly charged).

## INSTRUMENTATION

The elemental analysis was carried out on a Perkin Elmer-2400 elemental analyzer. The infra red spectra were recorded on a Shimadzu FTIR-8900 spectrophotometer. A Shimadzu UV-160, UV-Visible spectrophotometer was used for spectral and optical density measurements with matched 1cm path length quartz cells. pH measurements were carried out on a digital ORION pH meter (model 520 A). Magnetic stirrer (Ruhromag) was used for continuous stirring.

## RESULTS AND DISCUSSION

Addition product together with its elemental analysis and some physical data is given in the Table 5. Percentage determination of iron(II) in the isolated product was spectrophotometrically carried out.

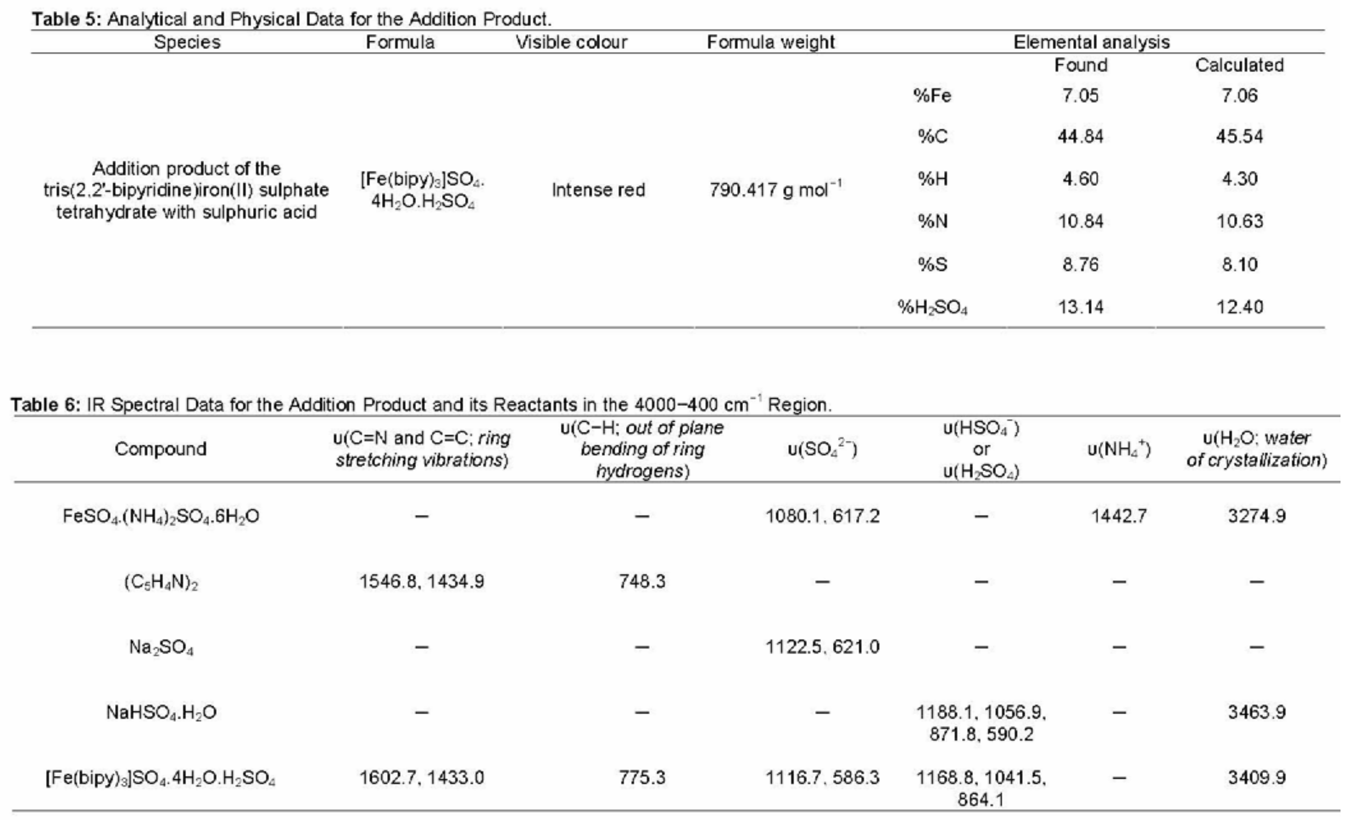

**Table 5:** Analytical and Physical Data for the Addition Product.

| Species | Formula | Visible colour | Formula weight | Elemental analysis | | |
|---|---|---|---|---|---|---|
| | | | | | Found | Calculated |
| Addition product of the tris(2,2'-bipyridine)iron(II) sulphate tetrahydrate with sulphuric acid | $[Fe(bipy)_3]SO_4.4H_2O.H_2SO_4$ | Intense red | 790.417 g mol$^{-1}$ | %Fe | 7.05 | 7.06 |
| | | | | %C | 44.84 | 45.54 |
| | | | | %H | 4.60 | 4.30 |
| | | | | %N | 10.84 | 10.63 |
| | | | | %S | 8.76 | 8.10 |
| | | | | %$H_2SO_4$ | 13.14 | 12.40 |

**Table 6:** IR Spectral Data for the Addition Product and its Reactants in the 4000−400 cm$^{-1}$ Region.

| Compound | u(C=N and C=C; *ring stretching vibrations*) | u(C−H; *out of plane bending of ring hydrogens*) | u($SO_4^{2-}$) | u($HSO_4^-$) or u($H_2SO_4$) | u($NH_4^+$) | u($H_2O$; *water of crystallization*) |
|---|---|---|---|---|---|---|
| $FeSO_4.(NH_4)_2SO_4.6H_2O$ | – | – | 1080.1, 617.2 | – | 1442.7 | 3274.9 |
| $(C_5H_4N)_2$ | 1546.8, 1434.9 | 748.3 | – | – | – | – |
| $Na_2SO_4$ | – | – | 1122.5, 621.0 | – | – | – |
| $NaHSO_4.H_2O$ | – | – | – | 1188.1, 1056.9, 871.8, 590.2 | – | 3463.9 |
| $[Fe(bipy)_3]SO_4.4H_2O.H_2SO_4$ | 1602.7, 1433.0 | 775.3 | 1116.7, 586.3 | 1168.8, 1041.5, 864.1 | – | 3409.9 |

## INFRARED SPECTRA

The IR-spectral study was carried out in the 4000−400 cm$^{-1}$ region, in KBr disc. For the study of different specie, only strong bands were considered. The principal IR bands for the addition product and its reactants are shown in Table 6.

In the spectra of diammoniumiron (II) sulphate-6-hydrate, 2,2′-bipyridine, sodium sulphate and sodium bisulphate monohydrate, four, three, two and five strong bands were observed respectively. The bands may be assigned to υ($H_2O$ of crystallization; 3274.9 $cm^{-1}$, $NH_4^+$; 1442.7 $cm^{-1}$ and $SO_4^{2-}$; 1080.1 and 617.2 $cm^{-1}$), υ(C=N and C=C ring stretching vibrations; 1546.8 and 1434.9 $cm^{-1}$, and C−H; out of plane bending of ring hydrogens; 748.3 $cm^{-1}$), υ($SO_4^{2-}$; 1122.5 and 621.0 $cm^{-1}$), υ($H_2O$ of crystallization; 3463.9 $cm^{-1}$ and $HSO_4^-$; 1188.1, 1056.9, 871.8 and 590.2 $cm^{-1}$) [Sawyer *et al.* 1984, Nakamoto 1978, Shilt and Taylor 1959] as shown in Figs. 4–7, respectively.

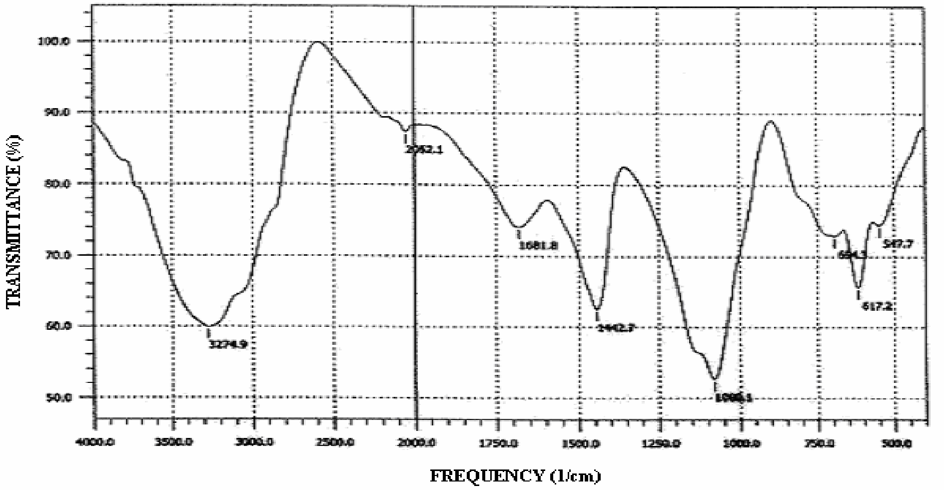

**Fig. 4:** The Infrared Spectrum of $FeSO_4.(NH_4)_2SO_4.6H_2O$ (in KBr).

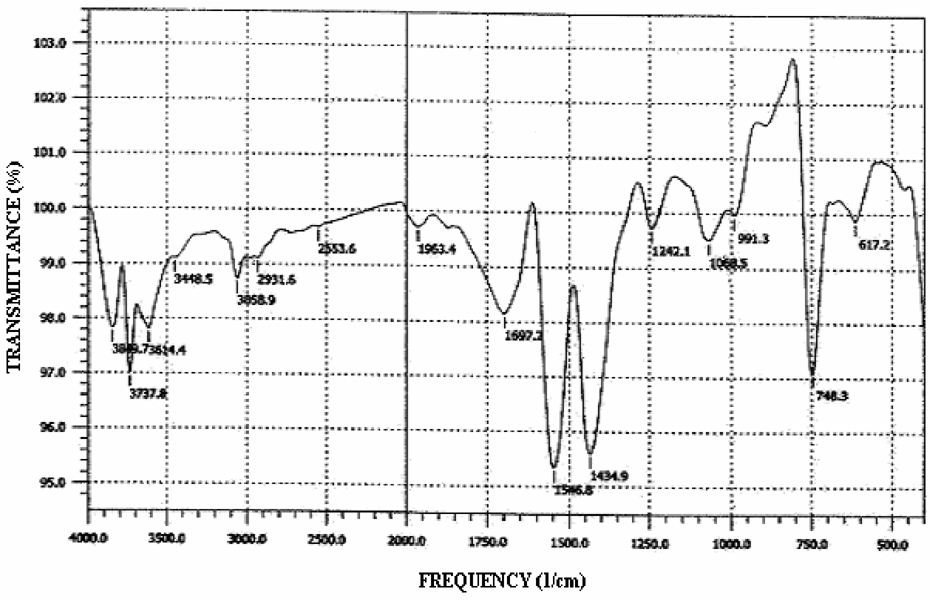

**Fig. 5:** The Infrared Spectrum of $(C_5H_4N)_2$ (in KBr).

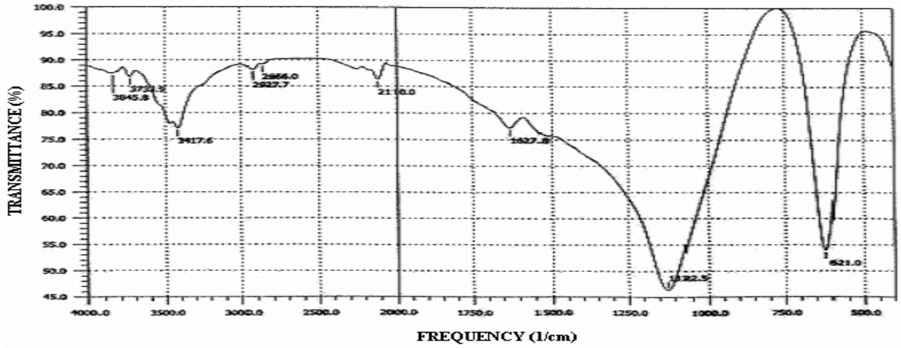

**Fig. 6:** The Infrared Spectrum of $Na_2SO_4$ (in KBr)

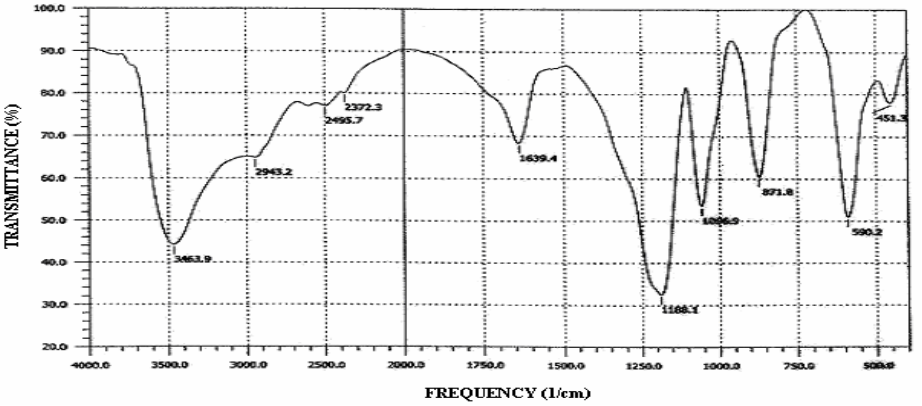

**Fig. 7:** The Infrared Spectrum of $NaHSO_4.H_2O$ (in KBr)

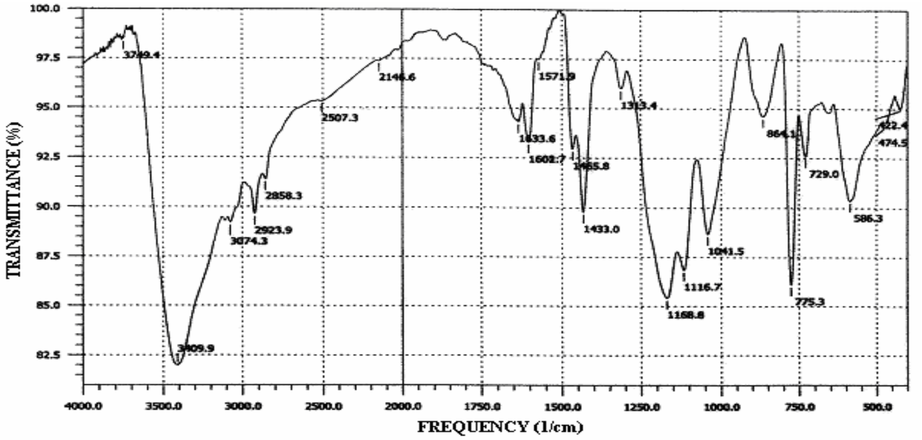

**Fig. 8:** The Infrared Spectrum of $[Fe(bipy)_3]SO_4.4H_2O.H_2SO_4$ (in KBr).

When 2,2′-bipyridine is complexed to a metal ion, changes in the IR spectrum of the ligand is observed, particularly in the regions 1650−1400 $cm^{-1}$ (C=N and C=C ring stretching vibrations) and 850−700 $cm^{-1}$ (C−H; out of plane deformations) [Shilt and Taylor 1959, Inskeep 1962, Sinha 1964, Ferraro and Walker 1965]. Addition product showed similar changes in these regions (Table 6 and Fig. 8), which gave a conclusion that bipyridine is coordinated as a bidentate ligand and the iron(II) has a coordination number of 6.

However the other bands observed in the IR spectrum of $[Fe(bipy)_3]SO_4$. $4H_2O$. $H_2SO_4$ (Table 6 and Fig. 8) may be ascribed to the υ($H_2O$ of crystallization; 3409.9 $cm^{-1}$, $SO_4^{2-}$; 1116.7 and 586.3 $cm^{-1}$, and $H_2SO_4$; 1168.8, 1041.5 and 864.1 $cm^{-1}$).

## pH METRIC (POTENTIOMETRIC) ANALYSIS OF $H_2SO_4$ IN THE ADDITION PRODUCT

Presence of $H_2SO_4$ in the addition product was determined by adding a weighed portion of the product to water, and the highly colored solution was titrated potentiometrically with a standard solution of sodium hydroxide (this solution was standardized against standard solution of oxalic acid). A 1:1 stoichiometry was found between $[Fe(bipy)_3]SO_4.4H_2O$ and $H_2SO_4$ in the addition product. Results are shown in Figs. 9−10.

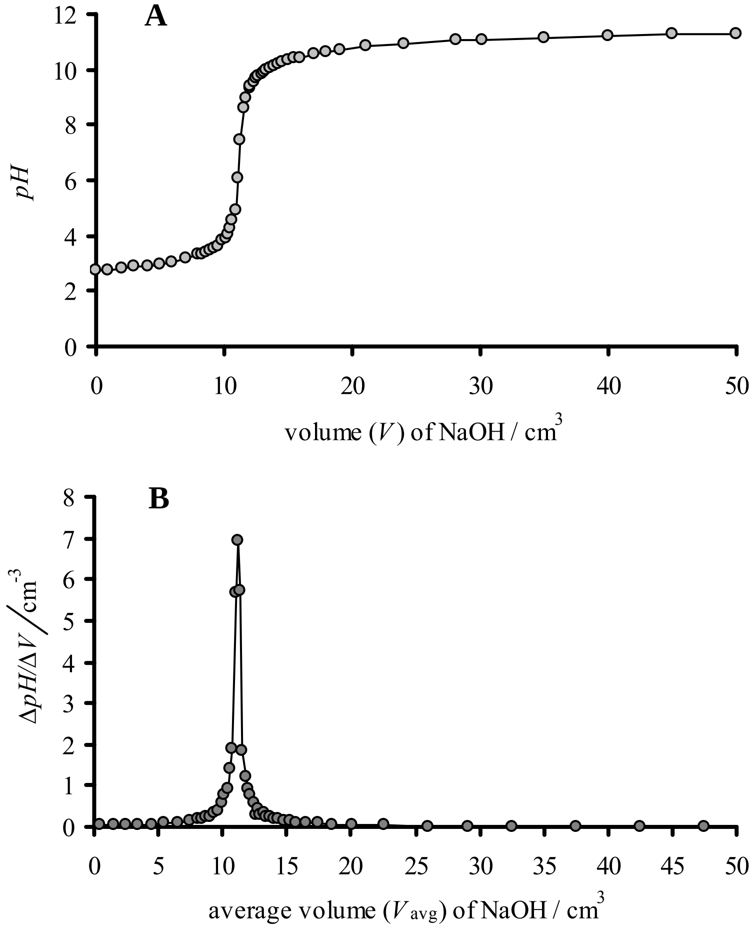

**Fig. 9**: Potentiometric Titration Curves of $[Fe(bipy)_3]SO_4.4H_2O.H_2SO_4$. A: Normal titration curve showing the region near the end point, B: First-derivative titration curve.

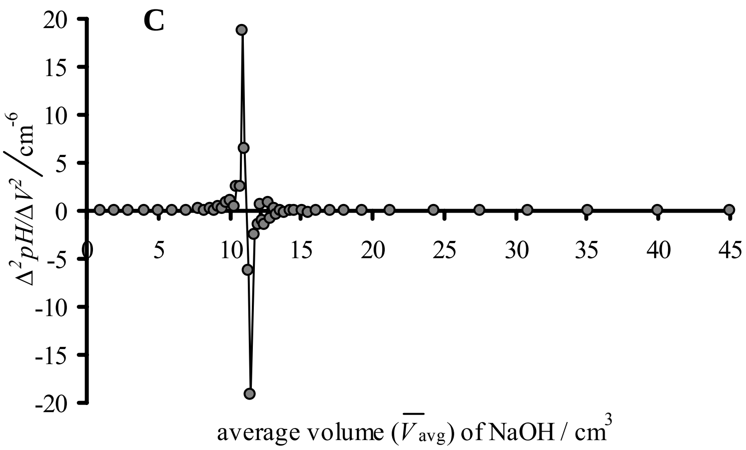

**Fig. 9** (continued)**:** Potentiometric Titration Curves of $[Fe(bipy)_3]SO_4.4H_2O.H_2SO_4$.
C: Second-derivative titration curve.

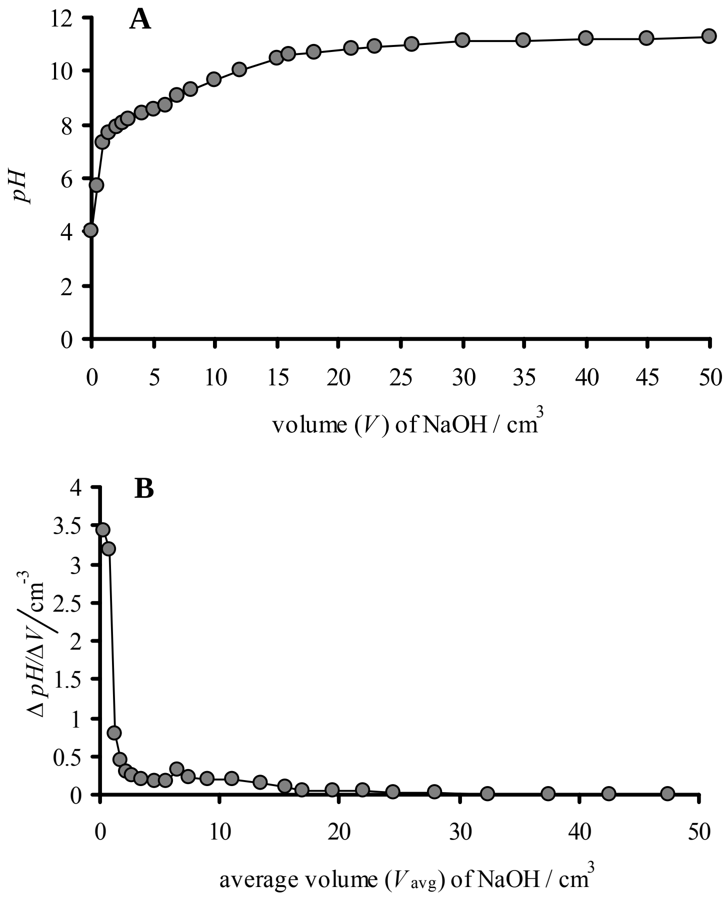

**Fig. 10:** Potentiometric Titration Curves of $[Fe(bipy)_3]^{2+}$. Curve A: Normal titration curve. Curve B: First-derivative titration curve.

## UV-VISIBLE ABSORPTION SPECTRAL CHARACTERISTICS OF THE ADDITION PRODUCT

UV-Visible absorption spectral characteristics of the tris(2,2′-bipyridine)iron(II) ion and the addition product of the tris(2,2′-bipyridine)iron(II) sulphate tetrahydrate with the sulphuric acid are reported in the Table 7 and Figs. 11−12. The data interpret that spectra of both the specie in different mediums are same which evidently corresponds to the chemical formula of the product as $[Fe(bipy)_3]SO_4.4H_2O.H_2SO_4$.

**Table 7:** UV-Visible Absorption Characteristics of the Iron(II)Bipyridine Complex Ion and the Addition Product in Various Solvents.

| Compound | Solvent | Band | Wavelength (λ), nm | Molar absorptivity (ε), $M^{-1}$ $cm^{-1}$ |
|---|---|---|---|---|
| $[Fe(bipy)_3]^{2+}$ | $H_2O$ | I | 522 | 8800 |
| | | II | 349 | − |
| | | III | 295 | − |
| | | IV | 244 | − |
| | | V | 210 | − |
| | 0.7 M $H_2SO_4$ | I | 522 | − |
| | | II | 349 | |
| | | III | 296 | |
| | | IV | 244 | |
| | | V | 210 | |
| | 0.68 M $HNO_3$ | I | 522 | − |
| | | II | 349 | |
| | | III | 269 | |
| $[Fe(bipy)_3]SO_4.4H_2O.H_2SO_4$ | $H_2O$ | I | 522 | 8120 |
| | | II | 349 | − |
| | | III | 293 | − |
| | | IV | 245 | − |
| | | V | 208 | − |
| | 0.7 M $H_2SO_4$ | I | 522 | − |
| | | II | 349 | |
| | | III | 293 | |
| | | IV | 245 | |
| | | V | 209 | |
| | 0.68 M $HNO_3$ | I | 522 | − |
| | | II | 349 | |
| | | III | 269 | |

## STABILITY OF THE ADDITION PRODUCT

Stability of the addition product was determined in the deionized water and found that the product is stable in the particular medium for a long period of time. Results are displayed in Table 8 and Fig. 13.

**Table 8:** Stability of the Addition Product of Tris(2,2′-bipyridine)iron(II) Sulphate Tetrahydrate with $H_2SO_4$. Medium = deionized water, $\lambda_{max}$ = 522 nm, ε = 8120 $M^{-1}$ $cm^{-1}$, Temperature = 25 °C

| S. No. | Time (days) | [Concentration] × $10^5$ M | | |
|---|---|---|---|---|
| | | [5.27] | [8.21] | [11.61] |
| | | Optical density | | |
| 1 | 0 | 0.428 | 0.667 | 0.943 |
| 2 | 4 | 0.425 | 0.664 | 0.941 |
| 3 | 10 | 0.434 | 0.670 | 0.965 |
| 4 | 31 | 0.442 | 0.685 | 1.015 |
| 5 | 53 | 0.440 | 0.707 | 1.005 |

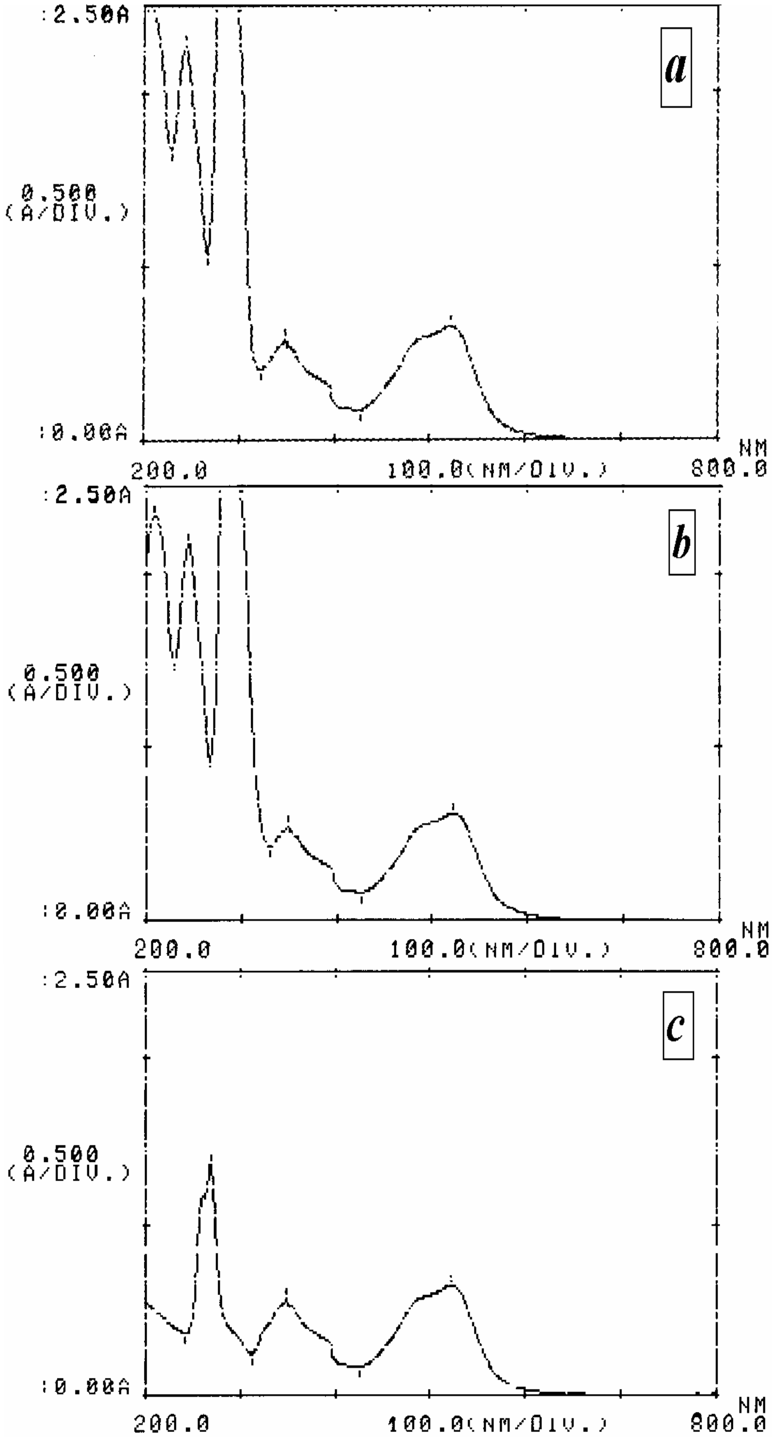

**Fig. 11:** UV-Visible Absorption Spectra of $[Fe(bipy)_3]^{2+}$;
(a): in $H_2O$, (b): in 0.7 M $H_2SO_4$, (c): in 0.68 M $HNO_3$.

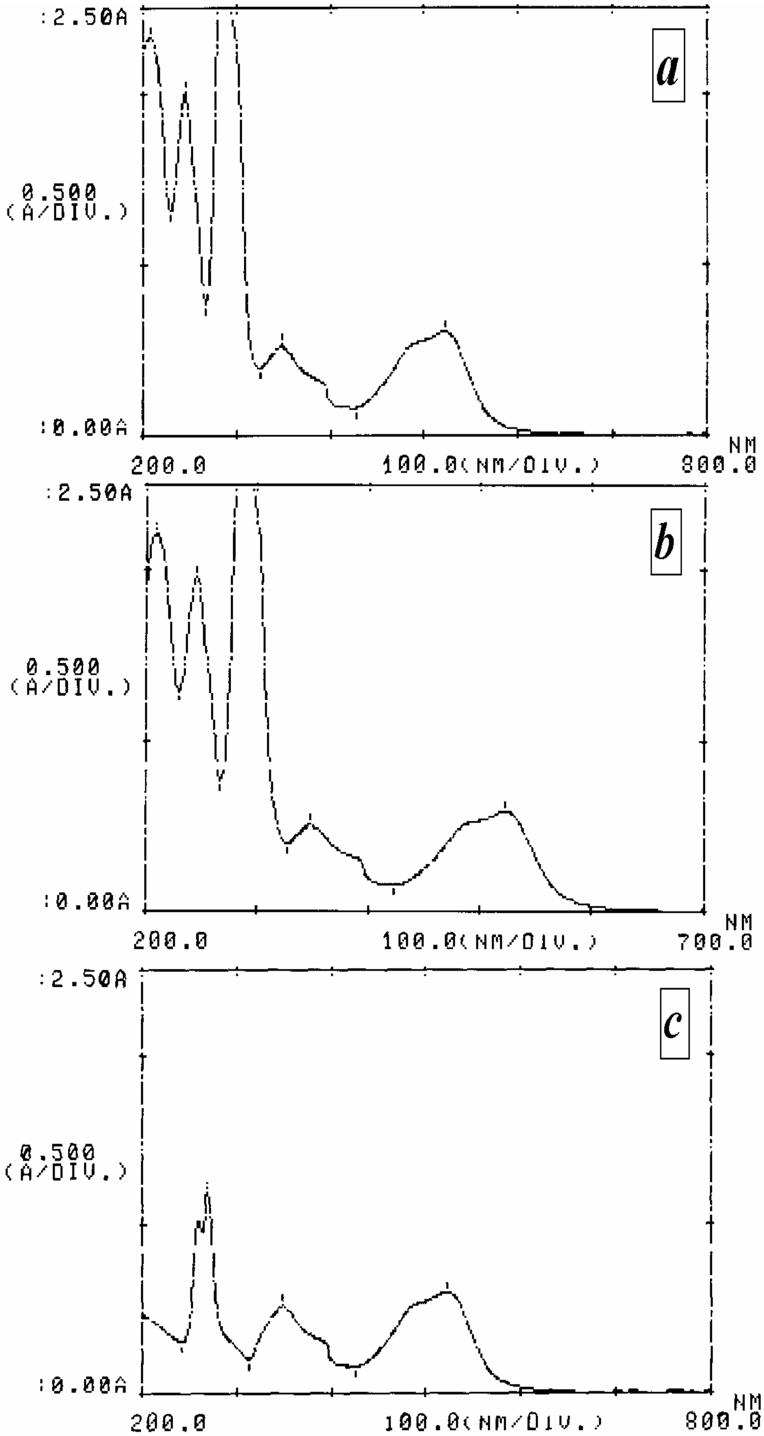

**Fig. 12:** UV-Visible Absorption Spectrum of $[Fe(bipy)_3]SO_4.4H_2O.H_2SO_4$; (a): in $H_2O$, (b): in 0.7 M $H_2SO_4$, (c): in 0.68 M $HNO_3$.

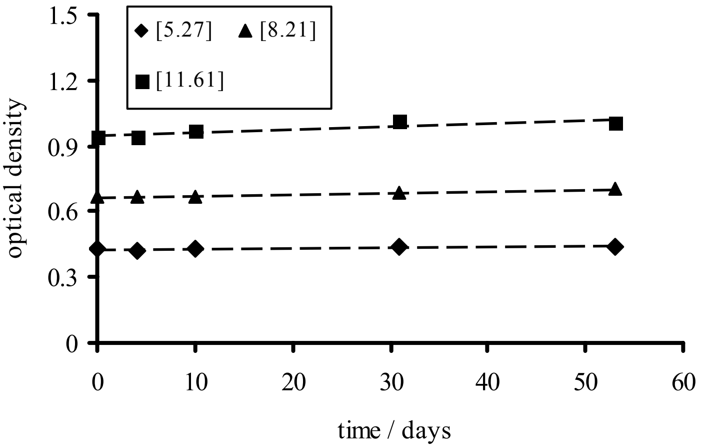

**Fig. 13:** Stability of $[Fe(bipy)_3]SO_4.4H_2O.H_2SO_4$ in the Deionized Water.

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