

Solvent Effects of the Electronic Absorption Spectrum of Ferroin Molecule

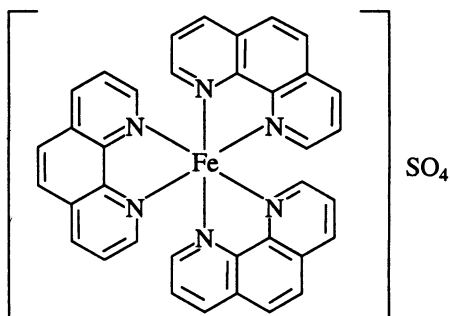
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In order to explore the role of the solvents on one of the best indicators, 1:10-phenanthroline ferrous sulphate, *i.e.*, ferroin, through ultraviolet spectroscopy, λ_{\max} , ϵ_{\max} and oscillator strength have been determined at room temperature. The present results together with values obtained from the experiments in water, methanol, acetone and orthophosphoric acid have been discussed in terms of ion-solvent interactions and solvent polarity. The intense long wavelength band which appears at about 510 nm in the visible region is referred to as the ${}^1A \longrightarrow {}^1A_1$ or $V \leftarrow N$ band. It is expected that the interaction affects the symmetry of the bidentate ligand with Fe^{2+} ion in the molecule to some extent depending on its nature.

INTRODUCTION

In continuation of our studies in electronic spectra of some redox dyes^{1, 2} we have selected a typical indicator ferroin, *i.e.*, 1:10-phenanthroline ferrous sulphate for such studies as this indicator is of great value in the titration *inter alia* of ferrous salts and other substances with ceric sulphate solution. From the literature³⁻⁷, we have found that no adequate attention has been given particularly to electronic absorption studies of ferroin molecule. Because of this situation, we have measured the effects of four different solvents, *viz.*, water, acetone, methanol and orthophosphoric acid. Such work has partly been studied in our laboratory some time before⁸ which has often been useful in assigning transitions and ultimately in evaluating the oscillator strength and we believe that it provides a good evidence of the nature of the orbitals involved in the transitions.



Ferroin Molecule

EXPERIMENTAL

Ferrioin, a fairly soluble compound⁹, is usually prepared by dissolving *ortho*-phenanthroline monohydrate, $C_{12}H_8N_2 \cdot H_2O$, in dilute solution of ferrous sulphate. The solutions of ferrioin of known concentration were prepared by weighing proper amounts of ferrioin on a chemical balance and dissolving in appropriate amounts of selected solvents.

A Shimadzu UV-VIS (model 160A, Japan) double beam spectrophotometer with automatic recording device was used and the spectra scanned through 200 nm to 1100 nm with an accuracy of 0.1 nm. They were run at room temperature using silica cell. The spectra were obtained in the shape of broad bands as plots of transmittance against wavelength from which the position of maximum absorption wavelength (λ_{max}) was estimated from the centre of symmetry of the graph. In case the graphs went beyond the scale, the solutions were diluted such that the peak position fell within the desired range.

Extinction coefficients (ϵ) were calculated at each wavelength using the Beer's Law equation. After converting the λ 's into wavenumber ($\nu \text{ cm}^{-1}$), the values of ϵ were plotted against ν . The area under the curves (ϵ vs. ν) calculated from the product $\epsilon \times 1/2$ bandwidth gave the value of the integrated absorption intensity I_a for the transition of the molecule¹⁰. From the ratio of $\frac{I_{obs}}{I_{theo}}$ the values of oscillation strengths of the transitions were calculated.

RESULTS AND DISCUSSION

From the spectra of ferrioin in different solvents, we have recorded the maximum absorption wavelength (λ_{max}) in Table-1. In each of these solvents the solution is red or light red. These spectra however exhibit bands in the visible as well as in the ultraviolet region.

TABLE-1
LIST OF BANDS OF FERROIN IN SOME SUITABLE SOLVENTS

Sl. No.	Solvents	Absorbance	λ_{max} (in nm)	Conc.	Colour
1	Water	1.669	511	0.04 g/L	Red
		2.219	236		
2	Methanol	1.164	509	4.00 g/L	No colour
		2.119	290		
3	Acetone	0.420	509	4.00 g/L	Light red
4	orthophosphoric acid	0.295	511	2.00 g/L	Light red
		2.180	261		
5	orthophosphoric acid	1.131	305	2.00 g/L	After 48 h the colour disappeared
		2.127	265		

TABLE-2
MOLAR EXTINCTION COEFFICIENT (ϵ) AT DIFFERENT FREQUENCIES (cm^{-1})
FOR BANDS OF FERROIN IN SOLVENT WATER

$$\text{Concentration } 0.04 \text{ g/L} = \frac{0.04}{651.84} \text{ g mole/litre} = C$$

$$l\text{-path length} = 1 \text{ cm and } \frac{1}{C} \cdot l = \frac{651.84}{0.04} = 1629.25 \text{ g mole}^{-1} \text{ cm}^2$$

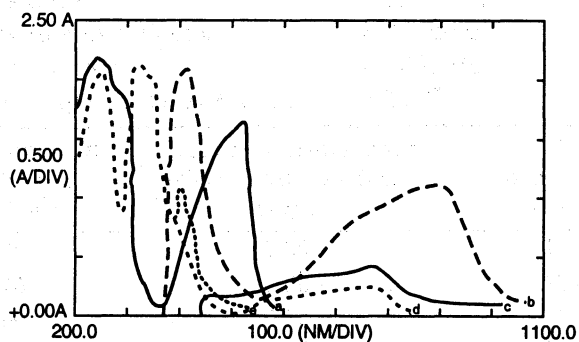
ν (cm^{-1})	$A = \log I_0/I$	$E = 1/C \cdot l \times \log I_0/I$
For band (a)		
17700	0.150	2444.43
18200	0.390	6355.53
18700	0.540	8911.08
19200	0.834	13600.00
19500	1.375	22400.44
20200	1.520	24770.00
20700	1.510	24618.45
21200	1.200	19555.50
21700	1.000	16296.25
22200	1.000	16296.25
22700	0.877	14296.25
23200	0.610	9940.71
23700	0.520	8474.05
For band (b)		
29000	0.056	912.59
29500	0.160	2607.40
30000	0.250	4074.06
30500	0.340	5540.72
31000	0.510	8311.08
32000	0.560	9125.40
33000	0.610	9940.71
34000	1.000	16296.25
35000	1.750	28518.43
36000	1.810	29496.21
37000	1.920	32288.88
38000	2.104	34288.00
39000	2.000	32592.50
40000	2.020	32918.00
41000	2.010	32385.00
42000	1.962	31980.00
42500	1.781	29023.17

TABLE-3
 MOLAR EXTINCTION COEFFICIENT (ϵ) AT DIFFERENT FREQUENCIES (cm^{-1})
 FOR BANDS OF FERROIN IN SOLVENT METHANOL

$$\text{Concentration } 4 \text{ g/L} = \frac{4}{651.84} \text{ g mole/litre} = C$$

$$1\text{-path length} = 1 \text{ cm and } \frac{1}{c} \cdot l = \frac{1 \times 651.84}{4} = 162.96 \text{ g mole}^{-1} \text{ cm}^2$$

ν (cm^{-1})	$A = \log I_0/I$	$\epsilon = 1/C \cdot l \times \log I_0/I$
For band (a)		
17800	0.410	66.81
18300	0.490	79.85
18800	0.530	86.35
19300	0.750	122.22
19600	1.164	189.68
20300	1.121	182.67
20800	1.000	142.96
21300	0.820	133.62
21800	0.750	122.22
22300	0.610	99.40
For band (b)		
28600	0.160	26.07
29100	0.190	30.96
29600	0.320	52.14
30100	0.500	81.48
30600	0.580	94.51
31100	0.630	102.66
31600	0.650	105.92
32100	0.780	127.10
32600	1.000	162.76
33100	1.350	219.99
33600	1.630	265.62
34100	1.900	309.62
34500	2.119	345.21
35000	1.630	215.62
35500	1.000	162.96
36000	0.130	21.18



U.V. SPECTRUM OF FERROIN IN SOLVENTS

(a) WATER (b) METHANOL (c) ACETONE

(d) α -PHOSPHORIC ACID (FRESH)(e) α -PHOSPHORIC ACID (AFTER 48 HOURS)

Fig. 1. UV spectrum of ferroin in solvents, (a) water (b) methanol (c) acetone (d) orthophosphoric acid (fresh) (e) orthophosphoric acid (after 48 h)

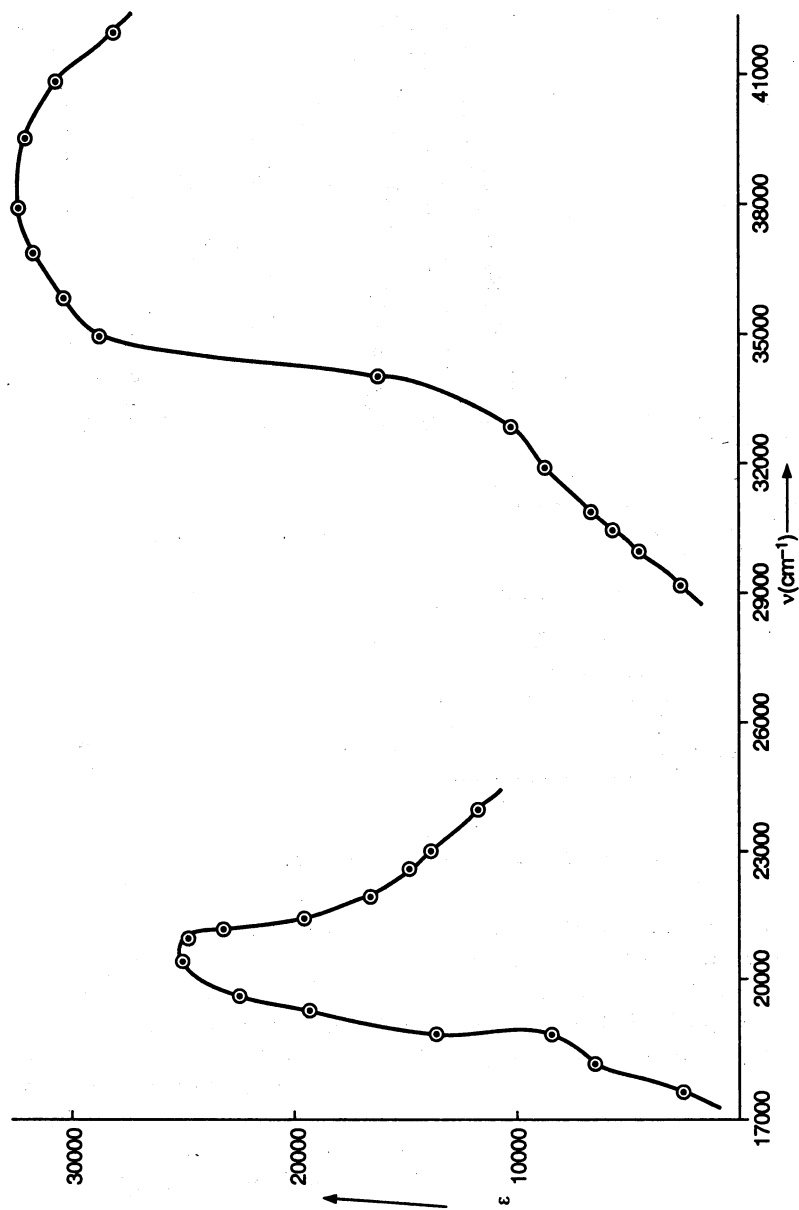
TABLE-4

MOLAR EXTINCTION COEFFICIENT (ϵ) AT DIFFERENT FREQUENCIES (cm^{-1}) FOR BANDS OF FERROIN IN SOLVENT ACETONE

$$\text{Concentration } 4 \text{ g/L} = \frac{4}{651.84} \text{ g mole/litre} = C$$

$$1\text{-path length} = 1 \text{ cm and } \frac{1}{c} \cdot l = \frac{1 \times 651.84}{4} = 162.95 \text{ g mole}^{-1} \text{ cm}^2$$

ν (cm^{-1})	$A = \log I_0/I$	$E = 1/C \cdot l \times \log I_0/I$
17400	0.150	24.44
18000	0.210	34.22
19000	0.350	57.03
19500	0.420	68.44
20000	0.420	68.44
21000	0.380	61.92
22000	0.350	57.03
23000	0.325	52.96
24000	0.300	48.88
25000	0.250	40.74

Fig. 2. (ϵ - ν) Graph for the bands of ferriin in water solvent

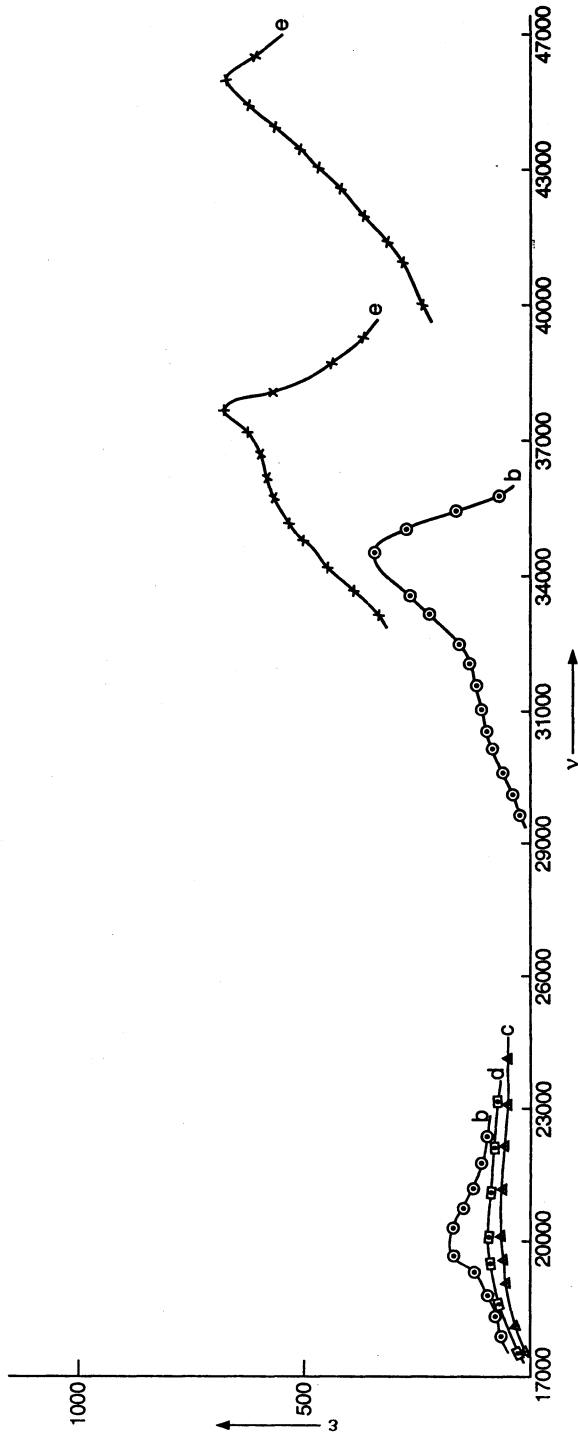


Fig. 3. (ϵ - ν) Graph for the bands of ferriin in solvent (b) methanol (c) acetone (d) *o*-phosphoric acid (fresh solution) and (e) *o*-phosphoric acid (after 48 h)

TABLE-5
MOLAR EXTINCTION COEFFICIENT (ϵ) AT DIFFERENT FREQUENCIES (cm^{-1})
FOR BANDS OF FERROIN IN SOLVENT ORTHOPHOSPHORIC ACID

$$\text{Concentration } 2 \text{ g/L} = \frac{2}{651.85} \text{ g mole/litre} = c$$

$$l\text{-path length} = 1 \text{ cm and } \frac{1}{c} \cdot l = \frac{1 \times 651.85}{2} = 325.92 \text{ g mole}^{-1} \text{ cm}^2$$

[Fresh coloured solution]

ν (cm^{-1})	$A = \log I_0/I$	$E = 1/c \cdot l \times \log I_0/I$
17400	0.043	14.01
18400	0.250	81.46
19400	0.295	96.14
20000	0.281	91.58
20500	0.250	81.48
21000	0.250	81.48
22000	0.240	78.22
23000	0.231	75.28
Solution after 48 h.		
40000	0.750	244.44
41000	0.910	296.58
41500	0.980	319.40
42000	1.138	371.10
42500	1.450	439.99
43000	1.500	488.88
43500	1.592	519.12
44000	1.740	567.76
44500	1.930	629.02
45000	2.059	671.06
45500	1.700	554.06
46000	1.638	531.24
46500	1.490	485.62

The visible band is around 510 nm (511 nm in water, orthophosphoric acid and 509 nm in acetone and methanol). The small shift of 2 nm is in our opinion more due to instrumental error than to any significant solute-solvent interaction. The transition in each case except in acetone is intense. In view of the non-availability of sufficient absorption data of ferroin it is not possible to make any comparison. However, the spectra of ferroin had been reported in solutions containing H_2SO_4 , HCl , HClO_4 , all inorganic acids¹¹. The principal peak of absorption decreases slightly and its λ_{max} shifts from 272 to 275 nm in which

they showed that the spectral modifications are not caused by the H^+ ion. Further studies in organic solvents seem to be lacking. We observe the bands in ultraviolet which seem to suffer displacements due to solute-solvent interaction. The shortest wavelength band which occurs in orthophosphoric acid (224 nm) is shifting to 236 nm in water and 290 nm in methanol. In acetone this band could not appear.

While the UV bands may be assigned to $\pi-\pi^*$ transition in view of the increasing red shift with increasing polarity of the solvents, the long wavelength visible band can be assigned only to the complex. The position and intensity of the bands support the transition to be of charge transfer type from the ligand to the d-orbitals of the ferrous ion. A transition between the d-orbitals themselves would be very weak because of symmetry restriction.

A special feature of the spectrum in orthophosphoric acid is that on being stored for 48 h, the solution loses the colour and the band in the visible region disappears. In its place a new band appears at 305 nm. This can be attributed only to the decomposition of the phenanthroline complex so that the new band is that due to free ligand molecule.

Oscillator strength and intensity of the bands

Table-6 gives the relative values of oscillator strength of the bands of ferroin molecule in different solvents, viz., water, methanol, acetone and orthophosphoric acid. The band in the present molecule of ferroin owes its origin to the longest wavelength transition of phenanthroline itself which is centred around 510 nm. In group theory notation this band in the visible region is referred to as ${}^1A_1 \leftarrow {}^1A_1$ or $V \leftarrow N$ band¹². The intensity of the band is therefore expected to be increased. The $\pi-\pi^*$, the $V \leftarrow N$ transition is very intense, the $\psi_i\psi_f$ product belonging to species A_i makes this transition allowed and geometric rough coincidence of the $\pi-\pi^*$ orbitals leads to very large values of $\psi_i\psi_f$ and hence to the usual high intensity of $V \leftarrow N$ transition.

TABLE-6
ELECTRONIC ABSORPTION SPECTRA OF FERROIN FOR
DIFFERENT BANDS IN DIFFERENT SOLVENTS

Sl. No.	Solvents	ν_{\max} (cm^{-1})	$1/2\epsilon_{\max}$	$I = 1/2\epsilon \times \Delta\nu$ [$\times 10^8$]	$f = O.S.$ [$\times 4.315 \times 10^{-9}$]
1.	Water	20500	3500	0.7175	0.3096
2.	Methanol	40000	11500	2.2000	0.9493
3.	Acetone	20000	1500	0.3000	0.1294
4.	orthophosphoric acid (Fresh solution)	34500 20500	3500 3500	1.2075 0.7175	0.5210 0.3096
5.	orthophosphoric acid (solution after 48 h)	20000	5500	1.1000	0.4746

Further solute-solvent interaction may be expected to affect the symmetry of the bidentate ligand with Fe^{2+} ion in ferrous molecule to some extent depending

on the nature of the molecule. In water the interaction is maximum because of the polarity of the solvent. The presence of H-bonding might be responsible for the higher intensity of the transition in the molecule. In acetone, the molecule does not seem to be affected in terms of symmetry to any significant extent. Therefore no increase in intensity is observed. Orthophosphoric acid seems to interact with the molecule and weak absorption in visible range is observed when the fresh solution is used. This being true the promotion of an electron from this orbital to the π^* orbital would be an x-polarized allowed transition¹³. But when the solution is stored for 48 h, the long wavelength band disappears. Thus, the longest wavelength $\pi-\pi^*$ transition is forbidden explaining the low intensity band which was observed at 305 nm.

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