

C H A P T E R - I I I

Section - 1

The importance of molecular spectroscopy needs no introduction now-a-days. In view of its relation to the fundamental studies as well as empirical studies of vast number of molecules, molecular spectroscopy is of great interest to the physicists and chemists at large.

The molecular spectra is intimately associated with the molecular behaviour which must be interpreted in terms of molecular properties. Thus the spectral aspects are important to organic or inorganic chemists for the identification or structure elucidation, to analytical chemists a convenient and rapid method of analysis of small quantities of the substance, to physical chemists-for various fundamental physico-chemical processes like bond-distance, force constants, energetics of chemical processes, spectral transitions, spectral solvent shifts, hydrogen bonding, charge-transfer process, determination of constants of association and dissociation, informations regarding solvation and intermolecular forces and a host of information¹⁻⁴.

The spectroscopic methods include electronic (ultraviolet and visible) spectroscopy, infra-red, Raman and microwave spectroscopy, nuclear magnetic and electron spin resonance spectroscopy and Mössbauer spectroscopy etc. The choice of instrument, however, depends upon the specific problem, the

structure and properties of the specimen and the nature of information sought.

We are particularly interested in the electronic absorption spectroscopy, and more precisely in the study of spectral solvent shifts of organic polyatomic molecules and their iron(II) complexes.

The shape, position and intensity of absorption bands are greatly modified by the solvents as a result of interaction of the solute with the solvent. Spectral solvent shifts are useful not only for making spectroscopic assignments but also for providing information for solute - solvent interaction³.

These aspects have received much attentions from the works like Kasha⁵, McConnell⁶, Supan and co-workers¹⁰⁻¹¹ and others^{1,12,13}. The works in this field have been well-summarised in different books and reviews.

We, would, therefore give only a brief outline of some of the important features of spectral solvent shifts.

Two different experimental approaches exist for investigations of solvent effects. One is to observe $\bar{\nu}_{\max}$ for a particular solute transition in a variety of solvents and compare the results with theoretical predictions. The other involves measuring $\bar{\nu}_{\max}$ for the band in a range of solvent

mixtures (usually binary) and comparing the shift with some functions of the mixed solvent. The limitations in either approach are the need for the solute to have transition with measurable shift with the change of solvent in an accessible spectral region and not overlapped by other bands. For these reasons mostly organic ions and molecules have been studied as there are very few inorganic ions with $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ or CTTS transitions not observed in many organic solvents.

Spectra of solutes in the solution and in the vapour phase are considerably different arising from the loss or blurring in solution of sharp vibrational bands in the vapour phase spectra. The wavelength and the intensity and shape of the absorption bands change due to unequal perturbation of the ground and excited electronic states of solute-molecules resulting from strong solute-solvent interactions (such as dipole-dipole, ion-dipole or hydrogen-bonding) in the two states. In solutions where dispersion forces are only significant (as in non-polar hydrocarbon solvents) solute spectra retain most of the features of the gas phase spectra.

It is quite natural that the interpretation of the solvent effects is extremely difficult due to small spectral shifts, precise measure of which is difficult. The solvent shifts are usually the resultant of several individual effects which may either cancel out or reinforce¹⁻⁴.

Kasha⁵ and McConnell⁶ have proposed the use of solvent effect as an aid to distinguish between $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions.

Stabilization of preferred resonance structure of solutes by certain solvents, dipole-dipole interaction, hydrogen bonding and the change in dipole moment during the solute-transition are some of the reasons of spectral solvent shifts.

The quantitative approach of the solvent effects on the absorption spectra has been made by Bayliss⁷. Treating the solvent as a continuous dielectric medium, an expression has been developed for its effect on the Franck - Condon absorption of light in terms of the polarization forces of the solvent.

The frequency shift $\Delta\nu$ caused by the solvent

$$\Delta\nu = \text{Const.} \times (f/\nu \cdot a^3) \frac{n^2 - 1}{n^2 + 1}$$

where f = oscillator strengths of the transition

a = radius of the spherical molecule

n = solvent refractive index

ν = frequency of absorption in the gas phase.

Good agreement has been observed in case of $\pi \rightarrow \pi^*$ transitions of benzene and isoprene.

Qualitative interpretation of solvent shifts has been proposed by Bayliss and McRae⁸ by considering

- a) The momentary transition dipole present during the optical absorption process
- b) The difference in permanent dipole moment between ground and excited states of the solute
- c) The Franck - condon principle
- d) The size of the solute and solvent molecules and
- e) London dispersion forces.

All organic electronic spectra in solution are subject to a generalized polarisation red shift which is due to solvent polarization by the transition dipole and which depends on the solvent refractive index. This can be obscured by the effect of dipole-dipole and dipole-polarization forces if the solute is polar when the application of Franck - condon principle shows that the solvent cage around the excited solute molecule is momentarily strained due to orientation strain and packing strain. Orientation strain (the important one) may be expected when solute and solvent are polar and when the solute dipole moment changes during the transition. packing strain is to be expected when the solute molecule is substantially bigger in the excited molecule. The absorption frequencies of polar solutes are shifted to the red in solution if the dipole moment increases during the transition, they may be shifted to

the blue (relative to the gas) if the dipole moment decreases. Four different situations are expected to arise for intramolecular transitions :-

I and II: Red polarization shift dependent on the solvent refractive index (n_s) expected when a non-polar solute is dissolved in non-polar or polar solvents. Slight packing strain may be important in polar solvents.

III : When a polar solute is dissolved in non-polar solvents solvent shift is dependent on dispersion forces and solvent polarization forces. If the solute dipole moment increases during the transition, the Franck - condon excited state is more solvated by dipole - solvent polarisation and a red shift dependent upon solvent n and change in solute dipole moment is expected. If the solute dipole moment decreases during the transition the Franck - condon excited state is less solvated, thus contributing a blue shift, again proportional to the above two factors. In the latter case the resultant shift may be red or blue depending on the relative magnitude of the polarisation red shift and blue shift.

IV : If a polar solute is dissolved in non-polar solvent, the ground state solvation energy results from dipole-dipole and ion-dipole forces, so there is an oriented solvent cage. A red shift is expected depending on the magnitude of the increase in dipole-moment during the transition, the value of the solvent dipole moment and the extent of solute - solvent interactions

(including H-bonding) A blue shift is observed when the dipole moment decreases during the transition.

Similar would be the case for intermolecular transitions.

Mc Rae⁹ has derived an expression for solvent-induced frequency shift from the second-order perturbation theory. The expression is

$$\Delta\nu = \text{dispersion terms} + B \frac{n^2 - 1}{2n^2 + 1} + C \left(\frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2} \right) + \text{stark effect term.}$$

where n is the refractive index, D is the dielectric permittivity of the solvent and B and C involve the molecular volume of the solute-molecule and its dipole-moment in the electronic ground and excited states.

The first term due to dispersion effects accounts for the effect of non-polar solvents on non-polar solutes. The second term represents the contribution from the interaction of the solute permanent dipoles with the solute induced solvent dipoles. The third term represents the interaction between permanent solutes and solvent dipoles.

The equation has been examined for both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition ^{of organic molecules. $n \rightarrow \pi^*$ transition} energies of C = O and C = S groups in different solvents are found to vary linearly with the stretching frequencies in the same solvent indicating the importance of group stabilization by solvent.

Nicol¹⁴ found linear plots of shifts in the absorption maxima of aromatic hydrocarbons using the relation

$$\Delta\nu = A \left(\frac{n^2 - 1}{2n^2 + 1} \right) + B \frac{(D - n^2)(2D + n^2)}{D(n^2 + 2)^2} + C \left(\frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2} \right)$$

Several other equations have also been suggested.

Better correlation of the results are generally observed if the absorption data is coupled with the emission data of the molecules. It is thus apparent that shifts in a variety solvents (usually arise from ion-dipole and dipole-dipole interactions) are linear in some function of dielectric constant $f(D) = \frac{\sqrt{2(D-1)}}{(2D+1)}$ or $(D-1)/(D+1)$ and this is generally the case. But solvents in which additional solute-solvent interaction occurs give results which do not lie on such plots of $\bar{\nu}$ against $f(D)$. Solvent effects on the energy of electronic transitions have been examined in details by Suppan¹⁰. The complexity of spectral-solvent shifts has been ascribed^{to} interactions of different types such as

- i) dispersion forces
- ii) dipole-induced dipole interactions
- iii) dipole-dipole interaction
- iv) multipole interaction
- v) specific interactions (hydrogen - bonding etc.)
- vi) solvent cage strains

Ledger and Suppan¹¹ also utilised the solvent shifts of absorption bands for the determination of electron distributions in excited states.

Analysis of spectral solvent shift in case of ketones show that neither the usual measure of solvent polarity such as dielectric constant and refractive index or spectral effects are satisfactory in correlating the $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transitions. By studying deviations from normal solvent behaviour, some unusual solvent shifts indicating the occurrence of specific solute-solvent interactions which could give information about details of molecular structure such as hydrogen bonding and conformational effects. Suppan¹⁰ observed that in a hydrogen bonding solvent, the amount of deviation from the $\bar{\nu}$ against $f(D)$ plot is different for different absorption bands of the same solute species. The most anomalous bands are those involving transitions of an electron which is specifically hydrogen-bonded in the ground state. The magnitude of the hydrogen bonded anomaly seems to depend both on charge-transfer to or from the bonded site and on the strength of the hydrogen bond.

It may be noted that with carbonyl $n \rightarrow \pi^*$ bands usually, both increase of solvent dielectric constant and increase of solvent hydrogen-bonding produce blue shifts whereas with the $\pi \rightarrow \pi^*$ bands_{of the} derived 2,4-dinitrophenyl-hydrazone's, although hydrogen bonding also produces blue shifts, increase of dielectric constant produces a red shift.

Solvent effect on certain charge-transfer transitions are sufficiently large for them to be used as defining scales of solvent polarity. A scale of solvent 'Z' values¹⁵ has been proposed using solvent shift ($1 \text{ kJ} = 6.832 \times 10^{-4} \bar{\nu}/\text{cm}^{-1}$) of the charge-transfer band of 1-ethyl-4-carbomethoxy-pyridinium iodide. Analysis of solvent shifts requires a knowledge of the transition concerned and how this changes the dipole moments of the absorbing species. In spite of limitations, useful information about both the ground and excited states can be obtained from spectral solvent shift.

Solvent effects upon spectral intensity cannot be interpreted in a simple qualitative fashion. However, some useful informations regarding solute-solvent interactions can be obtained from studies of solvent effects on spectral intensity.

In case of inorganic complexes, metal d - d transitions are comparatively insensitive to the environment of the complex although not completely so. They are, of course sensitive to the changes in symmetry at the metal ion, and changes in ligands, aspects frequently used in determining transition metal-ion solvation and in kinetic and theoretical studies.

A short discussion given above indicates the importance of spectral solvent shift and the complexity of proper interpretation.

In order to throw light on this important aspect of spectral solvent shift, we studied the spectra of 2,2'-bipyridine

and 1,10-phenanthroline in different solvents. The solvent effect of their tris-bipyridine or phenanthroline iron(II) complexes have also been studied.

These are described in subsequent chapters.

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Section - II

Studies on the spectral solvent shifts are not only useful for spectroscopic assignments but also in understanding different factors influencing solute-solvent interactions. These have been well-emphasized by different workers¹⁻³. However, the small spectral solvent shift and the lack of proper knowledge of the different factors associated with solute-solvent interactions often reinforcing or cancelling each other make the study complicated and the clear picture is yet to come.

In order to have some understanding regarding spectral solvent shifts particularly of $\pi \rightarrow \pi^*$ transitions, generally known to exhibit little spectral solvent shift, we studied the spectra of 2,2'-bipyridine⁴, 1,10-phenanthroline⁴ and 5-nitro-1,10-phenanthroline⁴ which we report in the present section. The spectral study also enabled us to examine the anomalous spectral behaviour of 2,2'-bipyridine as reported recently by Henry and Hoffman⁵. A discussion on the existing knowledge on $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions has been made and the spectral solvent shifts of 2,2'-bipyridine, 1,10-phenanthroline and 5-nitro-1,10-phenanthroline are interpreted in the light of the discussions based on solute-solvent interactions and ground and excited state solvations of the solute molecules.

Experimental Section

2,2'-bipyridine, 1,10-phenanthroline (G.R.E. Merck) and 5-

nitro-1,10-phenanthroline (Sigma) were used without further purification. Methanol (G.R.E. Merck) and Isopropanol (A.R. B.D.H.) were distilled and the middle fractions were used. Formamide (G.R.E. Merck), dimethylsulphoxide (Baker Analyzed Reagent) and propylene carbonate (K. Light Puriss) were dried over freshly ignited quicklime for several hours and then distilled under reduced pressure, the middle-fraction of the distillate being retained. N,N'-dimethyl formamide, n-heptane, iso-octane, cyclohexane (Uvasol grade) were used without further purification. Methyl cellosolve was treated with lithiumhydride until the evolution of H_2 ceased and finally distilled. The middle fraction was used. Dioxane (A.R. B.D.H.) was refluxed for 48 hours with NaOH, distilled twice. It was then treated with metallic sodium, kept overnight and distilled. The middle-fraction was collected and utilised within several hours. Absolute ethanol was treated with little excess of freshly ignited quicklime, kept overnight and distilled. It was refluxed with Zn-dust and caustic potash for 48 hours and finally distilled. The middle-fraction was utilised.

$HClO_4$ (G.R.E. Merck) used was estimated in the usual way.

The spectra of the ligands 2,2'-bipyridine and 1,10-phenanthroline in different solvents were measured (figs 1 and 2) and the main features are recorded in Table - 1.

In formamide and in the dipolar aprotic solvents, the peaks

around 230 nm are not available as the cut-off points of these solvents are at higher wavelengths.

The spectra of BH^+ and PhH^+ in different mixed solvents containing 90% by volume of organic solvents were measured in N/10 $HClO_4$. The absorption maxima are recorded in Table - 2 and 3.

In order to have approximate idea regarding the basicity of the solvents, we noted the pH-meter readings of the solutions standardizing the glass-electrode with phthalate buffer in aqueous solutions. Addition of water to these solvents generally lowers the meter-reading considerably. The meter readings of B in N/10 $HClO_4$ are ~ 2 in $dmsO-H_2O$, ~ 0.6 in $MC-H_2O$, ~ 4.2 in $F + H_2O$ and ~ 4.6 in $dmf-H_2O$ mixtures. Though the meter readings in no way measure the hydrogen ion activity in mixed solvents or non-aqueous solvents but definitely give an approximate idea regarding the basicity of the solvents.

The meter readings were taken with a Digital pH-meter (Systronics). The spectra were recorded with a Beckman DU-2 spectrophotometer maintained at $298^\circ K$.

Results and Discussions

(a) Spectra of 2,2'-Bipyridine and 1,10-phenanthroline and the Anomalous Behaviour of 2,2'-Bipyridine

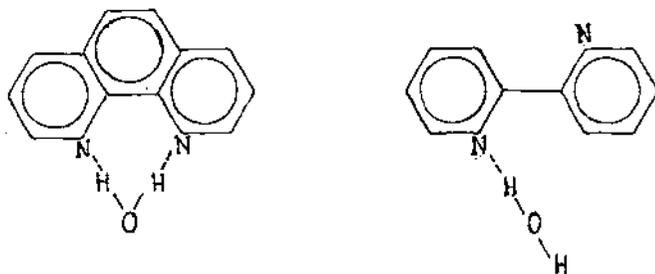
All the ligands have two very intense bands in the U.V.

region. The long wave-length band is ascribed to β' -band and the short wavelength band is assigned as β -band. The assignments of the bands had been made by Gondo⁶, Mason⁷, Bray et.al.⁸ and Lahiri et.al.⁹⁻¹¹.

In addition to 233 and 281 nm bands, Henry and Hoffman⁵ observed an absorption band at 308 nm in neutral aqueous solution of B. They attributed the band at 308 nm to be due to covalent hydrate formation according to the equation



However, they found no evidence of $Ph \cdot H_2O$ though Ph is known to retain water tenaciously. Spectra of Ph and $Ph \cdot H_2O$ were found to be the same. Their suggestion of covalent hydration of aromatic N-Heterocycles should be applicable more in case of Ph due^{to} its fixed coplanarity and better feasibility of hydrate formation than trans B (Fig. 3).



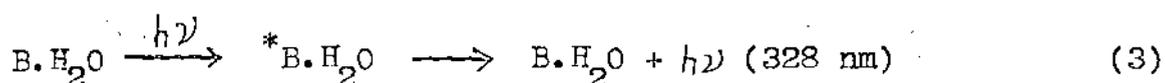
We found no band for B corresponding to α or ρ - band observed in case of Ph. However, no question of obtaining pure B spectra arise in solutions of pH 4.5 ($pK_B = 4.48$)¹² or even at higher pHs as it would be the result of the combined spectra of B and BH^+ , BH^+ having much higher ϵ than B and at 308 nm, ϵ of BH^+ is extremely high compared to that of B. Above pH 7, the spectra of B would be obtained. The reason that the disappearance of the 308 nm band on addition of OH^- is not accompanied by any change in extinction coefficient of the 281 nm band of B within the experimental precision 3% is due to the fact that the isosbestic point of B and BH^+ is in the region 282 ± 1 nm and is not due to the supposed reaction:



In fact, the authors have adduced no evidence for $B.H_2O$ or $B.OH^-$. It is natural that 308 nm band would be absent in non-aqueous solvents but the addition of H_2O changes the acid-base character of the solvents and the possibility of BH^+ formation increases with addition of H_2O due to changed pK in the altered conditions.

We are not in a position to run the emission spectra. The emission spectra of B ($\lambda_{max}^{ab} = 281$ nm) is undetected whereas BH^+ has a λ_{max}^{em} at 335 nm ($\lambda_{max}^{ab} = 301$ nm). The observed strong 328 nm emission seen from pH 4-10 in aqueous solutions have been ascribed to originate from the hypothetical covalent hydrate

* $B.H_2O$ according to the scheme



However, it is to be noted that the acid-base behaviour in the excited state is appreciably different^{13,14} from the ground state (pK^* of B = 9.5). Thus in the pH-range (4-10), B should exist as ${}^*\text{BH}^+$ or a mixture of ${}^*\text{B}$ and ${}^*\text{BH}^+$ but not as ${}^*\text{B.H}_2\text{O}$.

The reason that both the 328 nm emission and the 308 nm absorption intensities appear to have the same pH-dependence is due to the gradual conversion of BH^+ to B. It is to be borne in mind that the acid-base character of different non-aqueous and mixed-solvents are appreciably different from water. DMF is highly basic and addition of water makes it comparatively acidic. The pK -values of the ligands are changed appreciably in non-aqueous and mixed solvents due to change in electrostatic and non-electrostatic characters of the solvents. The pK^* value in the excited state also increase appreciably^{13,14}. Much of the derived conclusions arise due to ignoring these simple facts. Moreover, in presence of high concentrations of H_2SO_4 or other acids solvent structures and the acid-base properties are changed enormously so that the derived conclusions are hardly justifiable.

For Ph $\lambda_{\text{max}}^{\text{em}}$ is reported to be at 360 nm ($\lambda_{\text{max}}^{\text{ab}} = 264$ nm, Stokes' shift = 10101 cm^{-1}) and $\lambda_{\text{PhH}}^{\text{em}}$ is at 410 nm ($\lambda_{\text{max}}^{\text{ab}} = 272$ nm, Stokes' shift = 12374.5 cm^{-1}). The abnormally large Stokes' shift (Stokes' shift = 12071.5 cm^{-1}). The abnormally large Stokes' shift

of PhH^+ compared to that of BH^+ (Stokes' shift = 3371.9 cm^{-1}) requires explanation and further study.

(b) Discussion on $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions

Before describing the spectral-solvent shift, it will be pertinent to discuss some salient aspects of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ shifts.

Kasha¹⁵ and McConnel¹⁶ have used the solvent shift as criterion for distinguishing $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. A large blue shift on going from a non-polar (hydrocarbon) to a polar (hydroxylic) solvent is indicative of $n \rightarrow \pi^*$ transitions (not vice-versa) whereas no or small red shift suggests $\pi \rightarrow \pi^*$ transitions.

The blue shifts of $n \rightarrow \pi^*$ transitions observed in case of acetone, formaldehyde etc. are attributed to hydrogen-bonding capability, the greater the hydrogen-bonding capability, the greater the blue shift. This is amply demonstrated by different workers¹⁷⁻²³. The increasing hydrogen-bonding capability can be attributed to increasing acidity of solvents and can be correlated to ρ -values²⁴ of solvent polarities. Any compound with hydrogen-bonding capability generally show this type of behaviour - the greater the hydrogen-bonding capacity of solute or solvent, the greater is the blue shift.

The classification is naturally due to the fact that $n \rightarrow \pi^*$ transitions usually involve less energy than $\pi \rightarrow \pi^*$ transitions and due to the presence of lone pair of electrons having high dipole moments, they are more susceptible to marked solute-solvent interactions and hydrogen-bonding (the capability of hydrogen-bonding is lost or reduced when one of the electrons is transferred to the π^* level) making spectral solvent shift possible. Slight solvent shift in case of $\pi \rightarrow \pi^*$ transitions involves a large change in energy and would be possible if $\pi \rightarrow \pi^*$ transitions are in the long wavelength region and energy changes due to solute-solvent interactions are high.

The interpretation of the spectral solvent shift requires the knowledge of the ground state energies (as well as excited state energies) of solutes in different solvents as the 'solvation energies' of a 'neutral molecule' in different solvents would be different.

The calculation of solvation energies²⁵ involves the following steps.

The energy changes i) to create a cavity of appropriate size in the bulk solvent ii) in the reorganisation of the solvent molecules around the cavity into various layers. iii) Solute-solvent interactions of different magnitude (e.g. dispersion forces, dipole-dipole interactions, dipole-induced dipole interactions and specific short range interaction like H-bonding, charge-transfer and inter-molecular energy transfer). iv) The energy changes due to change in the standard states from gas to

solution which, however, vanishes for comparison.

The third step, obviously, is most important.

The absorption measurements involve excitation of electrons with ground state solvent cage to Frank Condon excited states, therefore proper interpretation of spectral shift should involve the knowledge of ground state energies.

$$\Delta\nu = \nu(\text{soln}) - \nu(\text{gas})$$

In absence of $\nu(\text{gas})$ data, we can consider $\nu(\text{heptane or hydro-carbon})$ roughly equal to $\nu(\text{gas})$, so that $\Delta\nu_{ab}$ can be a measure of solute-solvent interactions (exothermic in case of blue shift and endothermic increase of red shift) or an approximate measure of the difference in ground state solvation energies of solute assuming the energies of the F.C excited states are the same in all the solvents. Similarly, $\Delta\nu_{em}$ is expected to give a rough estimate of the difference in the excited state solvation energies of the solute^{14,26}.

Thus, the large blue-shifts observed in case of $n \rightarrow \pi^*$ transition of ketones or azo compounds in going from hexane to ethanol have been ascribed by Haberfield^{27,28} to increased ground state solvation (which is greatest in case of H-bonding solvents) accompanied by diminished excited state solvation in going from the non-polar to the polar solvents.

But greater ground state solvation by hydrogen bonding solvent or greater Frank-Condon strain in case of the hydrogen bond donor solvent is not always responsible for blue shift as is apparent from the observed blue shifts of nitro aromatics like 1-nitronaphthalene²⁹ etc, on transfer from dimethyl-formamide to methanol (where nitrogroup weakens the hydrogen bond formation but enhances dipole-dipole interaction). Haberfield et.al.²⁹ calculated the enthalpies of transfer of the F.C. excited states and relaxed excited states (from dmf to MeOH) by combining calorimetric and spectroscopic data as given below

$$\begin{aligned} \delta \Delta H \text{ F.C Excited State} &= \delta \Delta E \text{ Gr.State} + \delta \Delta E \text{ ab} \\ \text{dmf-MeOH} &\text{dmf-MeOH} \text{dmf-MeOH} \\ \text{or } \delta \Delta E \text{ relaxed Excited State} &= \delta \Delta E \text{ Gr.State} + \frac{1}{2} \delta \Delta E \text{ ab} \\ \text{dmf-MeOH} &\text{dmf-MeOH} \text{dmf-MeOH} \\ &+ \frac{1}{2} \delta \Delta E \text{ F} \quad 14, 26, 30 \\ &\text{dmf-MeOH} \end{aligned}$$

The enthalpies of transfer from F.C excited state (or relaxed excited state) of these compounds are uniformly endothermic into the hydrogen bonding solvent and larger than the ground state transfer enthalpies resulting in the blue shifts.

Thus, the blue shift is not always indicative of $n \rightarrow \pi^*$ transitions nor it always implies greater hydrogen-bonding capability. If the hydrogen bonding capability of solutes are weakened by the nitro, chloro-groups etc. red-shift may also be observed.

(c) Spectral Character and Spectral Solvent Shifts of 2,2'-Bipyridine, 1,10-Phenanthroline and 5-Nitro-1,10-Phenanthroline

All the transitions are $\pi \rightarrow \pi^*$ transitions rather than $n \rightarrow \pi^*$ transitions. From the measurement of absorption spectra, Badger and Walker and others found no evidence for $n \rightarrow \pi^*$ transitions based on the absence of solvent shift with variation of solvent polarity³¹⁻³³. We observed no shift in MeOH + H₂O, EtOH + H₂O and dioxane-water systems⁹. However, Harriman and co-workers^{34,35} observed spectral solvent shift (emission) ascribed to $n \rightarrow \pi^*$ transitions. This has been repudiated by Henry and Hoffman⁵ who found no solvent shift for B and Ph. It is apparent that all solutes are to some extent modified by solvents. Spectral solvent shift is thus always probable be it $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transitions. The transitions, however, are $\pi \rightarrow \pi^*$ transitions due to reasons cited below.

Unlike $n \rightarrow \pi^*$ transitions, 1) these bands are located at relatively short-wavelength regions characterized by high intensities, 2) transitions are insensitive to heteroatom substitution, 3) in acid solutions the bands show large red shifts due to protonation contrary to large blue shifts or disappearance of the bands in case of $n \rightarrow \pi^*$ transitions, 4) The long-wavelength transition of Ph and 5-n-Ph show almost no shift or slight red shift in going from non-polar to polar solvents.

In spite of similar linkages, the spectral behaviour of

three ligands are quite different and can be attributed to

i) fixed coplanarity and resonance stabilization of Ph compared to B.

ii) capability of free-rotation of 2,2'-bipyridine and preferred trans configuration of the molecular form (in neutral solutions, organic solvents or in the solid state) and slightly twisted cis configuration in the ionic form. The geometry of the molecule may be changed in the excited state and twisting of the molecule may take place.

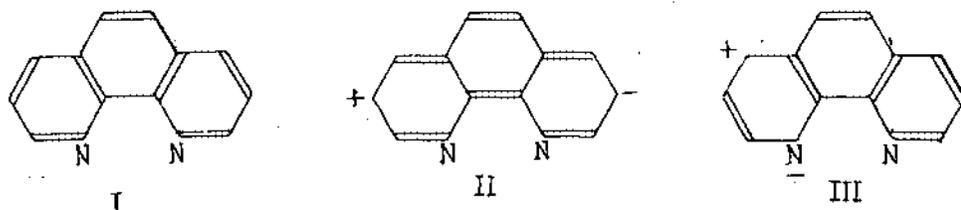
iii) The trans form of B has a dipole moment 0.91 D where cis- B has $\mu = 3.80$ D and Ph has $\mu = 4.11$ D^{36,37}.

Thus, due to greater dipole-dipole interactions, hydrogen-bonding and resonance stabilization, Ph is in the lower energy level in the ground state compared to B (even in the gaseous state), requiring much more energy for spectral solvent shift. 5-n-Ph will be in the higher energy level as the resonance stabilization is disturbed and the capability of hydrogen bond formation is weakened. This is well reflected in the spectra. Though nothing specific can be said regarding solute-solvent interactions but small shift indicates little solute-solvent interaction.

In spite of slight anomalies, both β' - and β - bands of B and

β -band of Ph show slight blue shifts in going from non-polar (having high intensities) to polar solvents (having low intensities), an indication generally ascribed to hydrogen-bonding in case of $n \rightarrow \pi^*$ transitions, though hydrogen-bonding solvents are also known to cause marked blue shifts of $\pi \rightarrow \pi^*$ transitions of chromophores^{3,38}. The reasoning that the band due to $n \rightarrow \pi^*$ transition is submerged in the main absorption band of high intensities does not solve the problem as we are unable to differentiate these bands (if any) in different solvents. The blue shifts could also arise from the differences of the ground state and excited state solvation energies arising from dispersion forces, dipole-dipole, dipole-polarization forces, orientation strain etc. If dipole moments of the solutes decrease during transition, the polarization red-shift is overshadowed by other forces resulting in blue shift whereas red shift would occur if dipole moment increases.

It is to be noted that the pK^* -values of B, Ph and 5-n-Ph are greater than pK values. The results suggest that the electron-densities on the nitrogen atom and dipole moments of the molecules increase in the excited states and may be due to the canonical structures like II, III, V, VI etc.



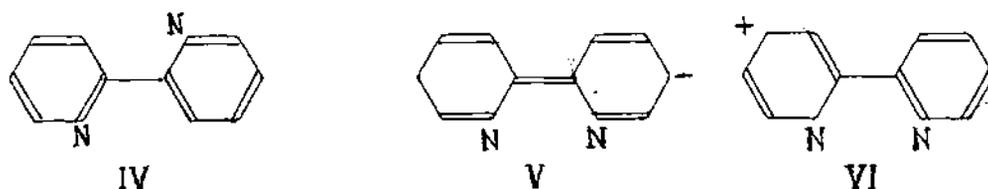


Fig. 4

similar to those suggested by Jackson and Porter³⁹ in case of acridine, naphthylamine etc. Electron densities and bond-orders in the ground and excited states calculated by Coulson and Jacobs⁴⁰ predict a migration of charge towards nitrogen of pyridine on excitation. This behaviour is expected in case of B and Ph also. Excited state dipole-moments can be calculated from absorption and fluorescence maxima of the compounds. Though no emission spectral data are available for B, but data exists for Ph in aqueous solution. Approximate calculation from large Stokes' shift show a considerable increase in dipole moment, the radius of the cavity for Ph has been calculated to be 3.70 \AA^0 . A red shift is thus expected in case of non-polar solvents but a resultant blue shift is expected in case of hydrogen-bonding solvents due to greater ground state solvation and orientation strain which is actually observed. In case of dipolar aprotic solvents, the polarization shift and the dipole-dipole interaction would be high in the excited state, a red shift is observed as expected. No useful correlation with the solvent refractive index, however, can be made. Due to increased electron-density and dipole moment in the excited states, the hydrogen-bonding and dipole-dipole interaction would be expected to increase in the excited states also. The small blue shift, or no shift,

however, suggests similarity of solvation in the ground and excited states²⁹.

The introduction of nitro group increases the dipole moment of 5-n-Ph which means an increase in solute-dipole interactions but weakening of the hydrogen-bonding making a resultant red shift in going from isoctane to water. The dipole-dipole interaction between 5-n-Ph and dipolar aprotic solvent increases considerably making considerable red-shift. Interaction energy between the nitro group and the dipolar aprotic solvent is greater than that between the nitro group and the polar protic solvent.

It is well-known that the spectral solvent shift can in no way be correlated with dielectric constant and solvent polarity. Though the solvent effects on U.V. transitions are poorly correlated by dielectric constant or functions of dielectric constant, transition energy has been found to be a linear functions² of $f(D) \int f(D) = \frac{2(D-1)}{D+1}$ where D is the dielectric constant of the medium⁷ within limitations. Deviations from linearity indicates 'specific associations'² which is usually stronger than dielectric stabilization. Hydrogen bonding is considered as the most important form of 'Specific association' and it is band specific. In the $\nu_{cm^{-1}}$ vs $f(D)$ plots, both B and Ph show hydrogen-bonding differing from each absorption band β' and β which is shown in fig. 5.

However, greater anomalies are also observed in solvents having lone pair of electrons (H_2O , dioxane, dmf, dmsO etc.) even if there is no question of hydrogen-bonding.

The deviations in case of dioxane has been ascribed to the presence of two non-adjacent dipolar groups whose moments cancel so that the effective reaction field is probably greater than indicated by the macroscopic property³⁹.

Due to strong electron repelling CH_3 -group, inductive effects of N and S atoms are increased enormously leading to a strong interaction of solute and solvent or complex formation between solvent and solute d-orbital of sulphur of dmsO may be involved in cases of dmsO which possesses polarized π -bonding.

The spectra of BH^+ show some interesting feature. The spectra of BH^+ in mixed solvents [90% by volume of organic solvents like MeOH, Pr^iOH , Dioxan, MC and dmsO] show red shift but blue shift is observed in case of mixed F and dmf (90% v/v) solvents.

In case of BH^+ , cis form predominates and dipole moments in the excited state are likely to be increased due to resonance stabilization⁴⁰ and a red shift is expected which is actually observed.

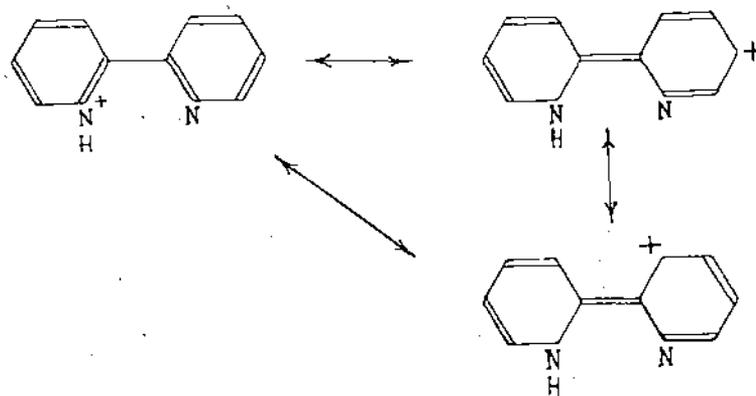


Fig. 6

But the blue shift as observed in $F + H_2O$ and $dmf + H_2O$ mixtures is due to the basicity of these solvents where both B and BH^+ coexist.

From the study it is apparent that for solute molecules with hydrogen-bonding ability, the spectral shift is dependent on the type of solvents and its degree of order. For non-polar solvents solute-solvent interaction is low, spectral solvent shift will be very small. Order in the solvent molecules are determined by (1) Hydrogen-bonding (2) dipole-dipole interactions (3) molecular shape⁴¹.

Order in hydrogen bonding solvents is due to hydrogen-bond formation. In this case, stabilization of solute molecule takes place predominantly due to hydrogen-bond formation which is generally small in the excited state, blue-shift is thus expected be it $n - \pi^*$

or $\pi \rightarrow \pi^*$ transition. If the hydrogen-bonding capability of solute or solvent is decreased, red shift may also be observed. In case of polar or dipolar aprotic solvents, order of the solvents is due to dipole-dipole forces, here the solvent shift would depend mainly on the dipole-dipole, dipole-induced dipole-interactions, blue shift may be expected if the dipole moment decreases in the excited state or red shift is expected if the dipole moment increases.

Conclusions

(a) The absorption band at 308 nm and the emission band at 328 nm arises from the combined effect of B and BH^+ and is not due to covalent hydrate $\text{B}\cdot\text{H}_2\text{O}$ or $\text{B}\cdot\text{H}_2\text{O}^*$. The fluorescence spectra observed are very much susceptible to the nature of the solution medium and not much reliance can be made on the emission spectra reported.

(b) The blue shift is not always indicative of $n \rightarrow \pi^*$ transitions nor it always implies greater hydrogen-bonding capability. For solutes with hydrogen-bonding capability, blue shift will be observed in going from non-polar to polar solvents be it $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transitions. The ground state solvation and excited state solvation is of prime importance in determining the spectral shift.

(c) The absorption bands observed in case of B, Ph and 5-n-Ph are due to $\pi \rightarrow \pi^*$ transitions. Slight blue shift is observed in

case of B and Ph in going from polar to non-polar solvents and also from dipolar aprotic to polar protic solvents. Due to the presence of nitro group, hydrogen-bonding is weakened in 5-n-Ph resulting in no or slight red shift in going from non-polar to polar solvents. Slight spectral solvent shift indicates similarity of solvation in the ground and excited states.

Table - 1

Absorption maxima $\bar{\nu}_{\max}$ 298 K cm^{-1} of 2,2'-bipyridine, 1,10-phenanthroline
5-nitro-1,10-phenanthroline

Solvents	$\bar{\nu}_{\max}$ in cm^{-1} of		$\bar{\nu}_{\max}$ in cm^{-1} of		$\bar{\nu}_{\max}$ in cm^{-1} of	
	2,2' - bipyridine		1, 10 - phenanthroline		5-nitro-1,10-phenanthroline	
n-heptane	42,370	35,460	43,290	38,020	43,290	37,740
Iso-octane	-	-	43,290	38,170	43,290	37,740
Cyclohexane	42,370	35,460	43,290	37,880	-	-
Isopropanol	42,370	35,340	43,480	38,020	43,290	37,590
Ethanol	-	-	43,670	37,880	-	-
Methanol	42,550	35,590	43,860	38,020	43,480	37,740
Water	42,920	35,710	44,050	37,880	43,230	37,450
Formamide	-	35,340	-	-	-	37,040
Dimethylformamide	-	35,460	-	-	-	36,900
Dimethylsulphoxide	-	35,090	-	37,740	-	37,450
Propylene carbonate	-	35,340	-	38,020	-	-
Methyl cellosolve	42,370	35,340	43,290	37,880	-	-
Dioxan	42,190	35,340	43,100	37,880	-	-

Table - 2

Absorption maxima $\bar{\nu}_{\max}^{298K}$ in cm^{-1} of 2,2'-
bipyridinium ion in different solvents

Solvent (90% v/v organic solvent)	$\bar{\nu}_{\max}$ in cm^{-1} of 2,2'-bipyridinium	
Water	41,490	33,220
MeOH - H ₂ O	41,490	33,110
Pr OH - H ₂ O	41,580	33,060
Dioxane - H ₂ O	41,150	33,000
F - H ₂ O	-	34,360
dmf-H ₂ O	-	34,900
dmsO-H ₂ O	-	32,790
MC - H ₂ O	41,240	32,890
PC - H ₂ O	40,820	33,330

Table - 3

Absorption maxima $\bar{\nu}_{\max}^{298K}$ in cm^{-1} of PhH^+ ion in different solvents

Solvent (90% v/v organic solvent)	$\bar{\nu}_{\max}$	in cm^{-1} of PhH^+
Water	45,450	36,760
F - H_2O	-	36,630
dmf - H_2O	-	36,630
dmsO - H_2O	-	36,860
PC - H_2O	45,450	36,900

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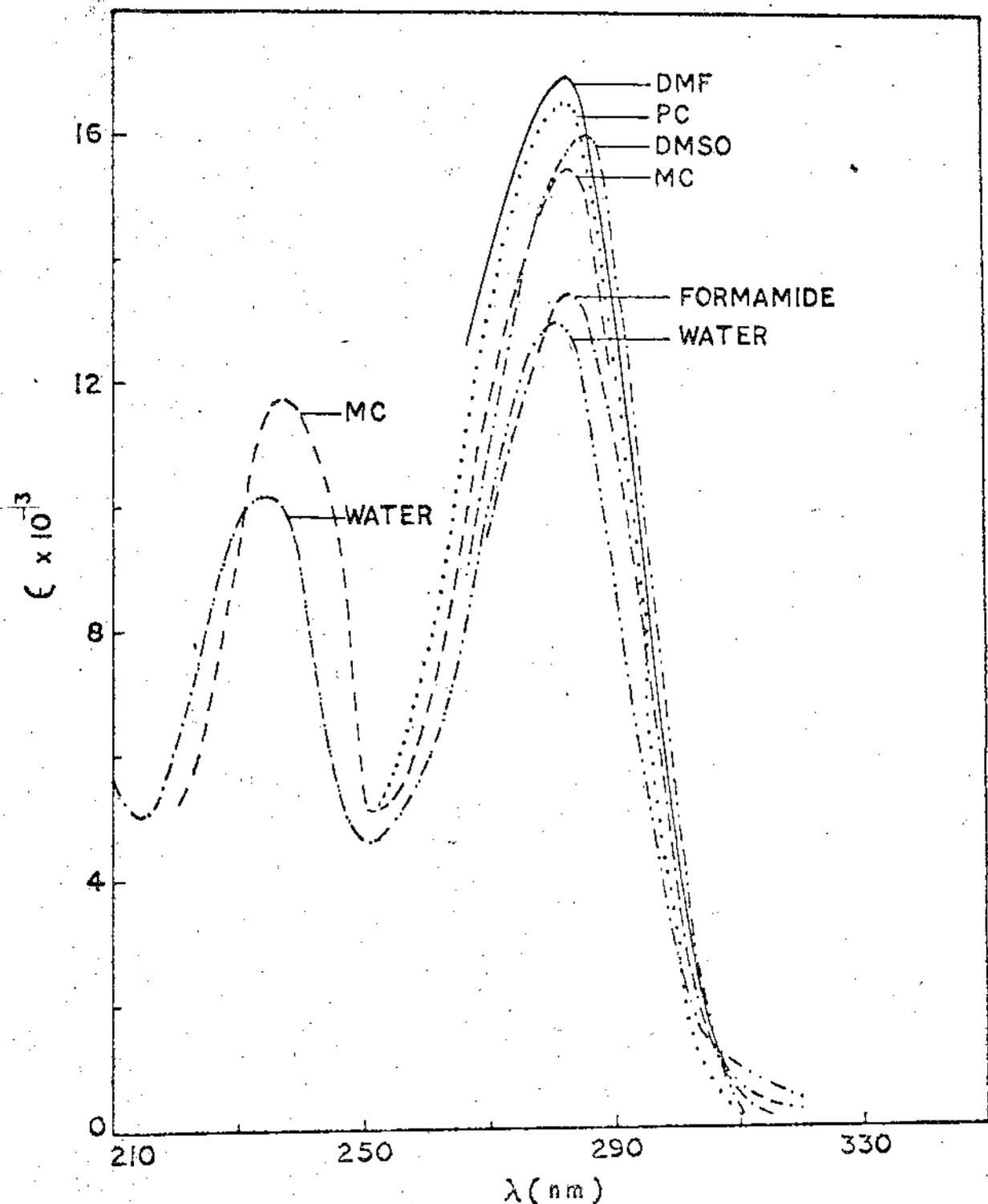


FIG. 1 THE SPECTRA OF 2,2'-BIPYRIDINE IN VARIOUS SOLVENTS.

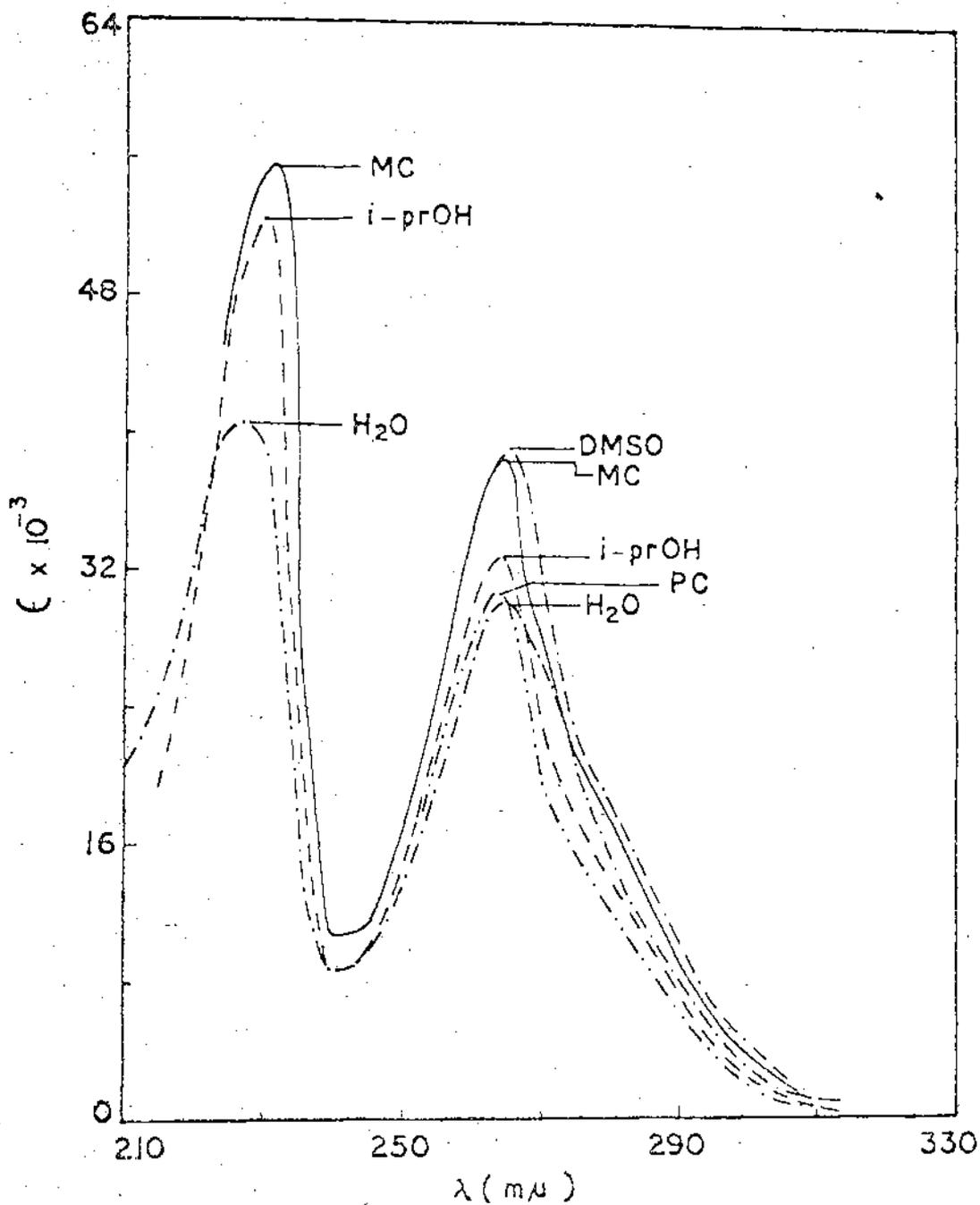
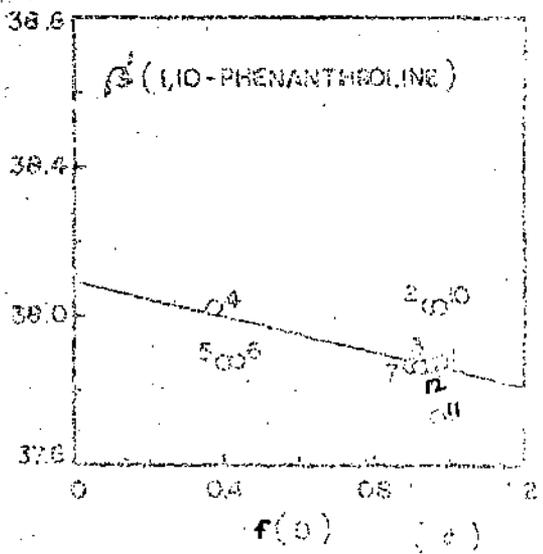
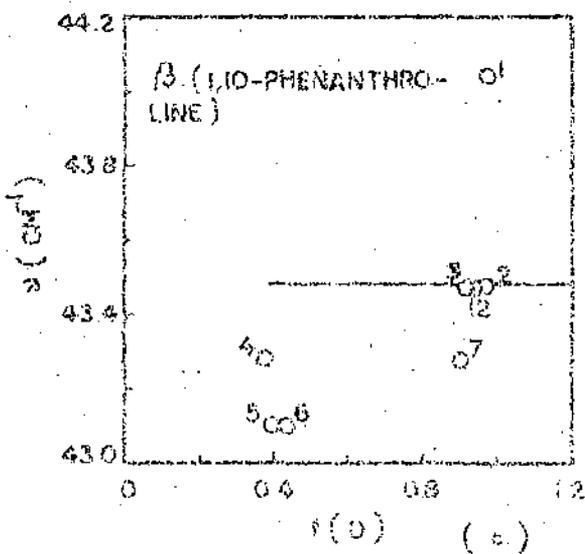
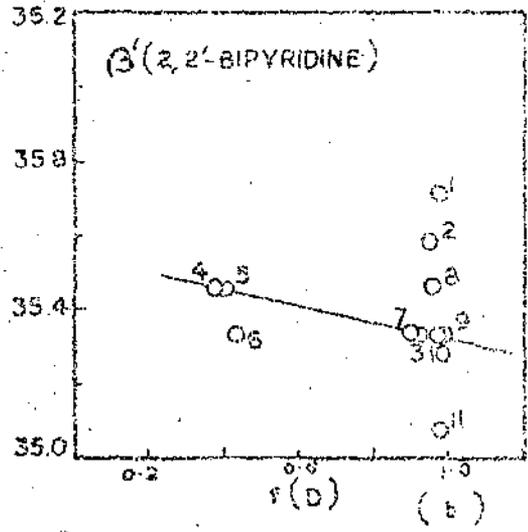
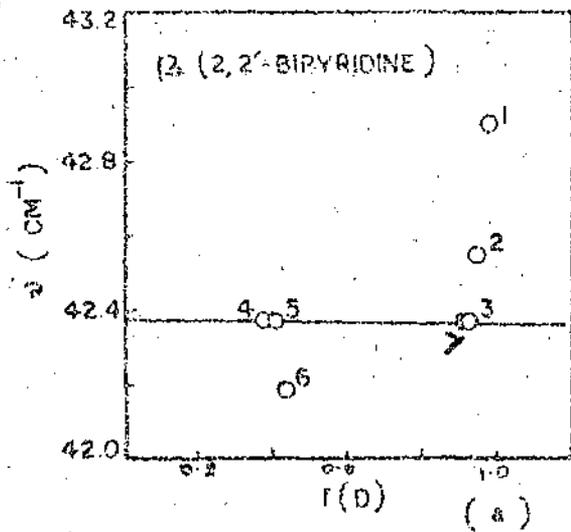


FIG. 2. THE SPECTRA OF 1,10-PHENANTHROLINE IN VARIOUS SOLVENTS.



1. WATER 2. METHANOL 3. ISOPROPANOL 4. n-HEPTANE
 5. CYCLOHEXANE 6. DIOXAN 7. METHYLCYCLOHEXANE 8. DIMETHYLFORMAMIDE
 9. FORMAMIDE 10. DIMETHYLACETAMIDE 11. DIMETHYL SULFOXIDE
 12. ETHANOL

FIG. 5. PLOT OF $n(D)$ VS $f(D)$.

Section - III

The dependence of charge-transfer maxima (ν_{\max}) on solvent has been investigated for a variety of diimine (LL) complexes $M(CO)_4(LL)$ and $Fe(LL)_2(CN)_2$ ($M = Cr, Mo$ or W , $LL = bipy, phen$ & substituted derivatives). In all these cases, the maximum absorption frequencies of the charge-transfer bands vary considerably with the nature of the solvent. Burgess, Chambers and Haines¹ recently summarised these results and examined the solvatochromic behaviour of intramolecular charge-transfer spectra of inorganic diimine complexes.

Though the intense red charge-transfer complexes of tris 2,2'-bipyridine and 1,10-phenanthroline with ferrous ion (ferrodiin and ferroin) are well known for their analytical applications, but the solvent effects on the spectra of ferroin and ferrodiin are very little studied though the spectral aspects have been extensively studied^{2,3}. Lahiri and co-workers²⁻⁷ have studied the spectra of ferroin and ferrodiin. The spectra of the complexes have been resolved into five distinct bands. For $Fe(bipy)_3^{2+}$ maximum absorption frequencies and extinction coefficients vary extremely little with solvent nature. However, it is premature to conclude that the solvent has no effect on the spectra of tris-complexes like ferrodiin and ferroin without further study. The extinction-coefficients of ferrodiin and ferroin have been found to vary with solvent compositions (within $\pm 3\%$) for variations of solvent compositions in case of methanol + H_2O , ethanol + water,

isopropanol + H₂O and t-butanol + H₂O). It is, therefore, reasonable to believe slight solvent dependence of the oscillator strengths of ferrodin and ferroin.

In order to throw more light on the solvatochromic behaviour of ferrodin and ferroin, we have run the absorption spectra of the complexes in solvents of different nature like $\text{dmso} + \text{H}_2\text{O}$, Formamide + H₂O and $\text{dmf} + \text{H}_2\text{O}$.

Experimental

Formamide, dmso and dmf were purified in the same way as described in section II.

The spectra of the ligands and their tris-Iron(II) complexes have been taken with the help of a Beckman DU2 spectrophotometer maintained at 298 K.

The complexes were prepared by the addition of excess of 2,2'-bipyridine or 1,10-phenanthroline (usually tenfold or more) to Mohr salt (dissolved in dilute HClO₄ acids). Complete complexation was ensured from the constancy in optical density readings.

Analysis of the absorption Curves

The resolution of the spectra into a number of Gaussian

curves is difficult. Fortunately the complex in the visible region have well-defined charge-transfer peaks and the spectra could well be resolved into a number of Gaussian curves indicating that a number of transitions are involved.

Attempts to fit equations to the absorption curves have been made by a number of workers⁸⁻¹⁰.

In the present case, the Gauss curves were very well fitted in the form

$$\epsilon = \epsilon_{\text{max.e}} - \left(\frac{\nu_0 - \nu}{\Theta} \right)^2 \quad \dots (1)$$

[Kuhn and Braun equation⁸]

where

ϵ = molar extinction coefficient at frequency ν , ϵ_{max} = maximum molar extinction coefficient at frequency ν_0 corresponding to the head of the band, Θ is defined in terms of ν' (range of frequencies corresponding to the half-width of the band) by the equation.

$$\nu' = 1.6651\Theta \quad \dots (2)$$

(Θ is equal to the difference of ν_0 and ν for which

$$\epsilon = \epsilon_{\text{max/e}})$$

The resolution was accomplished by fitting the most intense

peak to a Gaussian form first and then subtracting the Gaussian form from the experimental curve. The process was then continued on the resultant curve. A representative curve is given in figure 4.

The curves were also found to be well-fitted in the equation

$$\epsilon = \alpha \nu_0 e^{-\beta (\nu_0 - \nu)^2} \dots (3)$$

[Bielecki and Henri⁹]

where $\alpha = \frac{\epsilon_{\max}}{\nu_0}$ and $\beta =$ constant embodying the half-width of the band.

The values of β for the bands are given in tables 2 and 3. It is to be noted that the values of β are of the same order of magnitude for corresponding bands of analogous compounds. The values of β increases as we proceed towards the shortwavelength regions similar to the observations by Mead¹⁰ in connection with the study of oxalate and ethylenediamine complexes of Cr and Co using simplified form of Lowry and Hudson¹¹ equation.

Lowry and Hudson¹¹ made extensive studies on the absorption spectra of a series of bornyl and methyl xanthates. The absorption curves were resolved into two well-separated bands. They tried the above equations but none of the calculated absorption curves represents the experimental data satisfactorily.

They proposed the equation

$$\epsilon = \epsilon_{\text{max.e}} - \int \frac{\nu_0}{\nu} \left(\frac{\nu_0 - \nu}{\theta} \right)^2 \dots (4)$$

where $\nu' = K\theta$

The values of K was adjusted to give closest possible agreements between observed and calculated values. Lowry and Hudson's expression, however, does not satisfactorily represent the absorption bands given in figures 1 - 4 and this equation was not used as the number of bands are quite large in numbers.

The area under each curve

$$A = \int \epsilon(\omega) d\omega$$

is obtained from the total area of the each extinction curve and also from the relations

$$A = \epsilon_{\text{max}/K\theta} = \epsilon_{\text{max}} (1.0645) h$$

where h = half-width is equal to $2\Delta\omega$ for which

$$\epsilon = \epsilon_{\text{max}/2}$$

The oscillator strengths can be obtained from the relationship

$$f = 432 \times 10^{-9} \int \epsilon(\omega) d\omega$$

The dipole strengths can also be obtained from the relationship

$$D = 3.98 \times 10^{-20} \frac{1}{\epsilon} \int \epsilon(\omega) d\omega$$

The spectra of ferrodiin and ferroin in different mixed aqueous

solvents are resolved (Fig 1 - 4). The spectra of the ligands were also resolved in the same way but it is a bit approximate.

Results and Discussions

The spectral solvent shifts of 2,2'-bipyridine and 1,10-phenanthroline has been reported by us. In view of the high absorption of the solvents in the u.v region, the full spectra of the ligands could not be measured. Only the spectra of the long wavelength bands were taken where possible. The results as given in table 1 show considerable decrease in the oscillator strengths in the organic solvents compared to those in water, though the absorption maxima are very little affected.

The number of absorption bands of ferrodin and ferroin have been found to be the same in water and in mixed organic solvents.

It has been found that the oscillator strengths increases (though not appreciably) as one go from aqueous to dipolar aprotic solvents (*dmso* and *dmf*) and polar solvent like formamide. The absorption maxima are slightly, affected. The oscillator strengths of $\text{Fe}(\text{bipy})_3^{2+}$ though almost the same in water and methanol + water solvents but decreases in case of isopropanol + water mixtures but increases in *dmso* and *dmf*.

The results indicated that there is slight solvent dependence of charge-transfer band (ν_{max}) of $\text{Fe}(\text{LL})_3^{2+}$

(iron-diimine complex) but not so pronounced as in $\text{Fe}(\text{LL})_2(\text{CN})_2$. Further, the behaviour of polar hydrogen bonding solvent is different from the behaviour in dipolar aprotic solvents.

Table - 1

<u>Solvent</u>	<u>2,2'-bipyridine (280 nm bands)</u>		<u>1,10-phenanthroline (264 nm band)</u>	
	Area ($\text{cm}^{-1} \times 10^{-6}$)	Oscillator strength(f)	Area ($\text{cm}^{-1} \times 10^{-6}$)	Oscillator strength(f)
Water	102.69	0.454	234.58	1.014
Dimethyl formamide	53.76	0.232	-	-
Dimethyl sulforide	44.30	0.191	152.23	0.658
Formamide	44.43	0.192	-	-

Table - 2

Complex	Area of the resolved bands (cm ⁻¹) X units X 10 ⁻⁶	Absorption maximum of the bands in cm ⁻¹	Extinction coefficient X 10 ⁻³	Half-band width(cm ⁻¹)	(β)	Oscillator strength	Total Oscillator Strength
1. Fe bipy ₃ ²⁺	1. 17.94	19075	8.43	2000	6.07 X 10 ⁻⁷	0.0775	0.2030
	2. 8.78	20725	5.50	1500	1.25 X 10 ⁻⁶	0.0379	
	3. 3.39	22000	3.35	950	3.28 X 10 ⁻⁶	0.0146	
	4. 4.16	23275	2.30	1700	8.55 X 10 ⁻⁷	0.0180	
	5. 12.74	26000	3.80	3150	2.63 X 10 ⁻⁷	0.0550	
2. Fe bipy ₃ ²⁺ in 90% v/v Formamide - H ₂ O	1. 18.94	19150	8.9	2000	6.39 X 10 ⁻⁷	0.0818	0.2187
	2. 8.34	20800	5.6	1400	1.34 X 10 ⁻⁶	0.0360	
	3. 4.45	22100	3.35	1250	1.70 X 10 ⁻⁶	0.0192	
	4. 3.78	23250	2.45	1450	1.26 X 10 ⁻⁶	0.0163	
	5. 15.15	26300	4.25	3350	2.16 X 10 ⁻⁷	0.0653	
3. Fe bipy ₃ ²⁺ in 90% v/v dmsO - H ₂ O	1. 20.66	19150	8.825	2200	5.24 X 10 ⁻⁷	0.0892	0.2220
	2. 6.91	20750	5.0	1300	1.57 X 10 ⁻⁶	0.0298	
	3. 4.63	22000	3.0	1450	1.26 X 10 ⁻⁶	0.0200	
	4. 3.79	23250	2.3	1600	1.03 X 10 ⁻⁶	0.0169	
	5. 15.32	26300	4.0	3100	2.63 X 10 ⁻⁷	0.0661	
4. Fe bipy ₃ ²⁺ in 60% v/v dmf - H ₂ O	1. 20.45	19200	9.15	2100	5.77 X 10 ⁻⁷	0.0883	0.2281
	2. 8.49	20800	5.7	1400	1.34 X 10 ⁻⁶	0.0366	
	3. 4.28	22150	3.35	1150	1.85 X 10 ⁻⁶	0.0184	
	4. 3.83	23250	2.4	1500	1.17 X 10 ⁻⁶	0.0165	
	5. 15.83	26300	4.25	3500	2.04 X 10 ⁻⁷	0.0683	

Table - 3

Complex	Area of the resolved bands (cm ⁻¹) X units X 10 ⁻⁶	Absorption maximum of the bands in cm ⁻¹	Extinction co-efficient X 10 ⁻³	Half-band width in cm ⁻¹	(3)	Oscillator Strength	Total Oscillator strength
1. Fe Ph ₃ ²⁺	1. 35.93	19620	11.34	2160	6.43 X 10 ⁻⁷	0.112	0.262
	2. 14.22	21480	8.20	1680	9.68 X 10 ⁻⁷	0.061	
	3. 11.51	23100	7.40	1500	1.09 X 10 ⁻⁶	0.050	
	4. 6.70	24540	4.85	1320	1.56 X 10 ⁻⁶	0.029	
	5. 2.42	25680	2.55	960	3.36 X 10 ⁻⁶	0.010	
2. Fe Ph ₃ ²⁺ in 90% v/v Formamide-H ₂ O	1. 27.48	19600	11.225	2300	4.78 X 10 ⁻⁷	0.1187	0.272
	2. 18.44	21750	7.75	2250	5.06 X 10 ⁻⁷	0.0796	
	3. 10.39	23650	6.3	1550	1.10 X 10 ⁻⁶	0.0448	
	4. 4.59	25000	3.6	1200	1.85 X 10 ⁻⁶	0.0198	
	5. 2.26	26000	2.2	900	3.34 X 10 ⁻⁶	0.095	
3. Fe Ph ₃ ²⁺ in 90% v/v dmsc-H ₂ O	1. 29.73	19600	11.4	2450	4.20 X 10 ⁻⁷	0.1284	0.276
	2. 16.36	21750	7.5	2050	6.14 X 10 ⁻⁷	0.0706	
	3. 11.06	23600	6.3	1650	9.65 X 10 ⁻⁷	0.0477	
	4. 5.43	25150	3.4	1500	1.18 X 10 ⁻⁶	0.0234	
	5. 1.75	26500	1.5	1100	2.22 X 10 ⁻⁶	0.0075	
4. Fe Ph ₃ ²⁺ in 60% v/v dmf = H ₂ O	1. 28.033	19600	11.7	2250	5.01 X 10 ⁻⁷	0.1210	0.286
	2. 17.032	21600	8.0	2000	6.45 X 10 ⁻⁷	0.0735	
	3. 12.66	23400	7.0	1700	9.10 X 10 ⁻⁷	0.0547	
	4. 6.26	24900	4.2	1400	1.36 X 10 ⁻⁶	0.0270	
	5. 2.44	26150	2.0	1150	2.03 X 10 ⁻⁶	0.0105	

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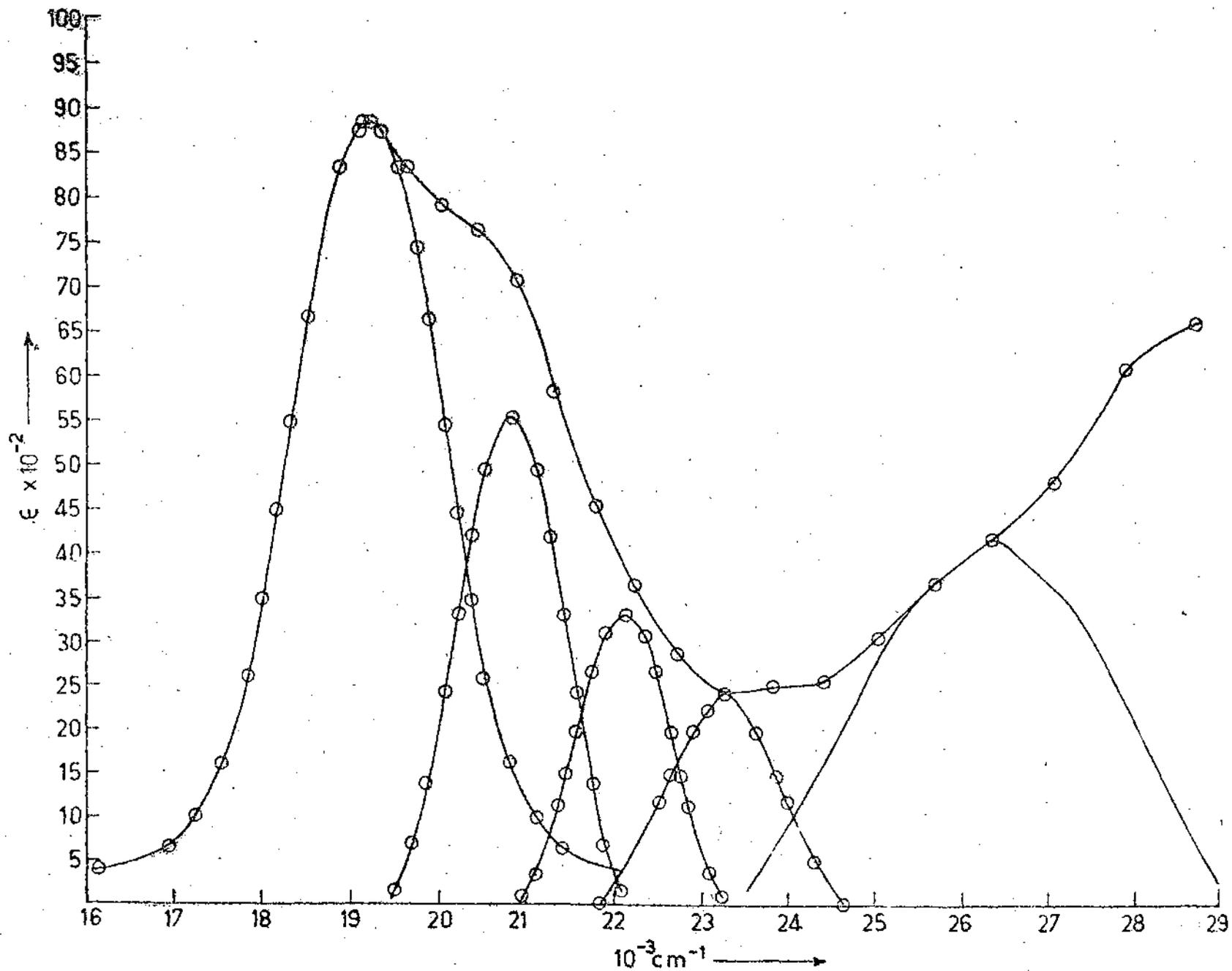


Fig. Absorption spectra of ferrodin in 90% v/v formamide-H₂O

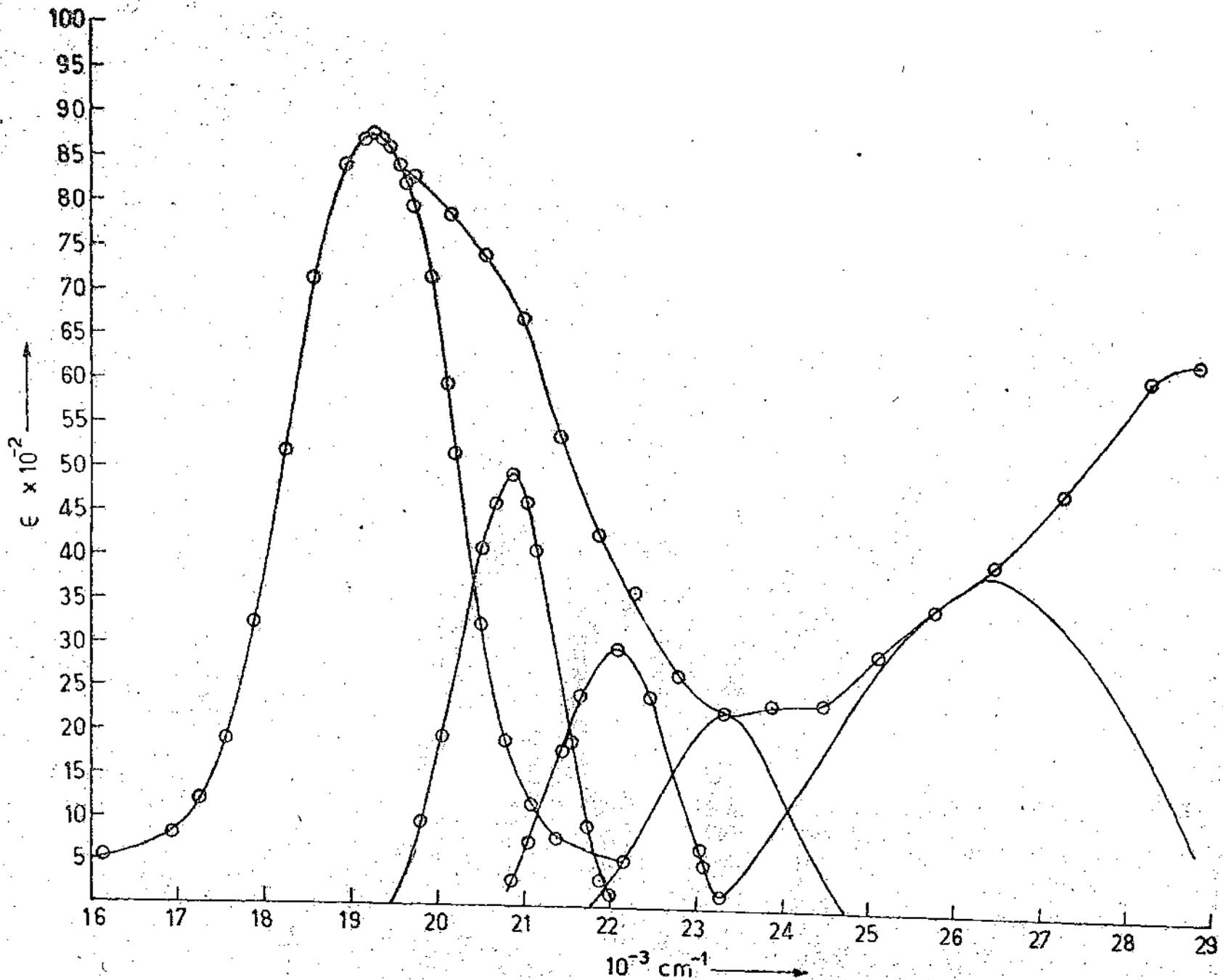


Fig. Absorption spectra of ferrodiin in 90% v/v dmsO-H₂O

Fig. 2

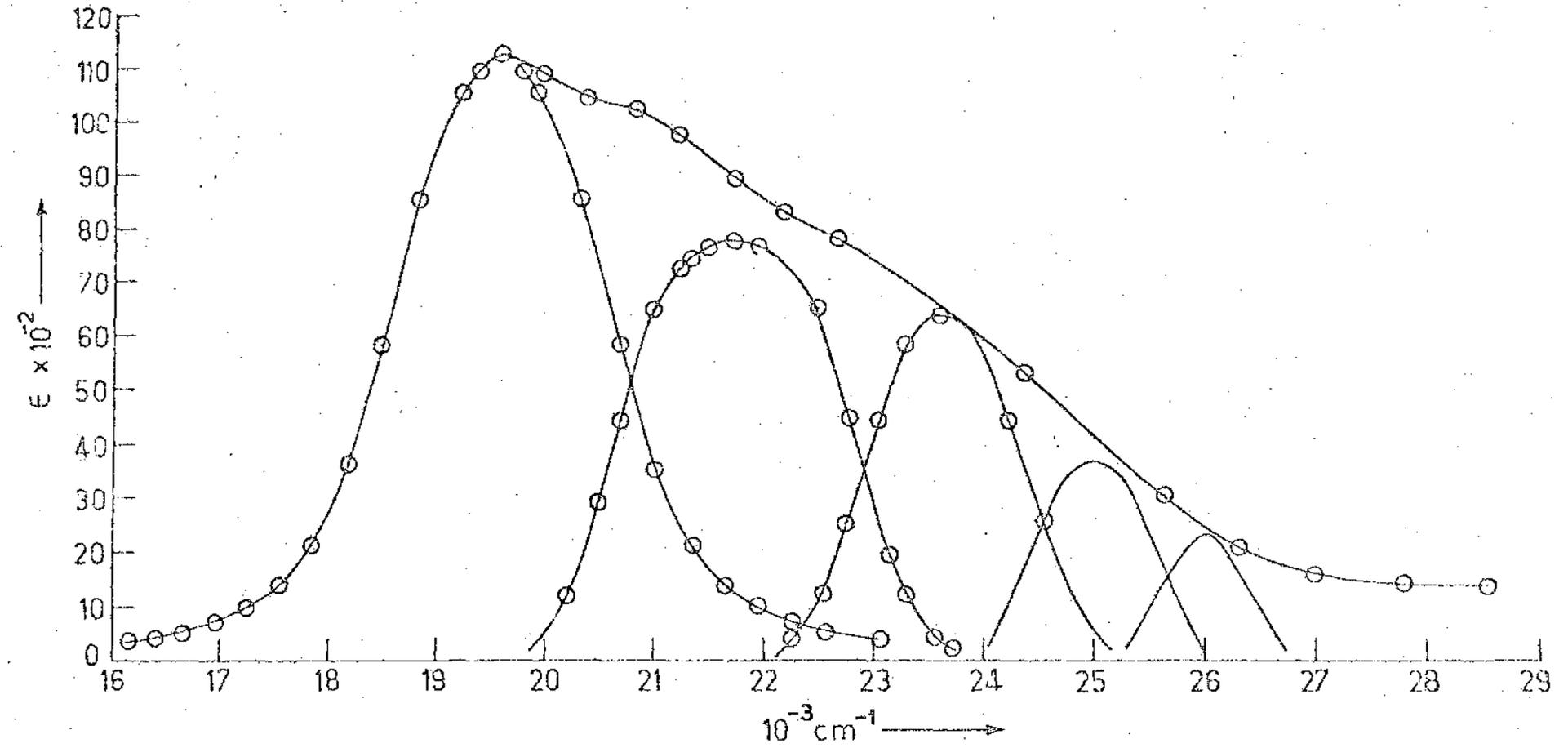


Fig. Absorption spectra of ferriin in 90% v/v formamide-H₂O.

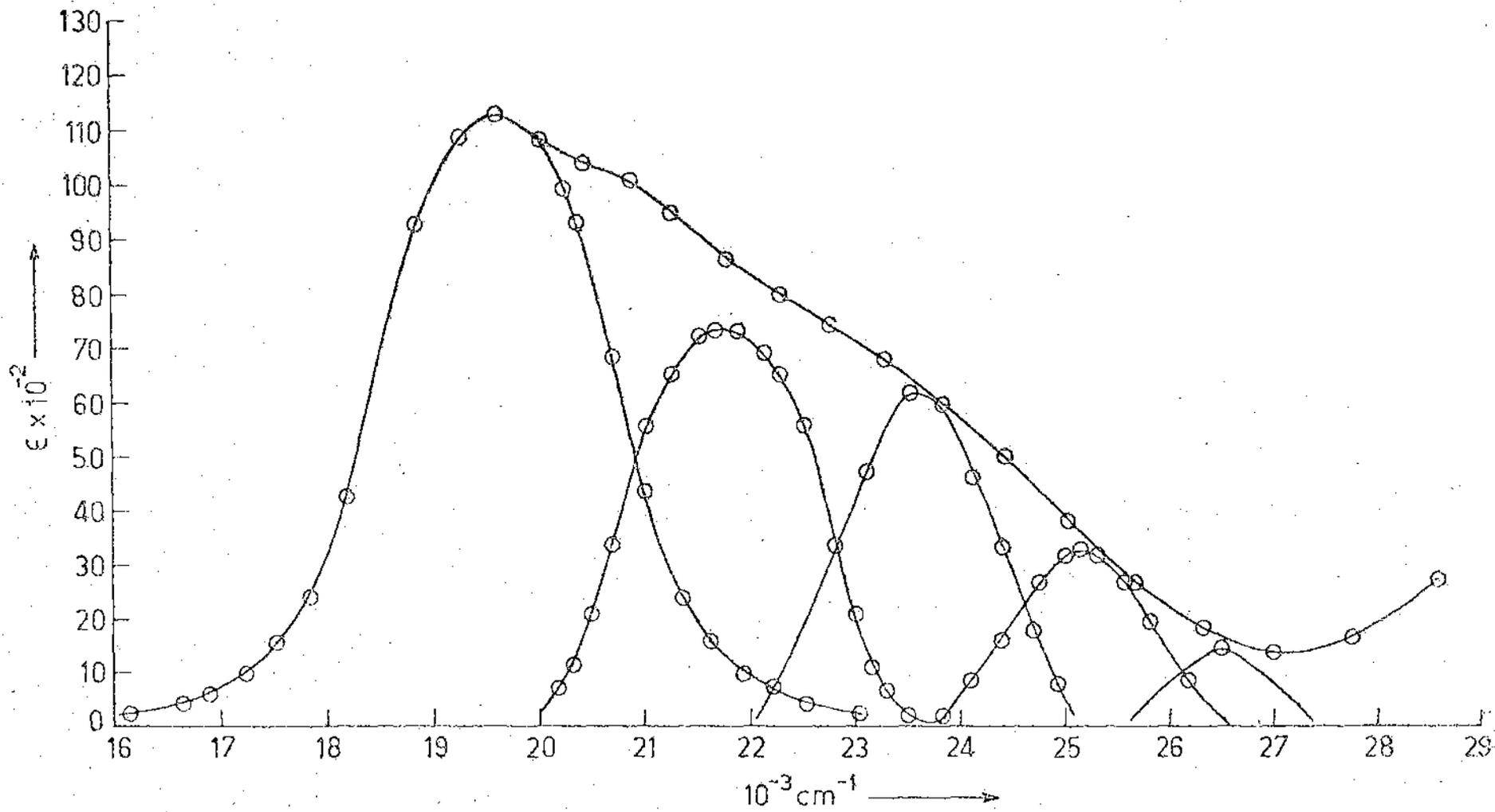


Fig. Absorption spectra of ferroiin in 90% v/v dmsO-H₂O.