

**STUDIES ON THE DISSOCIATION CONSTANTS, SPECTRAL
ASPECTS AND REACTION KINETICS OF AROMATIC
NITROGEN—HETEROCYCLES AND THEIR
COMPLEXES IN SOLUTION**

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C O N T E N T S

	Page
PREFACE	- i - viii
CHAPTER - I	- 1 - 128
Section - I : Introduction	
Section - II: Studies on the dissociation constants of 2,2'-bipyridine & 1,10-phenanthroline in dimethylsulphoxide + water mixtures and free-energies of transfer of hydrogen ions.	
Section-III : Studies on the dissociation constants of 2,2'-bipyridine and 1,10-phenanthroline in dimethylformamide + water and formamide + water mixtures.	
Section -IV : Studies on the dissociation constants of tris-(2,2'-bipyridine)-Fe(II) Complex in dimethyl sulphoxide + water and Formamide + water mixtures.	
CHAPTER - II	- 1 - 65
Section - I : Introduction	
Section - II: Studies on the kinetics of formation and dissociation of ferrodiin in dimethylformamide + water mixtures.	
Section-III : Studies on the kinetics of formation and dissociation of ferroin in dimethylformamide + water mixtures.	
CHAPTER - III	- 1 - 51
Section - I : Introduction	
Section - II: Absorption spectra of 2,2'-bipyridine, 1,10-phenanthroline and 5-nitro-1,10-phenanthroline in different solvents.	
Section-III : Solvatochromic behaviour of ferrodiin and ferroin.	
Some concluding remarks	- i - vii

PREFACE

Scope and Object of the work :-

The importance and uses of the chemistry of electrolytes in non-aqueous and mixed solvents were well-recognized. The applications and implications of the studies of reaction in non-aqueous and mixed solvents have been summarized by Meck¹, Franks^{2,3}, Popovych⁴, Bates^{5,6}, Parker^{7,8}, Criss and Salomon⁹ and others^{10,11}. The ion-ion and ion-solvent interactions have been subject of wide interest as apparent from recent Faraday Transactions of the Chemical Society¹².

Studies on properties of aqueous solutions have provided sufficient information on the dissociation constants and thermodynamics of the ligands and their complexes, the effects of variation of ionic structure, ion-mobility and common ions on the properties of aqueous solutions and to predict fairly accurately the types of species present in solution when a solute is dissolved in water. However, comparatively little work has been done to obtain the same type of information about the nature of non-aqueous solutions.

Recently, the atomic energy projects have helped to stimulate the interest in co-ordination chemistry in non-aqueous and mixed-solvents, since often the key to a successful purification or separation of the heavy metal ions involves complex formation and solvent extraction. Thus, information concerning the nature of the ionic species present in non-aqueous and mixed solvents is required for any fundamental understanding of the

chemistry of these systems. The careful measurements which are necessary to understand how solute-solvent interactions vary with widely different dielectric constants and solvating abilities have become frequent only during the past few years¹.

The study of physico-chemical processes in non-aqueous and mixed solvents is useful from the point of view of phase studies involving binary, ternary and quaternary solvent systems which find application in various analytical techniques e.g., chromatography and extraction^{2,3}.

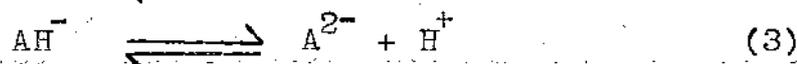
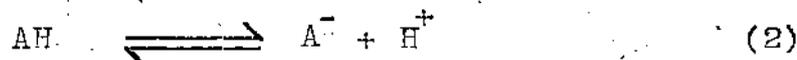
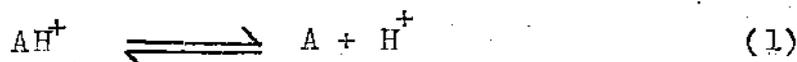
The mixed solvents are increasingly used in the elucidation of reaction mechanisms. Formerly, it was used to widen considerably the range of reactions². The most important but elusive aspect of the solution chemistry is the determination of 'single ion' thermodynamics or more particularly 'medium effect' of ions (particularly of hydrogen ions) in mixed and non-aqueous solvents. This would form basis of explaining quantitatively the influence of the solvent and the extent of interactions of ions in solvents and thus the way for the real understanding of the different phenomena associated with solution chemistry.

Since single ion-values can not be obtained thermodynamically, various theoretical and semi-empirical extra-thermodynamic attempts have been made. The use of extra-thermodynamic assumptions to estimate ion-solvent interactions is important both from theoretical and practical point of view. Estimates of free-energies of transfer for ions have enabled us to refine our models of

ion-solvent interactions. Additionally, armed with acceptable values of free-energies of transfer Chemists can choose solvents that will enhance the rates of many chemical reactions, the solubility of minerals in leaching operations or reverse, the direction of equilibrium reactions and give new methods of processing metals such as Copper⁷.

We are, however, interested in the study of the effects of the various solvents on the dissociation constants of weak acids and bases and their complexes. Compared to most organic solvents, the dielectric constant of water is comparatively large. One of the principal effects produced by adding a miscible organic solvent to water is the reduction of dielectric constant and the change in coulombic interactions between ions.

For the reactions,



it is possible to predict qualitatively the effect of addition of an organic solvent which lowers the dielectric constant.

The addition of the organic solvent means a change in the 'medium effect' due to change in acid-base character of the organic solvent. This undoubtedly changes the non-electrostatic contributions. It is, however, difficult to say qualitatively and quantitatively to what extent it affects the dissociation constants of the ligands. Measurements of the dissociation

constants in various mixed solvents give us an idea regarding the non-electrostatic contributions in various solvents. Bates and Robinson¹³ have shown an uniformity in the non-electrostatic contributions in the case of different methanol-water mixtures from the study of the dissociation constants of the various ligands.

Studies on the dissociation constants of ligands in different solvent may throw some light on the ion-solvent interactions as well as solvent basicity. Till recently only very qualitative idea regarding the non-electrostatic parts have been obtained in solvents like dimethyl sulphoxide (dmsO), N,N'-dimethyl formamide(dmf) and formamide. Quantitative values are still lacking.

The kinetic studies provide the most powerful methods of investigating detailed reaction mechanisms. Though absolute informations are rarely obtained but the postulations of reaction mechanisms is of the great help in understanding and systematizing the study of an area of chemistry. The effect of solvents on the reaction kinetics is extensive and varied.

The importance of spectral studies are enormous. The studies are not only helpful for assignments of spectral transitions and the nature of $n - \pi^*$, $\pi - \pi^*$ transitions etc they also provide us an approximate idea of solute solvent interactions.

It is apparent that the solution chemistry embraces a wide range of topics but we concentrated only on some of the aspects with the limited resources at our disposal. These are described in the subsequent chapters.

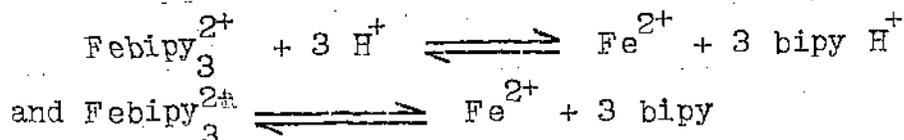
Summary of the work done :-

The dissertation consists of three chapters which are subdivided into several sections.

The section I of chapter I contains a fairly comprehensive and up-to-date review of the works done in the field of non-aqueous¹ and mixed solvents. The importance of the determination of the single ion thermodynamics have been stressed.

In the subsequent sections of chapter I, we have described our studies on the dissociation constants for the reactions

$AH^+ \rightleftharpoons A + H^+$ (where A = 2,2'-bipyridine or 1,10-phenanthroline) in different aquo-organic solvents like dmsO + H₂O, dmf + H₂O and formamide + water mixtures. The results have been discussed in terms of solvent - basicity and ion-solvent interactions. The free-energy of transfer of H⁺ ions $[\Delta G_{t(H^+)}^{\circ}]$ in different mixed solvents have been determined. The equilibrium constants for the reactions



in dmsO + H₂O and formamide + water have also been determined.

The chapter II of the present dissertation consists of a brief discussion on the different aspects of kinetics and reaction mechanisms of the inorganic reactions and the results of our investigations on the formation and dissociation reactions of ferrodin and ferroin in different dmf + water mixtures (0 - 100% dmf).

The last chapter begins with a brief introduction of spectral behaviour of compounds in different solvents particularly emphasizing spectral solvent shifts.

Studies on the spectral aspects of the (1,10-phenanthroline and 2,2'-bipyridine) particularly the spectral solvent shifts and solvatomachromic behaviour of ferrodin and ferroin have been incorporated in sections II and III of chapter III. The results indicate that both solute and solvent are responsible for spectral solvent shifts and for solutes with hydrogen-bonding capability, blue shift is observed in going from non-polar to polar solvents be it n — π^* or π — π^* transitions.

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CHAPTER - I

Section I

In recent years there has been increasing interest in the study of the behaviour of electrolytes in mixed solvents. The effect of solvent structure and solute-solvent interactions on equilibrium constants and rate constants of chemical reactions in mixed solvents is not well-understood. Addition of organic solvent in water brings about a radical change in the properties of the medium. Theories¹ of the structure of water, an extensively used and studied solvent, are inadequate and this is further complicated by the addition of organic components. It is now agreed that the thermodynamics of solute-solvent interactions will help in throwing more light on the nature of ionic solutes. Attempts are being made to identify the factors determining specific solvation of ions. Inadequate models for the structure of solvents and an incomplete understanding of the forces in the immediate vicinity of the surface of the ions make the theoretical treatment^{2,3} of the problem of solvation difficult.

Acid-base equilibria are particularly suited for such studies. The effect of solute-solvent interactions on chemical equilibria have been investigated both by alteration of the solvent composition and by variation of solute-structure and charge type.

The determination of dissociation constants of the ligands

in different mixed solvents and non-aqueous solvents provides an important step in this direction. Such studies in mixed solvents may throw light on the structure of the liquid molecules, the effect of the dielectric constant and the acid-base properties of the organic solvents on the dissociation constants of the ligands and ion-solvent, solvent-solvent interactions etc.

The addition of an organic solvent to water makes the situation much more engrossing and anomalous than water. The mixed solvents show a wide range of dielectric constants. Extensive studies on the physical properties of different solvent systems have been made. A lamentable gap still exists. Several classifications of organic solvent systems based on their dielectric constant, organic group type, acid-base properties or association through hydrogen-bonding⁴, have been proposed as a result the properties of different mixed solvent systems would show a wide divergence of properties which would naturally be reflected on the thermodynamic properties of ligands and their complexes. The determination of the thermodynamic properties of the ligands and their complexes in different solvent systems are very limited, though a considerable amount of work has been done in methanol-water, ethanol-water mixtures. This inspired us to undertake the studies of acid-base equilibria in mixed solvents. The classical researches of Harned and co-workers⁵⁻¹⁰, Bates, Robinsons and co-workers¹¹⁻²³, Ligny and co-workers²⁴⁻³³, Shedlovsky³⁴, Grunwold³⁵⁻³⁷, Feakins and others³⁸⁻⁴⁸, Lahiri and others⁴⁹⁻⁷², Strehlow⁷³, Das, Kundu and co-workers⁷⁴⁻⁸⁵, and others⁸⁶⁻¹²⁷ led to further investigations in this direction.

A brief survey of the investigations in mixed solvent systems, and the problems associated with such studies is presented to highlight the importance of such studies.

Dissociation constants of ligands in mixed solvents :-

Stability constants of chelate compounds and the dissociation constants of chelating agents have often been measured in mixed solvents because of the insolubility of one or more of the reactants in water. However, since these constants vary with the solvent compositions, the comparison and correlation of these constants are very difficult owing to the wide range of experimental conditions. In addition, the thermodynamic quantities for these reactions calculated from these data are limited to specific solvent systems. Consequently, studies have been made to determine the effect of the solvent on the dissociation constants.

The quantitative approach correlating the dissociation constants of a series of acid with that for a reference acid and the dielectric constant was made by Wynne - Jones.¹²⁸ If we consider the equilibrium constant K of the reaction between two acid - base systems, viz.,



we find

$$K = \frac{a_{A^-} \times a_{HA_o}}{a_{A_o^-} \times a_{HA}} = \frac{K_a}{K_o} \quad \dots \quad (2)$$

(K_a and K_o are the dissociation constants of the acids HA and the corresponding reference acid HA_o in the same solvent.)

The standard free energy change of the process is given by

$$\Delta G^\circ = -RT \ln K = \Delta G_{el}^\circ + \Delta G_{non-el}^\circ \quad \dots (3)$$

$$\text{or, } -\log K = \frac{\Delta G_{non-el}}{2.303 RT} + \frac{a}{\epsilon} \quad \dots (4)$$

$$\text{where } a = \frac{Ne^2}{2 \times 2.303 RT} \left(\frac{1}{r_{A^-}} - \frac{1}{r_{A_o^-}} \right)$$

(according to Born¹²⁹ equation).

∟ assuming the effective radii of the ions to remain approximately constant in a series of solvents 7.

The plots of $-\log K$ against $\frac{1}{\epsilon}$ should thus be a straight line which have been found to be true in several cases when ϵ is > 30 . The intercept for $\frac{1}{\epsilon} = 0$, i.e., for infinite dielectric constant, should give a measure of the dissociation constant free from electrostatic effects. The slope of the line, however, varies with the nature of the acid, so that an acid which is stronger than another in one solvent may be weaker in a second solvent¹³⁰⁻¹³³. The comparison of the dissociation constants of a series of acids in a given solvent may consequently be misleading, since a different order of strengths would be contained in another solvent. It has suggested, therefore, that

when comparing the dissociation constants of acids, the values employed should be extrapolated to infinite dielectric constant; in this way the electrostatic effect, at least, of the solvent should be eliminated.

However, Elliot and Kilpatrick¹³⁴ and Harned¹³⁵ find that the relationship ($-\log K$ vs $\frac{1}{\epsilon}$) fails in dioxane-water.

Other theoretical approaches using the dielectric constant as a parameter in describing any solvent system may be found in the Bjerrum - Fuoss^{136,137} ion-pair model and Denison and Ramsey's¹³⁸ model. Though the variation of $\log K$ with $\frac{1}{\epsilon}$ has theoretical bearing, some authors¹³⁹⁻¹⁴⁵ have favoured of the plot of $\log K$ against mole - fraction of the organic solvents because the constants exhibit linearity with the latter over a wide range, even though it has no theoretical basis.

The thermodynamic formulation for the dissociation constant of the acid-base equilibrium $A \rightleftharpoons B + H^+$ on the molal scale is given by

$$K = \frac{m_{H^+} \times m_B}{m_A} \times \frac{\gamma_{H^+} \times \gamma_B}{\gamma_A} \quad \dots (5)$$

The numerical value is fixed by the choice of a standard state in which the activity co-efficients are assigned values of

unity. In aqueous solutions, the customary standard state is so chosen that γ_i approaches unity as m approaches zero.

When the compositions of the solvent media and the solute concentrations change (and ionic strength), it is convenient to separate each activity co-efficient γ_i into factors $\gamma_i = m\gamma_i \cdot s\gamma_i$ ^{14,23,146}. γ_i is measured relative to the standard state in pure water and becomes unity only in infinitely dilute aqueous solution. On the contrary, the activity co-efficient $s\gamma_i$ in equation above becomes unity when $m=0$ in the solvent s , where $m\gamma_i$ has a value different from unity whenever the solvent differs from pure water.

The 'salt effect' $s\gamma_i$ varies with the solute concentration. To determine the thermodynamic dissociation constant in mixed solvents, $s\gamma_i$ is to be determined. Simple Debye-Hückel equation with appropriate allowance for the effect of altering the dielectric constant of the medium s , can be used to estimate $s\gamma_i$ when ionic species are involved. The thermodynamic dissociation constant can also be determined in very dilute solution when $s\gamma_i \rightarrow 0$ and this is the best method for the determination of the thermodynamic dissociation constant as it involves no error in estimating $s\gamma_i$.

The 'medium effect' $m\gamma_i$ is a function of the free energy of the species 'i' in the two standard states,

$$\Delta G_i = G_i^s - G_i^w = RT \ln m \gamma_i \quad \dots (6)$$

In spite of the limitations of Born's equation due to the complexity of medium effect, considering only the electrostatic contribution to the free energy using Born's equation, we have

$$\ln m \gamma_i = \frac{N z_i^2 e^2}{2 RT \epsilon} \left(\frac{1}{\epsilon_s} - \frac{1}{\epsilon_w} \right) \quad \dots (7)$$

The mass law equation for equilibrium yields

$$K_s = K_w K_x \frac{m \gamma_A}{m \gamma_A \cdot m \gamma_B},$$

where K_w and K_s are the dissociation constants referred to the standard states in water and in solvent respectively. Combining equations above, we obtain

$$p(K_s) - p(K_w) = \frac{N e^2}{4.6052 RT} \left(\frac{1}{\epsilon_s} - \frac{1}{\epsilon_w} \right) \left(\frac{z_B^2}{r_B} - \frac{z_A^2}{r_A} + \frac{1}{r_{H^+}} \right) \dots (8)$$

(Charges on r_A etc omitted).

with the dissociation equilibrium of the charge-type $A^{\circ}B^{-}$ (for example, A° = uncharged acetic acid, B^{-} = acetate anion, $z_A = 0$) equation predicts that $p(K_s)$ will be greater than $p(K_w)$ if the dielectric constant ϵ_s is lower than that of water (as it is in methanol - water and ethanol - water solvents and in pure methanol and ethanol). Actually the pK for acids of this charge type has been found to vary from 3 to 5 units higher in methanol and ethanol than in water^{23,34,147}. The observations are also true in other alcohols and dioxane.

If the equilibrium is of the charge type A^+B^0 (for example, A^+ = anilinium cation, B^0 = uncharged aniline, $z_B = 0$) and γ_{H^+} is about equal to γ_A , however, the electrostatic treatment alone would lead one to expect pK to be almost unaffected by changes in the dielectric constant of the solvent. It is unlikely γ_A will often be less than γ_{H^+} and therefore, an increase in pK would be more easily explained on electrostatic grounds than a decrease would be.

Selective Solvation and Ion-Solvent Interaction:

The question of specific solvation is of great importance in solution chemistry^{106,148-159}. The solvation and preferential or selective solvation of ions in different solvents were used in interpreting data on conductivity, transference, solubility, u.v. visible spectra and other results^{106,149-159}.

The importance of anion solvation in determining the relative strengths have been stressed by Grunwald and Price¹⁶⁰⁻¹⁶² and Parker and co-workers¹⁶³.

The relative strengths of picric, acetic and trichloroacetic acids in different solvent environments have been ascribed to strong London-dispersion interactions of the solute molecules with the surrounding medium.

The results of the investigations of clare et.al.¹⁶³

(on the relative strengths of a series of acids HA and HB in dimethylformamide and methanol) confirm the belief that acid-base equilibria and medium effects are very sensitive to a change from a dipolar aprotic solvent to a polar protic solvent presumably because of hydrogen bonding interactions between anions and the molecules of the protic solvent.

For each of the species participating in reaction, the free-energy change on the transfer from dimethylformamide to methanol is given by (according to Parker and co-workers)

$$\Delta G_t^0 = RT (\ln 10) \log_m \gamma_i = RT (\ln 10) \log \gamma_i^H \gamma_i^*$$

The co-efficient γ_i^H embodies the changes in chemical potential of i due to hydrogen-bonding by methanol on transfer from dimethylformamide, Whereas other changes in the transfer energy are included in γ_i^* .

The ratio of the rate constant for the reaction



in methanol to that in dimethylformamide has been taken to be a measure of $\gamma_{A^-}^H$. The excellent correlation between the hydrogen-bonding coefficient and to changes of the equilibrium constant of reaction on transfer from dimethylformamide to methanol emphasizes the importance of solvent anion interaction.

In view of the solvation properties, the free-energies of transfer in different solvents can be written as

$$\Delta G_t^\circ = \Delta G_{t(\text{el})}^\circ + \Delta G_{t(\text{solv})}^\circ$$

$\Delta G_{t(\text{solv})}^\circ$ includes the contribution of solvation and other specific ion-solvent interactions¹⁶⁴.

Solvation and free-energy of transfer of single ions :

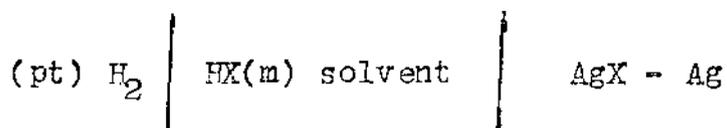
The applications and implications of the studies of reactions in non-aqueous and mixed solvents¹⁶⁵ and ion-solvent interactions have been described in details^{1-4,23,45,73,99,166-171}. But the most important but elusive aspect of the solution chemistry in the determination of 'single ion' thermodynamics or more precisely the 'medium effects' of ions in mixed or non-aqueous solvents.

The experimental methods, however, yield the transfer thermodynamic changes of neutral combinations but offer no means of separating them into single-ion characteristics. According to Strehlow⁷³ "single ion thermodynamics is a legitimate branch of physical chemistry. This division of thermodynamic functions of electrolytes into single ion values may reveal correlation between measurable but from a thermodynamic point of view unrelated quantities".

Various theoretical and semiempirical¹⁷²⁻¹⁷⁷ extra thermodynamic attempts have been made to obtain single ion thermodynamics with moderate success. However, the free-energy of transfer or 'medium effect' of ion in different solvents is yet to be determined in an unambiguous way. This aspect is a

matter of continuous review^{73,99,166,178-181}, the most recent being the extensive review made by Lahiri and Aditya¹⁸².

The free-energy changes associated with the transfer of a chemical entity (HX) from solvent (1, say water) to solvent (2, say S) is known as "total medium effect"¹⁸³ (ΔG_t^0) which is splitted into primary medium effect or medium effect and secondary medium effect or salt effect as exemplified from the consideration of the cell of the type



The measurement of e.m.f. of cells of the type in two different solvents namely water(W) and solvent(S) gives the total medium effect of any electroneutral combination HX

$$\begin{aligned} \Delta G_t^0 &= \Delta G_t^0 + 2RT \ln \frac{{}^S \gamma_{\pm}}{{}^W \gamma_{\pm}} \\ &= \Delta G_t^0 + 2RT \ln m \gamma_{\pm} \end{aligned}$$

$\Delta G_t^0 = -ZF({}^S E^0 - {}^W E^0)$ is the primary medium effect and measures ion-solvent interactions whereas the logarithmic term is known as secondary medium effect denoting ion-ion interactions and solvation.

The 'medium effect' $\log m \gamma_i$ of an ion is the reversible work of transfer of 1 mole of ion i from the standard state in solvent 1 (water) to the standard state in solvent 2(s) by the

expression

$$\log m \gamma_i = \frac{s\mu_o - w\mu_o}{RT} \dots (11)$$

obviously, the primary medium effect is independent of molality but the exact value of 'medium effect' could only be determined in absence of appreciable concentrations of electrolytes which changes not only the structure of the solvent molecules but also the solvent concentration due to solvation of ions. The secondary medium effect (salt effect) is a function of solute-concentration and can be determined with the help of theoretical equations like Debye-Huckel or Davies equations with appropriate values of A and B arising from the changed values of dielectric constants of the solvents. The equations fail at higher concentrations. Thus, it is desirable to work in dilute solutions so that $\gamma_{\pm} \rightarrow 0$ and the measurements account for the 'Primary medium effect' only.

Real free-energy of solvation

The 'medium effect' of an ion is actually related to the real free-energy of solvation¹⁷⁰.

The real free-energy of solvation Δ_1 ¹⁸⁴⁻¹⁸⁷ is defined as the change in ion-energy upon transfer from the gas phase into the solution. It is expressed by the relationship

$$\begin{aligned} \alpha_i &= \mu_i + z_i F = \mu_i + RT \ln a_i + z_i F \chi \\ &= \alpha_i^0 + RT \ln a_i \end{aligned}$$

where α_i is the standard real free-energy of solvation of ion.

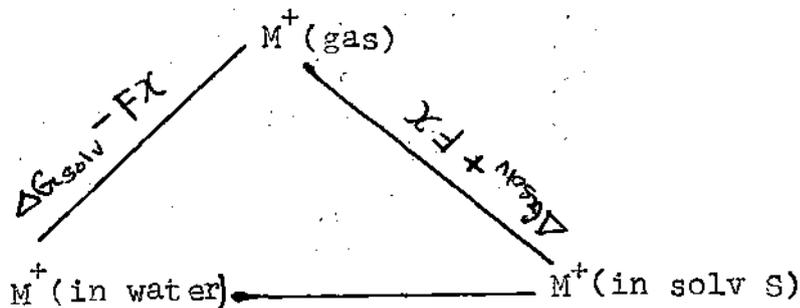
μ_i (or μ_i^0) represents the free-energy of ion-solvent interaction or chemical solvation. χ represents the surface potential of solvent and the term $z_i F \chi$ is the electrostatic work owing to the passage of the ion through the surface potential at the vacuum solvent interface. The surface potential cannot be measured directly or calculated.

The real free-energy of transfer of an ion from water to a second solvent have been determined from the volta potential measurements as done by Case and Parsons^{185,186}.

$$\Delta \alpha_i = \alpha_i^s - \alpha_i^w$$

From $\Delta \alpha_i$ and Randle's values of α_i^w , α_i^s can be determined.¹⁸⁴

The medium effect of an ion M^+ and the real free-energy of transfer can be correlated from the consideration of Born-Haber Cycle as follows :



Born-Haber Cycle

$$\begin{aligned}
 \Delta \alpha_t &= \Delta \alpha_{\text{solv}}^{(M^+)S} - \Delta \alpha_{\text{solv}}^{(M^+)W} \\
 &= \Delta G_{\text{solv}}^{(M^+)S} + zF \chi_s - \Delta G_{\text{solv}}^{(M^+)W} - zF \chi_w \\
 &= \Delta G_t^{(M^+)} + zF (\chi_s - \chi_w) \quad \dots (13)
 \end{aligned}$$

If both the solvents have the same ionic concentrations, then the "total medium effect" $\Delta \alpha_t$ can be represented as

$$\begin{aligned}
 \Delta \alpha_t &= \Delta \alpha_t^{\circ} + RT \ln \left(\frac{\gamma_{\pm}^S}{\gamma_{\pm}^W} \right) \\
 &= \Delta G_{t(\text{ion})}^{\circ} + zF (\chi_s - \chi_w) + RT \ln \left(\frac{\gamma_{\pm}^S}{\gamma_{\pm}^W} \right) \quad \dots (14)
 \end{aligned}$$

$\Delta \alpha_t^{\circ}$ is the primary medium effect and log term represents the "secondary medium effect" having a negligible contributions (~ 0.1 K.Cal or less) under ordinary conditions and is neglected compared to $\Delta \alpha_t^{\circ}$. ($\chi_s - \chi_w$) values are generally of the order of $\sim 0.1V$ so that $F (\chi_s - \chi_w) \sim 2$ K.Cal/mole which is of the same order of magnitude as $\Delta G_{t(\text{ion})}^{\circ}$ values.

ΔG_t° values cannot be experimentally determined but $\Delta \alpha_t^{\circ}$ (ions) are experimentally measurable inspite of limitations. However, it is to be noted that for electroneutral combinations

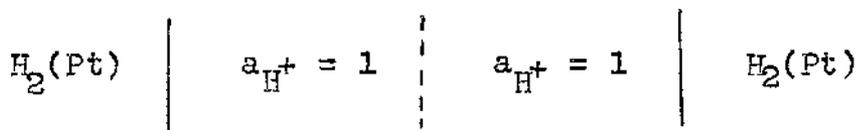
$$z_M^{+} + z_X^{-} = 0 \text{ so that } \Delta \alpha_t^{\circ} (\text{MX}) = \Delta G_t^{\circ} (\text{MX})$$

Determination of the medium effect

Thermodynamic properties of single ions in aqueous and

non-aqueous solvents and thermodynamics of transfer have been presented by a number of workers¹⁸⁸⁻²⁰¹. It is apparent that the 'medium effect' of individual ions can only be obtained from the measured "medium effect" of electroneutral combinations using various extrathermodynamic assumptions.

The determination of "medium effect" of H^+ ions ($\log_m \gamma_H$) evoked considerable interest as it determines directly the relative basicities of two solvents and can be obtained from the direct measurement of the cell



where $E = -\frac{RT}{F} \ln_m \gamma_H + E_{LJ}$

In view of limitations of having liquid-junction potential of uncertain magnitude, the "medium effect" of proton was first determined by Bjerrum and Larsson²⁰² from e.m.f. measurement of Cells composed of hydrogen electrode in a non-aqueous medium and aqueous calomel reference electrode connected with a bridge of aqueous 3.5 N KCl on the assumption of negligible liquid junction potential.

The values are of academic interest. The systematic efforts to determine the "medium effect" are given as what follows.

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Models based on modification of Born Equation :-



The medium effect of an ion can be obtained from the simple Born equation

$$\log_m \gamma_i = \frac{NZ_i^2 e^2}{2 RT} \left(\frac{1}{\epsilon_s} - \frac{1}{\epsilon_w} \right) \quad \dots (15)$$

It is to be noted that solvent molecules become inhomogeneous due to strong influence of solute molecules near the solvent molecules. Two extreme cases are dielectric saturation in the vicinity of ions²⁰³ and formation of a Clathrate²⁰⁴ by water molecule in the vicinity of a non-polar solute due to hydrophobic bonding effects.

The equation consists of two disposable parameters like radius and dielectric constant. Refinements are based on

a) Increase in crystallographic radii due to solvation²⁰⁵⁻²¹⁰. The model is due to Voet and successfully applied by Latimer et.al. Strehlow and co-workers and Coetzee et.al. in non-aqueous solvents where ionic radii are adjusted to account for the differences between the free-energies of transfer of pairs of alkali metal ions.

$$\begin{aligned} \Delta G_t^0 &= (G_{t,s} - G_{t,w}) \\ &= \frac{NZ^2 e^2}{2} \left[\frac{1 - \frac{1}{\epsilon_s}}{r_+ + R_+(S)} - \frac{1 - \frac{1}{\epsilon_w}}{r_+ + R_+(W)} \right] \quad \dots (16) \end{aligned}$$

However, the equation lacks theoretical significance and is restricted to differences between very similar cations and similar solvents.

b) Dielectric solvation in the vicinity of the ion reducing the

effective dielectric constant of the solvent²¹¹⁻²¹⁷. Noyes²⁰³ found that for cations having the electronic structure of an inert gas, the effective dielectric constant is given by

$$\epsilon_{\text{eff}} = 1.000 + 1.376 (\gamma^2 - 0.054)$$

and the local dielectric constant is given by

$$\begin{aligned} \epsilon_{\text{loc}} &= 78.30 \text{ for } r > 2.86 \text{ \AA} \\ &= \frac{1}{0.6009 + 0.1163/r} \text{ for } r < 2.86 \text{ \AA} \end{aligned}$$

Graham's relations²¹⁰ for differential dielectric ($\epsilon_d = \frac{d\epsilon}{dE}$) constant is $\epsilon_d = n^2 + \frac{\epsilon_o - n^2}{1 + b E^2}$ where E is the field strength at a distance r , n is the refractive index and b is a parameter independent of ϵ . It has been found that ϵ_d becomes equal to ϵ_o , above a certain initial value of r and ϵ_{sat} below a certain critical value of $r = r_o$. The radii for dielectric saturation of water and a number of alcohols are known.

Hepler²¹³ expressed ϵ as a function of r and took Hasted et.al.'s²¹⁴ value $\epsilon_{\text{sat}} = 5$ for $r < 1.5 \text{ \AA}$, $\epsilon_o = 78.30$ for $r > 4.0 \text{ \AA}$ and expressed $\epsilon = (\epsilon_o - \epsilon_{\text{sat}}/2.5) (r - 1.5) + \epsilon_{\text{sat}}$ in the range of $1.5 \text{ \AA} < r < 4.0 \text{ \AA}$.

The free-energy change due to hydration of an ion is given by

$$\Delta G_{\text{el}} = \frac{Ne^2}{2} \left[\int_r^{1.5} \frac{dr}{\epsilon_{\text{sat}}} \cdot r^2 + \int_{1.5}^4 \frac{dr}{(Xr - Y)r^2} + \int_0^\infty \frac{dr}{\epsilon_o r^2} \right] \dots (17)$$

$$X = \frac{\epsilon_0 - \epsilon_{\text{sat}}}{2.5} \text{ and } Y = 1.5 X - \epsilon_{\text{sat}}$$

The corresponding Stoke's²¹⁵ equation is

$$\mu_{\text{aq}}^{\text{el}} = \frac{N^2 e^2}{2} \left[\frac{2nr_w}{r_e(r_e + 2nr_w) \epsilon_{\text{eff}}} + \frac{1}{\epsilon(r_e + 2nr_w)} \right] \dots(18)$$

where $2nr_w$ is the thickness of n layers of water molecules around the ion, r_e is the crystal radius, ϵ = bulk dielectric constant

$$\epsilon_{\text{eff}} = \frac{1}{2} \left(\frac{1}{5} + \frac{1}{78} \right).$$

It is likely that partial or complete solvation of ions by other non-aqueous solvents may occur leading to changed values of r , ϵ_{sat} or ϵ_{eff} and ΔG_t° . The equation should, therefore, be restricted to water-rich solvents. The equations were utilized by Bates and co-workers^{14,15,18,217} to calculate $\Delta G_{\text{el}}^\circ$ values and the basicities of different methanol + water mixtures.

All the treatments consider the interactions of the ions with solvents to be predominantly electrostatic and neglects specific solute-solvent interactions and non-specific "neutral" component of the solvation energies of ions. Complete understanding require the knowledge of ion-dipole, ion (induced) dipole, ion-quadrupole, dipole-dipole and London dispersion forces which are functions of r^{-2} , r^{-4} , r^{-3} , r^{-3} and r^{-6} in that order where r is the corresponding interaction distance which contain the ionic radius term but not always equal to it²¹⁸. An actual calculation of solvation energies thus requires knowledge of radii of ions and solvents. The various interaction distances, the polarizabilities and multipole moments of the solvent molecules and the ions, the co-ordination numbers for the

primary solvation shell and various geometric factors. The reliable quantitative calculation of hydrational and solvational energies are thus very difficult.

The other methods of calculation of hydrational energies but not ΔG_t^0 (in most cases) are due to Noyes²⁰³, Goldman and Bates²¹⁹, Padova^{220,221}, Beveridge and Schnulle^{222,223}. A number of mathematically complex molecular orbital and statistical mechanical methods²²⁴⁻²³⁴ have also been suggested but they are relatively little used due to complexity of the models.

Methods based on measurement of oxidation-reduction potential and the E.M.F. of different cells :-

The search a suitable reference electrode having the same e.m.f. value in all solvents thus appears imperative. Pleskov²³⁴ proposed that the potential of Rb/Rb⁺ couple, because of low polarizability and large radius of Rb⁺ ion, should be equal in all solvents. However, both electrostatic considerations and experimental free-energy transfer values of halides (having larger radii), Rb⁺ and Cs⁺ in different solvent point the inherent limitations of the assumption. Strehlow and co-workers^{73,206,235} made appropriate allowances for the changed dielectric constants in different solvents and for the residual electrostatic free-energy terms and developed a modified Rb - scale which was utilized by Coetzee et.al.²³⁶ for measurements of polarographic half-wave potentials of a series of cations present as perchlorates in seven solvents.

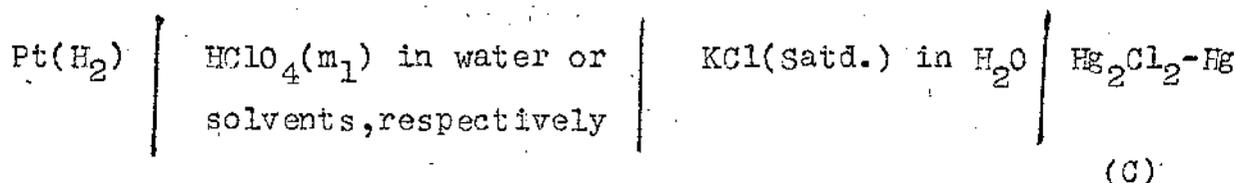
Koeppe, Wendt and Strehlow^{73,208,235} (also studied by Kuwana et.al.²³⁷) selected the redox - systems of large symmetrical complexes Ferricinium | Ferrocene and Cobalticinium | Cobaltocene, having very little residual charges on the surface, so that the standard e.m.f. of the Fic | Foc or Cic | Coc [i.e. $\Delta G_t^{\circ}(\text{Foc}) - \Delta G_t^{\circ}(\text{Fic})$] can be regarded to be solvent - independent. Thus the measurement of standard oxidation potentials in water and solvents gives the value of $\Delta G_t^{\circ}(\text{H}^+) - \Delta G_t^{\circ}(\text{Fic}) + \Delta G_t^{\circ}(\text{Foc})$

According to Strehlow,

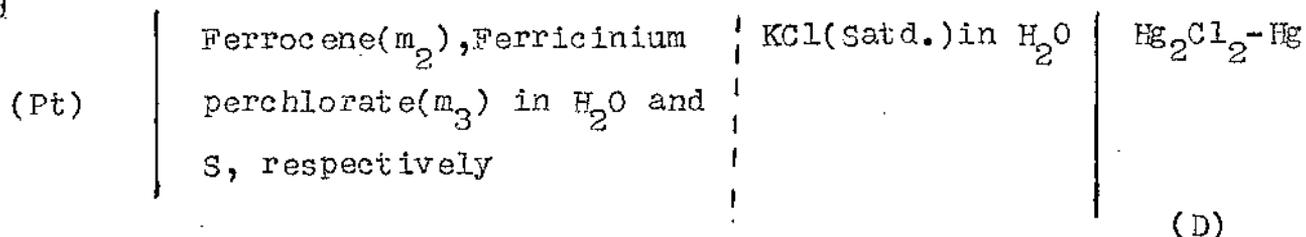
$$\Delta G_t^{\circ}(\text{Fic}) - \Delta G_t^{\circ}(\text{Foc}) = \frac{Nz^2 e^2}{2} \left[\left(\frac{1 - \frac{1}{\epsilon_1}}{r + a_1} \right) - \frac{1 - \frac{1}{\epsilon_2}}{r + a_2} \right] \dots (19)$$

where a_1 and a_2 are constants, specific for the solvents in question Strehlow used $a_1 = 0.85$; $0.72 \leq a_2 \leq 0.90$ based on data of alkali ions. In addition to the inherent limitations due to liquid-junction potentials, the contributions due to surface potentials in measuring the real free-energies of transfer have been neglected²³⁸.

In spite of the limitations, the method seems to be one of the most useful method for the determination of the 'medium effect' of single ions and widely used by de Ligny and co-workers^{28-32,238-240}. They used the cells of the type



and



to get

$$E_S^O(\text{Fic}) - E_W^O(\text{Fic}) = \frac{1}{F} \left[\Delta G_t^O(H) - \Delta G_t^O(\text{Fic}) + \Delta G_t^O(\text{Foc}) \right]$$

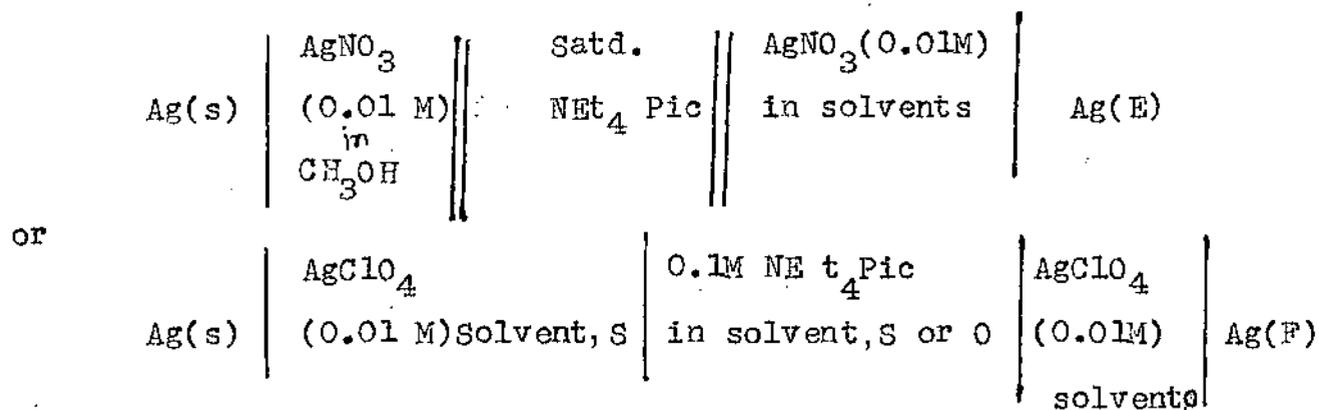
However, due to low solubility of ferrocene and instability of ferricinium in water, the determination of E is generally supplemented by the polarographic half-wave potentials, $\text{Foc} \rightleftharpoons \text{Fic}^+ + e$ have been proved to be diffusion controlled and the ratio of diffusion constants of ferrocene and the ferricinium ion appeared to be independent of solvent composition. The method has been used to determine the ΔG_t^O of H^+ and the other ions in different solvents. The method has been recently used by Kalidas et.al.²⁴¹ to measure $\Delta G_t^O(H^+)$ in different methanol - water, propylene glycol - water and methanol - propylene glycol mixtures.

However, the presence of considerable amount of indifferent electrolyte should change the solvent structure, E^O - values and thus the medium effects. The diffusion constant of ferrocene and ferricinium ions may be unequal. It has been shown by Alfenaar et.al.²⁴⁰ that the contribution of the solvent molecules to the diffusion potential cannot be neglected and is a function of solvent composition and the nature of electrolyte. The primary medium effect is the most important contribution to the diffusion potential. The diffusion potential of electrolyte solutions in methanol - water mixtures cannot be suppressed by salt - bridge.

Ferrocene may have residual electrostatic component of the ion¹⁶⁷ and the specific interactions of the redox couple with water and other solvents are also known²¹⁰. There may be uncertainties in the crystal radii of ferrocene²³⁸ (3.8 Å) and ferricinium³² (3.3 Å) ions.

Other redox couples studied are ferrocene /ferricinium picrate; ferroin/ ferriin couple²⁴³, (4,7-dimethylferroin/(4,7-dimethyl) ferriin couple²⁴⁴, bisdiphenyl chromium (0,1) couple²⁴⁵,²⁴⁶ with relative little success.

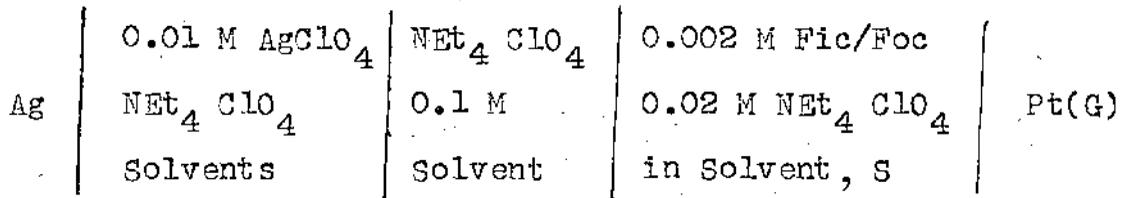
Parker and co-workers^{168,188,191} feel that the ferrocene assumption is not valid when water is one of the solvents. Parker & Alexander recommended the cells of the type



to determine medium effects. The bridge electrolyte contains tetraethyl ammonium picrate having large and comparable anion and cation size with no specific interactions with the solvents as apparent from roughly equal molar conductances in all solvents studied. Thus there is a negligible liquid-junction potential E_j .

Parker and co-workers^{168,169} also measured the potential of fic/foc couple against the Ag^+/Ag electrode in fifteen solvents

using the cell



Thus the values based on the ferrocene assumption can be readily converted to the negligible E_j assumption.

However, the suppression of E_j by means of a salt-bridge is impossible as the liquid-junction potential E_j at an interface of two different media is itself primarily a function of the medium effects for the single ions transported across it²⁴².

Extrapolation Method : The extrapolation method has its origin in the works of Izmaylov^{104,246,247} who assumed G° of an infinitely large ion to be zero and all significant components of the solvation energy G° of an ion are functions of $\frac{1}{r^n}$ (r = crystallographic radii, $n = 1 - 4$ or 6). He plotted thermodynamically allowed combinations like $(G_M^\circ - G_H^\circ)$ vs $\frac{1}{r_M}$ and $-(G_H^\circ + G_X^\circ)$ vs $\frac{1}{r_X}$ (M = alkalimetal ions, X = halide ions) and used extrapolations to get $-G_M^\circ$ at $(\frac{1}{r}) = 0$. The plot of $\left[-G_H^\circ + \left(\frac{G_M^\circ - G_X^\circ}{2} \right) \right]$ vs $\frac{1}{r_{av}} = \frac{1}{2} \left(\frac{1}{r_M} + \frac{1}{r_X} \right)$ improve the value of G_H° . Izmaylov^{104,247} also considered solvation of ions as complex formation between solvent molecules (donors) and ions with vacant orbitals as acceptors.

He determined the solvation energies of anions and cations from the plots of $(G_M^\circ + G_X^\circ)$ vs $\frac{1}{r^2}$, $(G_M^\circ - G_H^\circ)$ vs $\frac{1}{r^2}$ and

$$\left[-G_i^{\circ} + \frac{G_M^{\circ} - G_X^{\circ}}{2} \right] \text{ vs } \frac{1}{n^2} \quad (n = 3, 4, 5 \text{ etc.})$$
 for different isoelectronic pairs like $(\text{Na}^+ \text{F}^-)$, $(\text{K}^+ \text{Cl}^-)$, $(\text{Rb}^+ \text{Br}^-)$ and $(\text{Cs}^+ \text{I}^-)$ where n is the principal quantum numbers of the lowest vacant orbital of the ion. He considered the second method to be more reliable. However, Izmaylov's assumption that $\Delta G_{(\text{neut})}^{\circ}$ account for 1 - 2% of the total solvation energy was found to be erroneous from the estimates of $\Delta G_{(\text{neut})}^{\circ}$ via inert gas assumption or experimental determination of $\Delta G_{(\text{neut})}^{\circ}$. Moreover, the calculations of Izmaylov^{104,246,247} were dependent on the large errors involved in the determination of the dissociation energies of molecular hydrogen, the sublimation energies of the metal and of atomic hydrogen in the gas phase and crystal lattice energies of silver halides. The extrapolations are non-linear and generally based on three points. Therefore, large errors in the determination of ΔG_t° or 'medium effect' are but expected.

Feakins and Watson and their associates^{39-46,248,249} used the e.m.f. methods to determine the ΔG_t° (free-energies of transfer from water to different solvents) values of HCl, HBr and HI on one hand and LiCl, NaCl and KCl on the other and utilized the extrapolations

$$\Delta G_t^{\circ}(\text{HX}) = \Delta G_t^{\circ}(\text{H}^+) + a r_X^{-1} \quad (21)$$

and

$$\Delta G_t^{\circ}(\text{MCl}) = \Delta G_t^{\circ}(\text{eL}^-) + b r_M^{-1} \quad (22)$$

to get $\Delta G_t^{\circ}(\text{H})$ at $\frac{1}{r_X} = 0$ and $\Delta G_t^{\circ}(\text{cl})$ at $\frac{1}{r_M} = 0$

Cations are found to be in lower free-energy states in the mixed solvents compared to water, while the anions show the reverse trend. However, linearity is poor in most cases due to incomplete compensation of ΔH_t and $T \Delta S_t$ terms which are complex functions of radius and estimations based on the dependence of $\frac{1}{r^2}$ appear to be oversimplification. The major contributions to free-energy of solvation arises from ion dipole interaction term $ze\mu / r^2$ in addition to Born charging energy beyond the solvation shell²⁵. In consistent values of ΔG_t° of individual ions result from the plots of $\Delta G_t^{\circ}(\text{M Cl})$ vs $\frac{1}{r_M^2}$ and $\Delta G_t^{\circ}(\text{HX})$ vs $\frac{1}{r_X^2}$. Other inconsistencies are also noted²³⁸. However, it has been now recognized that the solvation energy of an ion is composed of an electrostatic part ΔG_{el}° and neutral part ΔG_{neut}° , i.e.,

$$\Delta G_t^{\circ} = \Delta G_{neut}^{\circ} + \Delta G_{el}^{\circ}$$

The assumption was originally put forward by Bjerrum and Larson²⁰² and applied by Haugen and Friedman²⁵¹ and most of the workers now a days. The neutral component was equated to the 'medium effect' of the uncharged species of similar size and structure as the ion (known as inert gas assumption). For benzoate ion, benzoic acid is the neutral analogue while for ions like Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ the isoelectric inert gases are the corresponding neutral analogues¹⁶⁷.

The method has been elegantly put forward by Alfenaar and de Ligny^{31,238} and more recently by Kim²⁵², Abraham and Liszi¹⁹⁹.

In view of the difficulty of calculation ΔG_{neut}° , it has

been determined experimentally. Alfenaar and de Ligny^{31,238} took $\Delta G_{\text{neut}}^{\circ}$ of very large ions to be equal to $\Delta G_{\text{neut}}^{\circ}$ of the corresponding uncharged particle of equal radius but for small ions, a difference arises from the changed solvent structure around the ions of the solvent molecules.

The free-energy of transfer of ions between two solvents including ion-ion, ion-dipole, ion-quadrupole interactions etc. are given by

$$\Delta G_{\text{I}}(\text{ion}) = \Delta G_{\text{neut}}^{\circ} + \frac{a}{r} + \frac{b}{r^2} + \frac{c}{r^3} + \dots \quad \dots (24)$$

The free-energy of transfer of electroneutral combinations of ions have been divided by Alfenaar and de Ligny into the contributions of the individual ions M and A as follows :

$$\Delta G_{\text{M}}^{\circ} + \Delta G_{\text{A}}^{\circ} - \Delta G_{\text{neut}}^{\circ}, \text{ A} = \Delta G_{\text{H}}^{\circ} + \frac{a}{r_{\text{A}}} + \frac{b}{r_{\text{A}}^2} + \frac{c}{r_{\text{A}}^3} \dots \quad \dots (25)$$

$$\Delta G_{\text{H}}^{\circ} - \Delta G_{\text{M}}^{\circ} - \Delta G_{\text{neut}}^{\circ}, \text{ M} = \Delta G_{\text{H}}^{\circ} - \frac{a}{r_{\text{M}}} + \frac{d}{r_{\text{M}}^2} + \frac{e}{r_{\text{M}}^3} + \dots \quad \dots (26)$$

The values of the left hand sides can be determined experimentally. a_{Born} is calculated using the Born equation from the slope at $\frac{1}{r} = 0$, and $\Delta G_{\text{H}}^{\circ}$, b, c etc can be estimated by the method of least square. When the left hand side of the two equations (25) and (26) are plotted against $\frac{1}{r}$, two curves will have a common intercept $\Delta G_{\text{H}}^{\circ}$, the larger the ions, the greater the accuracy of the results.

The extrapolations, however, are non-linear. The contributions of $\Delta G_{t(\text{neut})}^{\circ}$ appear to be considerable and the reliability of the determination of $\Delta G_{t(\text{neut})}^{\circ}$ via 'inert gas assumption' have not been proved.

de Ligny and co-workers^{28-32,238-240} later slightly modified the method by incorporating ideas of Buckingham²⁵³, Halliwell and Nyburg²⁵⁴, Muirhead-Gould and Laidler²⁵⁵.

Salomon^{180,196,257} determined the individual free-energies of solvation from plot of differences in conventional free-energies vs $\frac{1}{r_i}$, where r_i is the gas-phase radius of Gouray and Adrion.

$\Delta G_{\text{solv}}^{\circ}(\text{H}^+)$ is obtained from

$$\left[\Delta G_{\text{conv}}^{\circ}(\text{M}^+) - \Delta G_{\text{conv}}^{\circ}(\text{X}^-) \right] = \frac{\text{constant}}{r_i} - 2 \Delta G_{\text{solv}}^{\circ}(\text{H}^+) \quad \dots (29)$$

$$\left[\Delta G_{\text{conv}}^{\circ}(\text{M}^+) = \Delta G_{\text{solv}}^{\circ}(\text{M}^+) - \Delta G_{\text{solv}}^{\circ}(\text{H}^+) \right]$$

$$\Delta G_{\text{conv}}^{\circ}(\text{X}^-) = \Delta G_{\text{solv}}^{\circ}(\text{X}^-) + \Delta G_{\text{solv}}^{\circ}(\text{H}^+) \quad \left. \right]$$

M^+ and X^- are ions of equal charge and radius.

It is known that the enthalpy and entropy terms are complex functions of r , but due to compensation of the enthalpy and entropy of solvation, the free-energy term is relatively independent of terms higher than r^{-1} . $\Delta G_{\text{solv}}^{\circ}(\text{H}^+)$ is found to be -235.0 K cal/mole.

Since $\Delta G_{\text{neut}}^{\circ}$ is dependent of ionic radius, the choice of crystal radii as determined by different workers are noted. Criss and salomon¹⁸⁰ considered it desirable to take differences in $\Delta G_{\text{t,conv}}^{\circ}(\text{ion})$ which automatically cancels $\Delta G_{\text{t,neut}}^{\circ}$, for anions and cations of equal charge and radius. The choice of crystal radius thus becomes less important.

Abraham and Liszi¹⁹⁹ determined the free-energy (and other thermodynamic properties) of solvation of gaseous univalent ions using a one-layer and two layer-continuum model for $\Delta G_{\text{t,el}}^{\circ}$ utilizing the equation $\Delta G_{\text{t}}^{\circ} = \Delta G_{\text{t,el}}^{\circ} + \Delta G_{\text{t(neut)}}^{\circ}$, $\Delta G_{\text{t(neut)}}^{\circ}$ is the free-energy of solvation of a non-polar gaseous solute of the same size as the ions in question.

Wells²⁵⁷ calculated the free-energies of transfer of H^+ ions from water to water + co - solvent mixtures (like MeOH, Pr^iOH , $t\text{-BuOH}$, ethylene - glycol, glycerol, acetone, dióxane, dmsO) assuming that $\Delta G_{\text{t}}^{\circ}(\text{H}^+)$ consists of two parts

$$\Delta G_{\text{t}}^{\circ}(\text{H}^+) = \Delta G_{\text{t}}^{\circ}(\text{H}^+)_e + \Delta G^{\circ}(\text{ROH}_2^+)$$

$\Delta G_{\text{t}}^{\circ}(\text{H}^+)_e$ is the free-energy change^{of} the transfer of a sphere containing the tetrahedral structure $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ (having $r = 3r_{\text{H}_2\text{O}}$) from ϵ_w to ϵ_s (dielectric constant of the mixture) using Born equation

$$\Delta G_{\text{t}}^{\circ}(\text{H}^+)_e = \frac{e^2}{6r_{\text{H}_2\text{O}}} \left(\frac{1}{\epsilon_s} - \frac{1}{\epsilon_w} \right).$$

$\Delta G^{\circ}(\text{ROH}_2^+)$ covers all subsequent structural changes induced by

the presence of the tetrahedral $\text{H}_3\text{O}^+ (\text{H}_2\text{O})_4$ in the mixed solvent.

However, the method is applicable only in water-rich media. The limitations of the method are discussed elsewhere.

Method based on 'Reference Electrolyte'

The most widely advocated and promising approach to the estimation of 'medium effects' for single ions (and also for the estimation of partial molar volume, the solvation enthalpies and other thermodynamic properties of single ions) are those based on 'reference electrolytes'. The reference electrolyte^{167,258-262} should be composed of large symmetrical counter ions of equal size and solvation properties, so that the 'medium effect' should be equally divided between the cations and the anions. The central atom and the charge of such counter ions should be shielded by large organic residues to minimize both the charge density and specific interactions with the solvent.

Tetraphenyl phosphonium tetraphenyl borate ($\text{Ph}_4\text{P B Ph}_4$) was first used by Grunwald and co-workers¹⁵¹ to estimate the 'medium effects' of single ions. If $\frac{dG_t^{\circ}}{dz_1}$ for the reference electrolyte is denoted G_t° , the equation separating the transfer energy into the individual contributions of positive and negative ions becomes

$$G_t^{\circ}(+) = G_t^{\circ}(-) = \Delta G_{t(\text{neut})}^{\circ} - \frac{Ne^2}{2r\epsilon} \cdot \frac{d \ln \xi}{dz} \quad \dots(32)$$

The Ph_4C was chosen as neutral analogue.

The experimental values chosen from the 'reference electrolyte' method agreed well with the values predicted by the equation. Slight positive G_t° values for alkali metal cations and negative G_t° values for inorganic anions indicate preferential solvation of ions. Popovych²⁵⁹ proposed tri-isoanyl-n-butylammonium tetraphenyl borate (TABB Ph_4) as 'reference electrolyte' based on the equality of the Stoke's radii of ions in water, methanol + acetonitrile, Tetraphenyl arsonium tetraphenyl borate ($\text{Ph}_4\text{As B Ph}_4$) has been proposed by Parker and co-workers^{188,191}.

Because of their low solubility in different solvents, the reference electrolytes are suitable for determining free-energies of solvation without uncertain activity corrections.

The limitations of the method can be summarized as follows :

- 1) The results are based on solubility data and errors may arise from the possible^{167,181}
 - a) formation of crystal solvents
 - b) micelle formation
 - c) formation of complex ions
 - d) ion-pair formation
- 2) Insufficient evidence or no direct experimental evidence for the equality of radii of counter ions.

3) Approximate equality of Stoke's radii or calculated radii from models are not real indices of ion-sizes or imply a direct correlation between transport or thermodynamic properties²⁶¹⁻²⁶⁴. Dielectric relaxation, size of secondary solvation effects must be taken into account to determine free energies of solvation¹⁸⁰.

4) The method should not be applied to dipolar aprotic solvent, which differentiates strongly between the relative solvation of anions and cations²¹⁰.

In spite of the defects, the results obtained with TABEP₄ of Popovych and co-workers and with Ph₄AsB Ph₄ assumption of Alexander and Parker are in good agreement, Discrepancies between two methods arise from Parker's use of formal solubility product rather than thermodynamic ion activity product used by Popovych¹⁶⁶.

Berne and Popovych²⁶⁵ studied the medium effects of tetraphenyl germane (Ph₄Ge), tetraphenyl methane (Ph₄C) and tetraphenyl silane (Ph₄Si) which are excellent neutral analogues of tetraphenyl borate (B Ph₄⁻), tetraphenyl arsonium (Ph₄As⁺) and tetraphenyl phosphonium ions (Ph₄P⁺), the 'reference ions' widely used in the estimation of 'medium effects' of single ions and whose ion-sizes roughly fall in the range of 4.0 - 5.5 Å. Thus, for ions with radii 4 - 5 Å

$$\Delta G_t^{\circ} = \Delta G_t^{\circ}(\text{neut}) + \Delta G_t^{\circ}(\text{Born})$$

(experimental)

the interactions expressed by higher order terms in r^{-1} appear to be unimportant.

Medium effects of Ph_4Ge , Ph_4C and Ph_4Si referred to standard states in ethanol were calculated from solubilities in acetonitrile methanol, ethanol-water solvents containing 60 - 100 wt% ethanol, when the 'medium effects' of tetraphenyl compounds are added to the corresponding estimates of $\log_m \gamma$ (Born) for an ion with $r = 4-5 \text{ \AA}$, the results are in fair agreement with the observed values of $\frac{1}{2} \log m \gamma$ for the $\text{Ph}_4\text{As}^+ \text{B Ph}_4^-$, $\text{Ph}_4\text{P}^+ \text{B Ph}_4^-$ and TABB Ph_4 in ethanol-water solvents, methanol but not in acetonitrile.

Recently, Kim²⁵² after a critical and extensive study strongly recommends $\text{Ph}_4\text{As}^+ \text{B Ph}_4^-$ as 'reference electrolyte' to calculate single ion thermodynamics. The electrostatic free energy of transfer $\Delta G_t^{\circ}(\text{Born})$ are calculated by the Buckingham theory, $\Delta G_t^{\circ}(\text{neut})$ are replaced by the experimental values of $\Delta G_t^{\circ}(\text{Ph}_4\text{Ge})$ and $\Delta G_t^{\circ}(\text{Ph}_4\text{C})$. Ph_4Ge and Ph_4C have proved to be by their size and structure f as determined from the determination of molar volume V , packing density(d) and volume co-efficients

$$f = \frac{V(\text{Ph}_4\text{Ge})}{V(\text{Ph}_4\text{C})} \quad \text{and} \quad f = \frac{V(\text{Ph}_4\text{As}^+)}{V(\text{Ph}_4\text{B}^-)} \quad \text{the ideal}$$

neutral analogues of Ph_4As^+ and Ph_4B^- respectively. Good agreement have been reported between ΔG_t° ($= \Delta G_{el}^{\circ} + \Delta G_{neut}^{\circ}$) values calculated and experimental values of ΔG_t° ($\text{Ph}_4\text{As B Ph}_4$) in various organic solvents.

The partition of the values for the reference cation and anion has shown slight and marginal difference in standard free energies of transfer, in most cases slightly greater for the cations than for the anion.

Miscellaneous Methods

A number of methods of minor importance have been suggested to obtain 'medium effect' of which the method based on linear free energy relationships suggested by Grunwald and co-worker is of importance.

For the ionization of acids HA (aliphatic acids, benzoic acids) and BH^+ (anilinium ion, toluidinium ions etc.) in alcohol + water mixtures and water, we have,

$$(\text{pk}_s - \text{pk}_w)\text{HA} = \log \gamma_{\text{H}^+} + \log \frac{\gamma_{\text{A}^-}}{\gamma_{\text{HA}}} = \log \gamma_{\text{H}^+} + m_{\text{A}} \gamma^- \dots (33)$$

and $(\text{pk}_s - \text{pk}_w)\text{BH}^+ = \log \gamma_{\text{H}^+} + \log m_{\text{B}} \gamma_0$, m_{A} and m_{B} are substituent constants independent of the nature of the solvent; γ^- and γ_0 are the solvent parameters dependent on the solvent only where

$$\gamma_- = (1 - w^2) \quad \dots (34)$$

and $\gamma_0 = -(1 - w)^2 \quad \dots (35)$

w = weight fraction of water in the solvent.

$$\text{Now, } (pk_s - pk_w)_{HA} - (pk_s - pk_w)_{BH^+} = m_A \gamma_- - m_B \gamma_0 \quad \dots (36)$$

m_A and m_B were determined by multiple-regression method which enables one to calculate $\log \gamma_{H^+}$.

The method, however, is of little value due to the inherent limitations regarding the assumptions of m_A, γ as pointed out by Wynne-Jones²⁶⁶ and Popovych^{166,260} and more recently by Maity and Lahiri²⁶⁷⁻²⁶⁹.

Basicity of the mixed solvents :

The complexity of ion-solvent interactions is well-illustrated by the conflicting evidence concerning the relative "basicities" of water and alcohols in the mixed solvents about which there is no general agreement. The investigation of transfer of free energies by Feakins and co-workers^{38-45,248} brings one to the conclusion that the anions are in a higher free-energy state in methanol-water mixtures than in water, whereas cations are in a lower free energy state indicating methanol to be more basic than water. Considering the charge distribution in the solvent molecules, Feakins suggests that due to the inductive effect of the methyl group, methanol is more basic than water and methanol will confer

"greater basicity" on water to which it is hydrogen bonded. This idea is in line with the views of Frank and Wen²⁶⁸. Similar conclusions have been drawn by Wells²⁶⁹ from the behaviour of p-nitroaniline in solutions of strong acids in methanol and in isopropanol. The medium effect for the proton, $\log m\gamma_H$ estimated by Popovych and co-workers^{166,258-261,265} is negative in ethanol-water mixtures containing from 10 to 98 wt% ethanol and passes through a minimum at 60% by wt. Negative values of $\log m\gamma_H$ between 10 and 98 wt% ethanol indicate that ethanol-water mixtures in that range are more basic than either of the pure liquids, with maximum basicity occurring at 60 wt%. Braude and Stern²⁷⁰ observed a similar variation in solvent basicity from the behaviour of the acidity function, H_0 in mixtures of ethanol, dioxane and acetone with water. In all three cases, $-H_0$ passes through a minimum (maximum solvent basicity) at approximately equimolar solvent composition and then rises sharply in the region of the pure organic solvents. Calculations by Paabo, Bates and Robinson¹⁵ point to the existence of a basicity maximum also in methanol - water mixtures, as do the estimates of $\log m\gamma_H$ by Alfenaar and deligny²³⁸. The conclusion of Braude and Stern²⁷⁰ was that water is more basic in mixtures with other solvents than in the pure liquid state, whereas its proton affinity is lowered by strong intermolecular hydrogen bonding. Addition of organic solvent to water is believed to bring about a gradual destruction of the water structure, thus liberating polymerised, condensed system having a considerable degree of structure, 2) the thermodynamic significance of K is doubtful¹⁴⁸. These apparently conflicting views have led Frank and Ives¹⁴⁸ to suggest that in a hydrogen bonded liquid system, it is not possible

or even meaningful to assign relative intrinsic basic or acidic strengths to molecular species which exist so strongly under each others influence.

According to Feakins⁴⁵, dioxane molecule is more basic than water and also enhances the basicity of water molecules to which it is bonded.

Feakins⁴⁵ also suggests that pK possibly measures basicity but only over part of the solvent-composition range and the basicity of the solvent may well change depending on their environment and therefore, change over the range of methanol-water concentration. Thus, it is apparent that pK can give some idea regarding basicity provided the full nature of the environment is known.

Muirhead, Gould and Laidler² have given the different types of forces which are present in solutions. In addition to an increasing number of basic sites on the water molecules for bonding with the protons. The effective proton affinity of the solvent reaches its maximum when the higher aqueous solvent $H^+(H_2O)_n$ are replaced by H_3O^+ ions. This condition corresponds to the minima in the plots of $-H_o$ or $\log m\gamma_H$ vs solvent composition. Beyond the minima, the H_3O^+ ions are gradually replaced by the organic oxonium ions, which the case of $C_2H_5OH_2^+$ are more acidic than H_3O^+ (positive $\log m\gamma_H$). The conductance of HCl²⁷¹ in alcohol-water mixtures however appears to indicate that protons

are bound more tightly to water molecule than to methanol. Calculation of the equilibrium constants for the simple proton transfer reaction $\text{ROH}_2^+ + \text{H}_2\text{O} = \text{ROH} + \text{H}_3\text{O}^+$ have given results (e.g. $K \sim 100$ for MeOH, ~ 250 for EtOH) supported by indicator²⁷², e.m.f. ²⁷³ and catalytic studies²⁷⁴ taken to mean that water is a much stronger base than alcohols. But 1) K -calculated for the hypothetical proton-transfer reaction is a gross oversimplification of something more complex happening in the ion-ion forces, ion-dipole forces, ion-induced dipole forces, ion-quadrupole forces (may be termed ion-solvent interactions in a broader sence), dipole-dipole forces, dispersion forces, and charge-transfer forces exist in solution. Parker¹⁷⁸ also suggested that there are four kinds of strong solute-solvent interaction : ion-dipole, dipole-dipole, π -complex forming and hydrogen bonding. Full and proper knowledge of these factors are necessary before we can say definitely about the basicity of the solvents.

In view of the complexities of the problem, Pal and Lahiri⁵³ determined the dissociation constants of salicyclic andsulphosalicyclic acids in a number of equidielectric mixtures of different solvent compositions to get the relative magnitude of the basicities of the different solvent mixtures.

In view of the uncertainties of the radii values of anions (specially in case of unsymmetrical electrolytes) and lack of exact knowledge of solvation⁵³, the basicity of the solvent mixtures could not be ascertained but only the relative idea regarding the non-electrostatic contributions could be made. Since "non-electrostatic

terms" (termed 'basicity' by Paabo et.al.) is predominantly negative for methanol-water mixtures, Pal and Lahiri⁵³ observed

ΔG_{e1}° term (- ve) is in the order dioxane > isopropanol > ethanol > methanol. But equidielectric mixtures invariably make the mole-fraction of different solvents to differ considerably. Though there is constancy in ΔG_{e1}° parts (assuming r to be same in equidielectric mixtures), only the difference in ΔG_{none1}° parts of different percentages of mixed solvents could be obtained. But ΔG_{none1}° changes with solvent-composition as the free-energy of mixing and solvent basicity change with solvent composition. Thus, the idea of even the relative basicity of the solvents could not be made from these measurements. They stressed the importance of determining the ion-solvent interactions to determine the basicity of mixed solvents.

Inspite of the progress that has been made in understanding ion-solvent interactions and their role in medium effects, there is yet no means of evaluating in a reliable way the proton affinity of one medium with respect to that of another. For this reason, a single pH-scale applicable more than one medium can not yet be considered a practical possibility.

A satisfactory treatment of the theoretical basis of complex formation in various solvents and mixed solvent does not yet seem possible. Complex formation occurs in a way analogous to corresponding reactions in water. A consideration of electrostatic effects involved will complicate the treatment appreciably. No systematic investigations have been done as to the effect of dielectric constant and change in acid-base character of the

solvents on the complexes. However, change in the stability constants of the complexes with solvent compositions are noted but the values are not simple functions of the dielectric constants^{53-55,67,141,275}.

Dioxane-water mixtures have been widely used for the determination of stability constant of complexes slightly soluble in water. Irving and Rossotti²⁷⁶ compared $\log K_{HL}$ and $\log K_{ML}$ in mixtures water + dioxane & in some other solvents. The thermodynamic significance of the difference between these constants was discussed. In aqueous dioxane and aqueous alcohols, the stability constant of the complexes containing an O-M linkage increases with increasing organic solvents whereas the stabilities of complexes containing N - M linkage decrease. But Irving and Rossotti found no simple relationship between stability and solvent composition for complexes of ammonia, ethylenediamine and pyridine, although the silver ethylenediamine complex is more stable in pure ethanol and isopropanol than water.

Complex formation in non-aqueous or mixed solvents and their systematic correlations offer possibilities for future research. The free energies of transfer^{of} metal complexes and ligands may be of great help to determine the free-energies of transfer of metal ions and metal complexes.

In recent years, free-energies of transfer of metal complexes (particularly alkaline metal complexes) of macrocyclic ligands like cryptands and crown ethers have been made²⁷⁷. A positive value of the transfer activity co-efficients $S_1 \gamma S_2$
LM⁺

[L = cryptands or crown ether, M^+ = alkali metal ion] denotes that [LM^+] is more strongly solvated in S_1 than in S_2 .

However, attempts for qualitative and quantitative correlations are still very few.

From the discussions, it is apparent that inspite of the extensive studies, the role of solvents on the dissociation constants of the ligands, the exact nature of ion-solvent, solvent-solvent interactions, and solvent basicities are yet proved to be elusive as a result nothing specific can be said about the 'medium effects' a quantity of fundamental interest.

Systematic and extensive studies are needed for the proper understanding of the solution chemistry in aqueous and mixed solvents. Studies on the dissociation constants of ligands and their complexes in mixed solvents may give us some idea regarding ion-solvent interactions, solvent-basicity and medium effects.

With the above objects in view, we have determined the dissociation constants of 2,2'-bipyridine, 1,10-phenanthroline in dmsO + water, dmf + water and formamide + water mixtures and ferrous-tris-2,2'-bipyridine complex in dmsO + water and formamide + water mixtures.

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Section - II

Studies on the dissociation constants of ligands in different non-aqueous and the binary mixtures give us insight regarding the role of solvents on the dissociation equilibria and ion-solvent interactions.

Most of the studies are in protic solvents like methanol, ethanol, t-butanol etc. and their aqueous binary mixtures. Studies in dipolar-aprotic solvents and their binary mixtures may be of some help to understand the nature of the solute-solvent interactions and other solvent properties.

The peculiar properties and the various uses of dipolar-aprotic solvent dmsO have led us to study the acid-base properties of ligands in dmsO + H₂O mixtures. We report in this section the results of our study on the dissociation equilibria for the "isoelectric" reactions of the type



where A is either 2,2'-bipyridine (bipy) or 1,10-phenanthroline (Phen) in dmsO + H₂O mixtures pH-metrically and spectrophotometrically. The evaluation of free-energies of transfer of H⁺ ion in mixed-solvents have been attempted.

Experimental :

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

were used without further treatment. Dimethylsulphoxide (Baker Analyzed Reagent) was dried over freshly ignited quicklime for several hours and then distilled under reduced pressure. The distilled solvent was used within 24 hours. HClO_4 , caustic soda and other chemicals used were of analar grade. Doubly distilled water was used to prepare the solutions.

The ligands are known to absorb strongly in the u.v. region. The absorption maxima were slightly changed indicating little solute-solvent interactions.

The pK-values of the ligands were determined potentiometrically and spectrophotometrically in the same way as described by Lahiri, Aditya and co-workers¹⁻⁴. Since the ligands absorb strongly in the u.v. regions, their optical density measurements were taken at 300 and 305 nms (for 2,2'-bipyridine) and 310 and 315 nms for 1,10-phenanthroline.

The weight percentages of the organic solvent at 298K were calculated from the known amounts of the two solvents by volume and the densities of the solvents.

The dielectric constant and density values of dmsO + H_2O mixtures were interpolated from the data compiled by Covington and Dickinson⁵.

Determination of H^+ ion in dmsO + H_2O mixtures :

The glass electrode has been reported to function satisfactorily in demethylsulphoxide up to a pH of 28. Ritchie⁶ Calibrated the glass electrode with solutions of p-toluene-sulphonic acid. Kolthoff et. al.⁷ used buffer mixtures of 4-Chloro - 2, 6-dinitrophenol and 2,6-dinitrophenol (pK values determined conductometrically and spectrophotometrically) and their tetraethylammonium salts. But such studies in dmsO + H₂O mixtures are not known. Since glass-electrodes work satisfactorily in dmsO, therefore, the method suggested by Van Uitert et.al.⁸ could be well utilised. The method has been extensively studied by Lahiri, Aditya and co-workers⁹⁻¹⁰. The instrument was first standardized with potassium-hydrogen-phthalate 0.05 mol dm⁻³ buffer and then with 10⁻⁴ mol dm⁻³ HClO₄ acid solution. The glass electrode was then kept immersed in the appropriate solvent medium for equilibration and the meter readings of 10⁻⁴ mol dm⁻³ HClO₄ in the particular solvent medium was taken. The method gives reproducible results. The correction factors log U_H in the particular medium were calculated by the relationship $-\log [H^+] = B + \log [U_H]$ where $[H^+]$ is the stoichiometric hydrogen ion concentration assuming 100% dissociation of the acid in the aqueous and in mixed solvents.

The correction factors log U_H in different percentages of dmsO + H₂O mixtures are presented in Table (1).

The optical density readings were recorded with a

Backman DU2 spectrophotometer maintained at 298K. The pH-meter readings were noted with a ECIL digital pH-meter having an accuracy of ± 0.01 .

Results :

The thermodynamic dissociation constants for the reaction(1) is represented by

$$K_T = \frac{a_A \times a_{H^+}}{a_{AH^+}} = \frac{C_A \times C_{H^+}}{C_{AH^+}} \times \frac{f_A \times f_{H^+}}{f_{AH^+}} = \frac{C_A \times C_{H^+}}{C_{AH^+}} \quad (2)$$

(in very dilute solutions)

$$\text{Thus } pK_T = pH + \log \frac{C_{AH^+}}{C_A} \quad (3)$$

$$= B + \log U_H + \log \frac{C_{AH^+}}{C_A} \quad (4)$$

$$= B + \log U_{H^+} \log \frac{d - d_M}{d_I - d} \quad (5)$$

(B = meter readings of the solutions)

where d_M , d_I and d are the optical densities of either 2,2'-bipyridine or 1,10-phenanthroline at pHs corresponding to molecular, ionic and mixtures of molecular and ionic forms respectively.

$$\text{Further } [H^+]_{\text{Total}} = [H^+]_{\text{free}} + [AH^+] \quad (6)$$

$$[A]_T = [A] + [AH^+] \quad (7)$$

Thus, from the known concentrations of $[A]_T$, $[H^+]_T$ and $[H^+]_{\text{free}}$ [determined experimentally] values, pK_T can be calculated using (4), whereas equation (5) has to be utilized

where d_M , d_I , d and $[H^+]$ ion concentrations are available. Tables 2 - 4 give the result of dissociation constants in mixed solvents. The average pK-values of 2,2'-bipyridine or 1,10-phenanthroline at different dmsO + H₂O mixtures are given in the Table 5.

Discussions :

In view of ion-pairing and homoconjugation of acids, it is desirable to work with very low concentrations in dmsO. But we always prefer to determine the dissociation constants of acids at very low ionic strengths and in absence of neutral electrolytes so that the thermodynamic dissociation constants could be determined.

In mixed solvents, the activity co-efficients of the ith species can be written as

$$\gamma_i = m_i \cdot s_i''$$

However, in very dilute solutions $s_i \rightarrow 1$ so that only the "medium effects" which could be properly assessed so that we get the role of solvents and the nature of the solute-solvent interactions.

The results in the table (5) show that the pK-values of 2,2'-bipyridine and 1,10-phenanthroline decrease as the percentage of organic solvents increase but the change is quite appreciable particularly at the beginning. The change is quite large when we compare ΔpK -change in comparable methanol-water

mixtures^{2,3} where the dielectric constants are considerably lower. The greater solubility of the ligands in organic solvents is one of the factors for change in pK-values. The pK of 1,10-phenanthroline decreases, reaches a minimum at about 80 wt% of organic solvent and then increases whereas no such minimum is observed in case of 2,2'-bipyridine.

The pK-values show linear relationship when plotted against weight percentage (Fig - 1). But the plots of pK vs 1/D or mole-fractions are linear at best up to 60 wt% beyond which considerable deviations arise (Fig 2,3). It is apparent that specific solute-solvent interactions are important to account for the variation of pK-values.

In order to have some understanding regarding the contributions of non-electrostatic parts, it is desirable to calculate

ΔG_t° (non-el). ΔG_t° (el) has been calculated using the simple Born¹² equation inspite of its limitations and uncertainty regarding the radii of ions.

$$\Delta G_t^{\circ}(\text{el}) = 166 \times 4.184 \left(\frac{1}{D} - 0.0127 \right) \left(\frac{1}{r_{H^+}} - \frac{1}{r_{AH^+}} \right)$$

r_{H^+} has been taken equal to 0.86 Å^{13,14}, $r_{\text{phen } H^+}$ or $r_{\text{bipy } H^+}$ has been calculated to be 3.70 Å. The change in pK-values in going from water to dmsO + H₂O mixtures have been usually ascribed to solute-solvent interactions. The effects due to dielectric constants in case of 'isoelectronic reactions' being negligible. However,

in view of the differences of radii of H^+ and AH^+ ions, the effects of the dielectric constants are quite appreciable.

In view of the limitations of Born equations, we have also utilised the 'one layer' solvation model as suggested by Abraham and Lisze¹⁵

$$\Delta G_{t(el)}^{\circ} = \frac{NZ^2}{2} \left(\frac{1}{\epsilon_1} - 1 \right) \left(\frac{1}{a} - \frac{1}{b} \right) + \frac{NZ^2}{2} \left(\frac{1}{\epsilon_0} - 1 \right) \left(\frac{1}{b} \right)$$

a = radius of the ion.

$b = a + r_s$ (r_s = radius of the solvent molecule)

$\epsilon_1 = 2$ and ϵ_0 = bulk-dielectric constant.

r_{dmso} and $r_{\text{H}_2\text{O}}$ have been taken from the literature¹⁵.

$r_{\text{dmso} + \text{H}_2\text{O}}$ has been assumed to vary with solvent compositions.

As expected, the differences between $\Delta G_{t(el)}^{\circ}$ values calculated using Born equation and Abraham's¹⁵ equation are quite large. The use of Born equation or other modified equations, which are appreciable to ions having spherical radii, in case of flat molecular ions like phenH⁺ or bipyH⁺ is likely to introduce some error. However, the limitations of the Born equation or other equations with adjusted radii or dielectric constant values are well-known¹⁶. However, there are also uncertainties in the radii values of simple spherical ions. The ion-dipole interactions may also be quite appreciable.

But whatever may be the method of calculating the $\Delta G_{t(\text{el})}^{\circ}$ values, $\Delta G_{t(\text{non el})}^{\circ}$ have been found to increasingly negative (Table 6) indicating the increased basicity of the solvent mixtures compared to H_2O . It is known that dms₂ is basic in nature and the dms₂ + H_2O mixtures are likely to be more basic than H_2O . But the correction factor ($-\log U_{\text{H}}$) increases as the percentage of organic solvent increases reaches a maximum at about 80 wt% of dms₂ and then decreases again. This means that the basicity is maximum at about 80 wt% of dms₂.

Since the $\Delta G_{t(\text{H}^+)}^{\circ}$ of transfer or 'medium effect' from water to dms₂ + H_2O mixtures would enable us to have better insight regarding the solvent basicity and ion-solvent interactions, attempts have been made to determine the $\Delta G_{t(\text{H}^+)}^{\circ}$ values utilizing the free-energies of transfer for the reaction (1). Since the work has been carried out in very dilute solutions, the solutions may be regarded to be their standard states.

Thus,

$$\begin{aligned} \Delta \Delta G_{t(1)}^{\circ} &= \Delta G_{s(1)}^{\circ} - \Delta G_{w(1)}^{\circ} \\ &= \Delta G_{t(A)}^{\circ} + \Delta G_{t(\text{H}^+)}^{\circ} - \Delta G_{t(\text{AH}^+)}^{\circ} \\ &= \Delta G_{t(\text{H}^+)}^{\circ} - \Delta G_{t(\text{el})(\text{AH}^+)}^{\circ} \\ \left[\text{as } \Delta G_{t(\text{AH}^+)}^{\circ} &= \Delta G_{t(A)}^{\circ} + \Delta G_{t(\text{el})(\text{AH}^+)}^{\circ} \right] \end{aligned}$$

Thus,

$$\Delta G_{t(\text{H}^+)}^{\circ} = \Delta \Delta G_{t(1)}^{\circ} + \Delta G_{t(\text{el})(\text{AH}^+)}^{\circ}$$

$\Delta G_{t(H^+)}^{\circ}$ values from H_2O to $dmso + H_2O$ mixtures have been presented in table 6 using the dissociation constant values of 2,2'-bipyridine and 1,10-phenanthroline and $\Delta G_{t(el)}^{\circ}(AH^+)$ values calculated from Born equation and one layer solvation model as described before. The limitations of determining the free-energies of transfer of ions are well known¹⁶. We have particularly chosen bipyridine and phenanthroline for the measurement of $\Delta G_{t(H^+)}^{\circ}$ as the solute-solvent interactions of the ligands are known to be very small from spectral measurements¹⁷.

In spite of the limitations of calculating $\Delta G_{t(el)}^{\circ}(AH^+)$ (we prefer Born equation than the one layer solvation model), $\Delta G_{t(H^+)}^{\circ}$ values calculated using bipy or phen are in good agreement qualitatively and almost quantitatively if one considers the limitations of such measurements. Assuming an error of ± 0.02 (at low percentages of organic solvent) - ± 0.04 (at high percentages) in pK-values, an error to the extent of $\pm (0.20 \text{ to } 0.40) \text{ KJ}$ are expected. In view of lack of data, it is difficult to compare our $\Delta G_{t(H^+)}^{\circ}$ values with those in the literature. However, the values can be compared with the values reported by Wells¹⁸. The values are qualitatively in agreement but not quantitatively. For better comparison, the $\Delta G_{t(H^+)}^{\circ}(\text{molar})$ values have been converted into mole-fraction scale and the values come closer. Still the differences are appreciable about -1.0 KJ at 10.89 wt% - 4.67 KJ at 42 wt% and about -3.8 KJ at about 72 wt% (Table 7). No values are available at higher percentages. The results thus can be

regarded to be in good agreement.

In view of the inherent limitations of the various extra thermodynamic models of calculating 'medium effects' of ions arising from simplified generalisation, the method suggested by us is simple and reliable. The $\Delta G_t^{\circ}(\text{H}^+)$ values calculated by Wells¹⁸ in dmsO + H₂O mixtures involve the use

$$\Delta G_t^{\circ}(\text{H}^+) = \Delta G_t^{\circ}(\text{H}^+)_e + \Delta G^{\circ}(\text{ROH}_2^+)$$

where $\Delta G_t^{\circ}(\text{H}^+)_e$ has been calculated by the application of Born equation to the transfer of a sphere containing the tetrahedral structure, H₃O⁺ (H₂O)₄ using

$$\Delta G_t^{\circ}(\text{H}^+)_e = \frac{Ne^2}{6 r_{\text{H}_2\text{O}}} (D_s^{-1} - D_w^{-1})$$

$r_{\text{H}_2\text{O}}$ is the radius of water ions. The reactions as suggested by Wells implies a change in radius values in mixed solvents. The generalisations and the use of data obtained at high ionic strengths are hardly justifiable for the determination of 'medium effects'. The $\Delta G_t^{\circ}(\text{H}^+)$ values are increasingly negative indicating the spontaneity for the transfer of H⁺ ions in mixed solvents. Thus the mixed solvents appear to be more basic compared to water. However, $\Delta G_t^{\circ}(\text{H}^+)$ increases above 80 wt% of dmsO indicating that 'the basicity' decreases beyond this region which is in good accord with the observed 'Correction factor' values.

Though it is hardly possible to throw light on the

solvent structures from the limited data, but attempts can be made.

It is expected that dmsO would first enhance the three-dimensional polymeric structure of water but unlike the alcohol + water mixtures, the maximum structure formation has been reported to be in the region of $X_{\text{dmsO}} \approx 0.35$ or higher^{19,20}. The changes of other physico-chemical properties are also in the region $X_{\text{dmsO}} \approx 0.35$ to 0.50 ¹⁹⁻²².

It is likely that after initial structure formation breakdown of water-structure and dissociation of dmsO and disruption of water structure take place with concomittant formation of hydrogen-bonded dmsO + H₂O system upto about 80 wt% of dmsO. Beyond this region, disruption of dmsO + H₂O occurs. That is why the changes in physico-chemical properties occur in this region. The $-\Delta G_t^{\circ}(\text{H}^+)$ or 'correction factor' ($-\log U_{\text{H}}$) is also maximum indicating the maximum solvent basicity in this region.

Table - 1

Correction factor of dmsO + H₂O mixtures

Wt% of dmsO	Mole-fraction	$\frac{1}{D} \times 10^2$	Correction factors
1	2	3	4
10.87	0.027	1.28	- 0.02
21.53	0.060	1.30	- 0.07
32.02	0.098	1.31	- 0.14
42.28	0.144	1.32	- 0.28
52.35	0.202	1.35	- 0.46
62.24	0.280	1.39	- 0.66
71.94	0.371	1.45	- 0.89
81.46	0.503	1.55	- 1.14
90.81	0.692	1.72	- 1.03

Table - 2

Dissociation Constants of 2,2'-bipyridine at 32.02% by wt% of dmsc

(pH-metric)

Concentration of 2,2'-bipyridine soln. = 5×10^{-3} mol dm⁻³

(Temp = 298 K)

Fraction of the ligand neutral- ised (10^{-3} mol dm ⁻³)	Meter readings	pH-after Correction	pK	Average pK
1	2	3	4	5
1.5	4.35	4.21	3.84	
2.0	4.17	4.03	3.85	
2.5	3.99	3.85	3.85	3.85
3.0	3.82	3.68	3.86	
3.5	3.63	3.49	3.86	

Table - 3

Dissociation Constants of 2,2'-bipyridine at 32.02% by wt of dmso
(Spectrophotometric)

Temp = 298 K

Cell length = 1 cm.

Analytical wave length = 300 nm

Optical density of the molecular form (d_M) = 0.062

Optical density of the ionic form (d_I) = 0.418

Meter reading	pH after correction	Observed d	$d - d_M$	$d_I - d$	$\log \frac{d - d_M}{d_I - d}$	pK
1	2	3	4	5	6	7
4.21	4.07	0.191	0.129	0.227	- 0.24	3.83
4.03	3.89	0.234	0.172	0.184	- 0.03	3.86
3.91	3.77	0.255	0.187	0.163	0.06	3.83
3.80	3.66	0.275	0.213	0.143	0.17	3.83
3.75	3.61	0.287	0.225	0.131	0.25	3.85
3.66	3.52	0.300	0.238	0.118	0.30	3.82

Average pK = 3.83 ± 0.01

Average pK value from O.d.'s at 300 nm = 3.83 ± 0.01 .

Table - 4

Dissociation Constants of 1,10-phenanthroline at 32.02% by wt of dmso
(spectrophotometrically)

Temp = 298 K

Analytical wave length = 310 nm

Optical density of the molecular form (d_M) = 0.235

Optical density of the ionic form (d_I) = 1.17

Meter reading	pH after correction	Observed d	$d - d_M$	$d_I - d$	$\log \frac{d - d_M}{d_I - d}$	pK
1	2	3	4	5	6	7
4.49	4.35	0.730	0.495	0.440	0.05	4.40
4.38	4.24	0.780	0.545	0.390	0.14	4.38
4.25	4.11	0.832	0.597	0.338	0.25	4.36
4.16	4.02	0.885	0.650	0.285	0.36	4.38
4.11	3.97	0.900	0.665	0.270	0.39	4.36
4.06	3.92	0.940	0.705	0.230	0.49	4.41

Average pK = 4.38 ± 0.01

Average pK value from O.d.'s at 315 nm = 4.38 ± 0.01

Table - 5

Dissociation constants of 2,2'-bipyridine and 1,10-phenanthroline
in dmsO + water mixtures

Temp = 298K

2,2'-bipyridine				1,10-phenanthroline		
Wt%	pK(pH-metric)	pK(Spectro- photometric)	Average	pK(pH-metric)	pK(Spectro- photometric)	Average
10.87	4.17	4.21	4.19	4.69	4.68	4.69
21.53	4.00	4.02	4.01	4.55	4.53	4.54
32.02	3.85	3.83	3.84	4.42	4.38	4.40
42.28	3.70	3.72	3.71	4.28	4.20	4.24
52.35	3.44	3.40	3.42	3.99	3.93	3.96
62.24	3.17	3.11	3.14	3.73	3.68	3.71
71.94	2.72	2.66	2.69	3.46	3.42	3.44
81.46	2.30	2.24	2.27	3.14	3.18	3.16
90.81	2.23	2.15	2.19	3.35	3.41	3.38

Table - 6

Free-energy of transfer of Protons and related properties in dmsO + H₂O mixtures.

Temp = 298K.

Wt% of dmsO	ΔG_t° (K Joules)		ΔG_t° (el) (KJoules)				ΔG_t° (H ⁺) (KJoules)					
	Bipy	Phen	A		B		A			B		
			r = 0.86	r = 3.70	r = 0.86	r = 3.70	Bipy	Phen	Average	Bipy	Phen	Average
10.87	- 1.60	-2.05	0.08	0.02	5.39	1.17	- 1.58	-2.03	- 1.81	-0.43	-0.88	-0.66
21.53	- 2.62	-2.91	0.24	0.06	10.09	2.29	- 2.56	-2.85	- 2.71	-0.33	-0.62	-0.48
32.02	- 3.59	-3.71	0.32	0.08	14.50	3.30	- 3.51	-3.63	- 3.55	-0.29	-0.41	-0.35
42.28	- 4.34	-4.62	0.40	0.09	18.62	4.27	- 4.25	-4.53	- 4.39	-0.07	-0.35	-0.21
52.35	- 5.99	-6.22	0.65	0.15	23.29	5.19	- 5.84	-6.07	- 5.96	-0.80	-1.03	-0.92
62.24	- 7.59	-7.65	0.97	0.23	26.35	6.40	- 7.36	-7.42	- 7.39	-1.19	-1.25	-1.22
71.94	-10.15	-9.19	1.45	0.34	29.74	7.24	- 9.81	-8.85	- 9.33	-2.91	-1.95	-2.43
81.16	-12.55	-10.78	2.26	0.53	32.94	8.07	-12.02	-10.25	-11.14	-4.48	-2.71	-3.60
90.81	-13.00	- 9.53	3.63	0.84	36.28	9.28	- 12.16	-8.69	-10.43	-3.52	-0.25	-1.89

A = Calculated using born Equation

B = Calculated using one layer continuum model.

Table - 7

- $\Delta G_{t(H^+)}^{\circ}$ (KJoules) (mol-fraction scale)

Wt% of dmsO	Wells	Our work
10.89	3.01	2.00
21.53	5.60	3.09
32.02	7.90	4.14
42.28	9.90	5.23
52.35	11.70	7.06
62.24	13.70	8.80
71.94	14.90	11.10
81.46	-	13.35
90.81	-	13.17

References

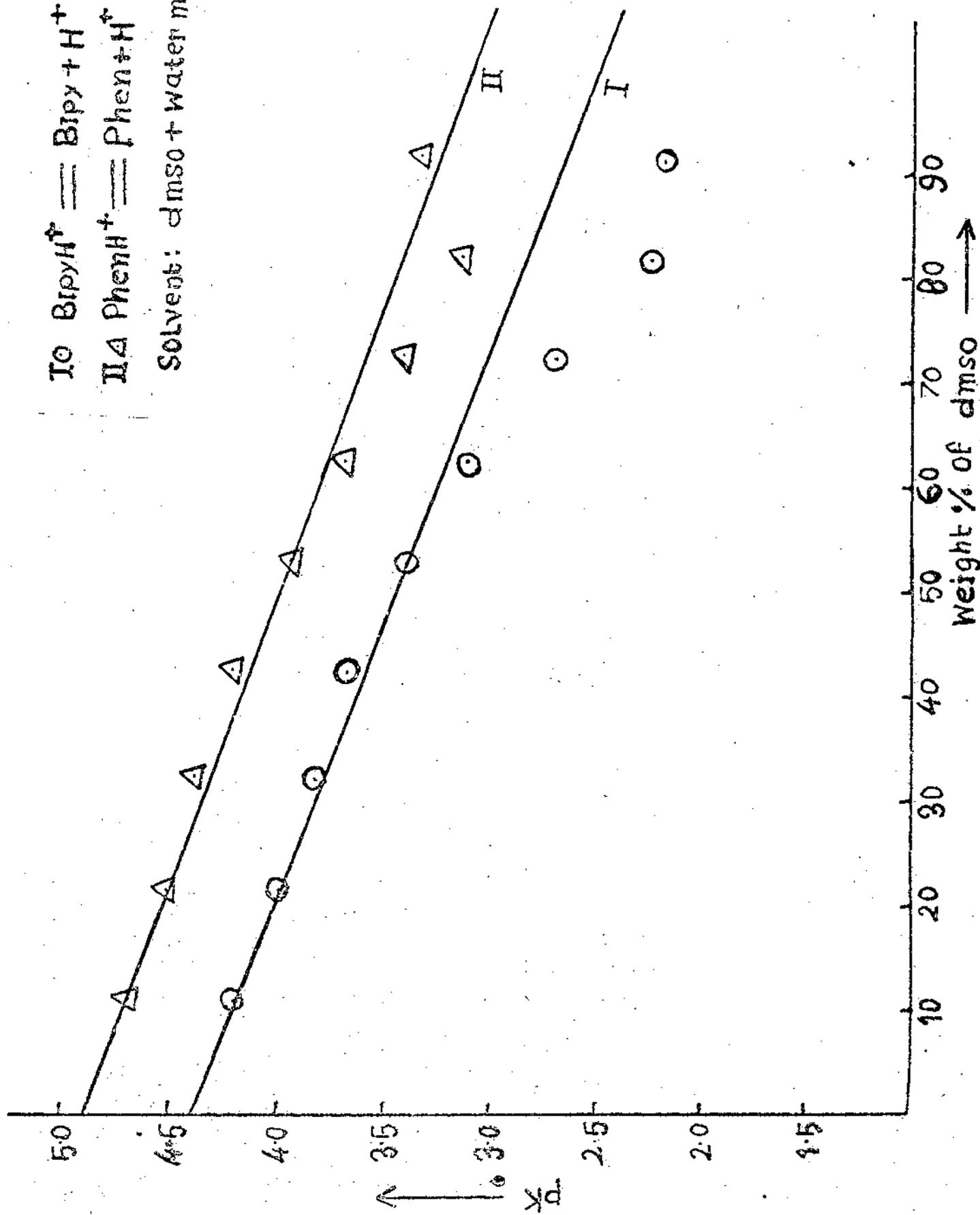
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Solvent: dmsO + Water mixture

Fig. 1



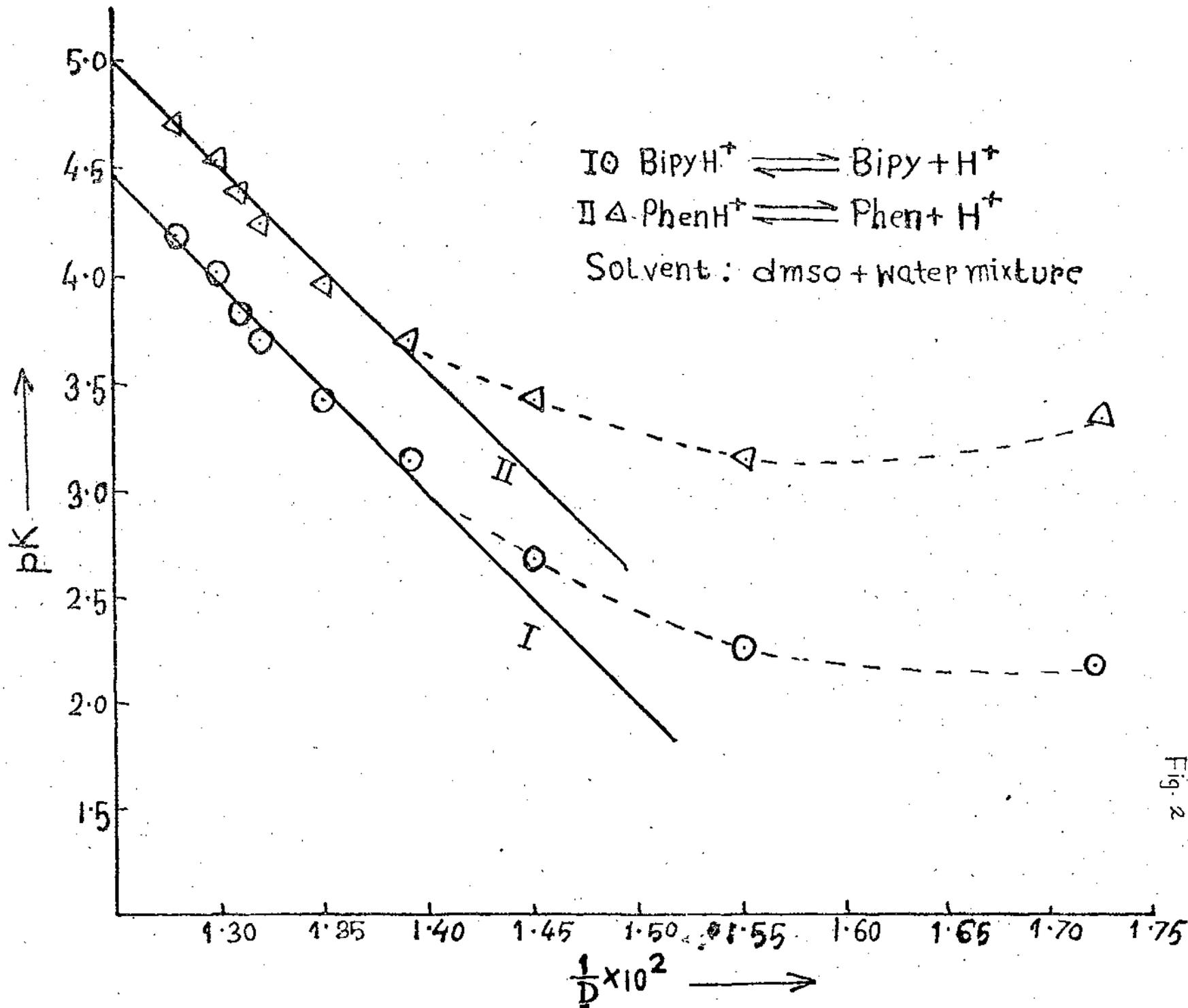
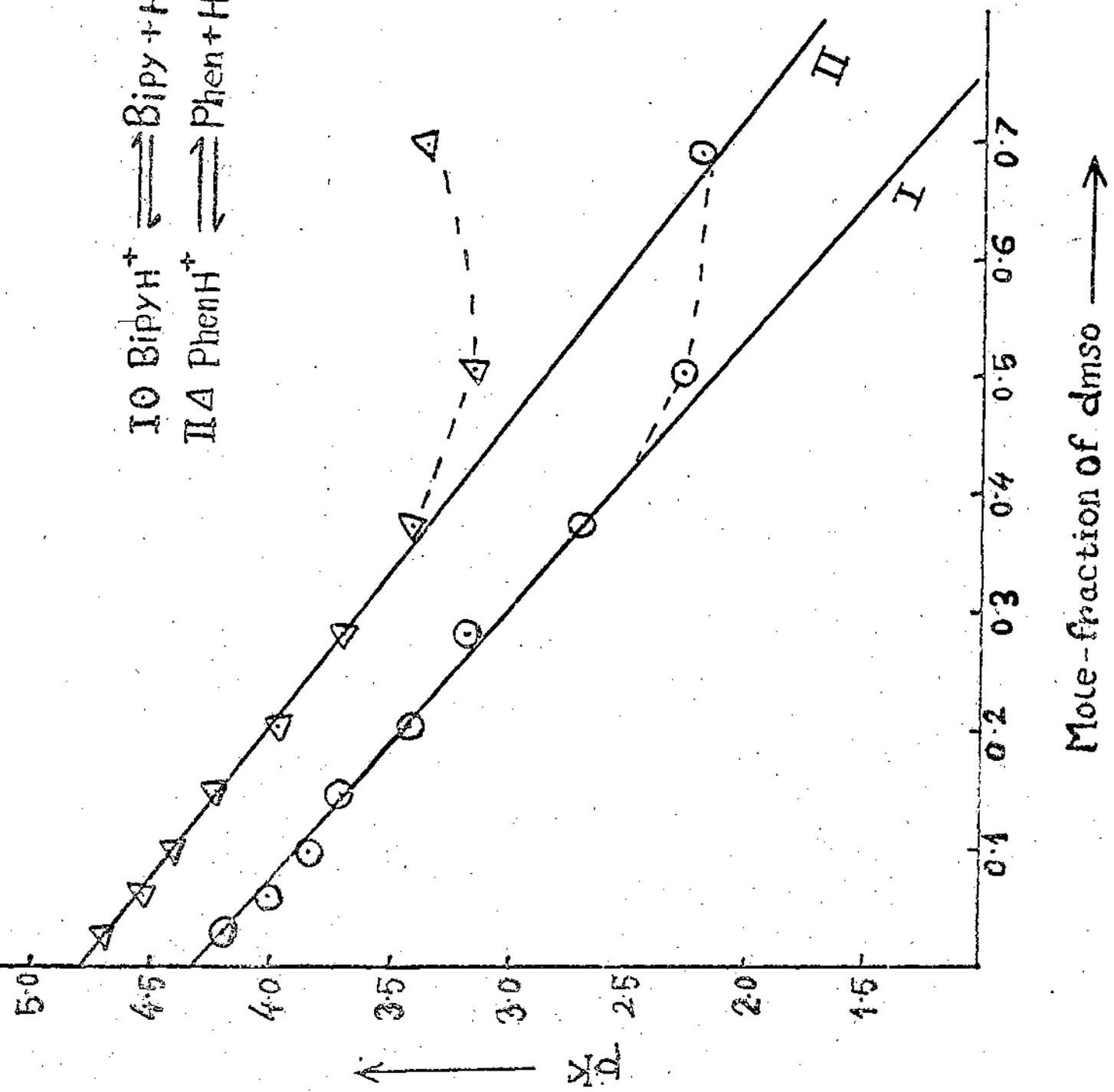
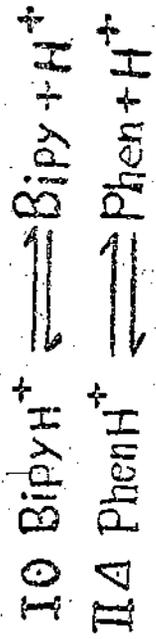


Fig. 2

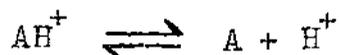
Fig. 3



Section - III

The effects of solvent structure and solute-solvent interactions on equilibrium constants and rate constants of chemical reactions in non-aqueous and mixed solvents are not well-understood. The effects could be investigated both by the alteration of the solvent composition and by variation of solute structure and charge type. Studies on the acid-base equilibria in different non-aqueous and their binary mixtures are particularly suited to study the role of the solvents and their solute-solvent interactions. The dissociation constants of ligands in different non-aqueous (mostly protic) solvents and their binary mixtures have been widely studied and attempts have been made to determine the free-energies of transfer of single ions. However, such studies in dipolar aprotic solvents like dmf and hydrogen-bonding amide solvent like formamide and their binary aqueous mixtures are relatively few.

This prompted us to study the dissociation equilibria for the "isoelectric" reactions of the type



where A = 2,2'-bipyridine (bipy), 1,10-phenanthroline in dmf + water and formamide + water mixtures pH-metrically and spectrophotometrically.

Attempts have been made to explore the role of the solvents and evaluate the values of the free-energies of transfer of H^+ ions from water to dmf + water and formamide + water mixtures.

The results are reported in the present section.

Experimental

2,2'-bipyridine and 1,10-phenanthroline (G.R.E. Merck) were used as such, Formamide (G.R.E. Merck) were dried over freshly ignited quicklime for several hours and then distilled under reduced pressure. N,N'-dimethylformamide i.e. dmf (E. Merck) was purified by fractional distillation under reduced pressure after drying the solvent over freshly ignited quicklime for several hours. The distilled solvents were used within 24 hours.

HClO_4 , Caustic soda and other chemicals were of analar grade. Doubly distilled water from all glass distilling set was used to prepare the solutions.

All the ligands absorb strongly in the U.V. region and the absorption maxima of the ligands are 280 (molecular) nm and 301 (ionic) nm for 2,2'-bipyridine and 264 (molecular) and 272 (ionic) nms for 1,10-phenanthroline. The solvents also absorb strongly in the U.V. region and optical density measurements are possible only at longer wave lengths. We have selected 300 and 305 nms for 2,2'-bipyridine and 310 and 315 nms for 1,10-phenanthroline.

The pK-values of the ligands were determined pH-metrically and spectrophotometrically in the same way as described in the previous sections.¹⁻³

In formamide solutions, the optical density corresponding to ionic forms of the ligands could not be determined as a white precipitate was observed with the addition of considerable amount

of HClO_4 to formamide. Therefore, pK-values in formamide solutions were determined only pH-metrically.

The weight percentages of organic solvents at 298K were calculated from the volumes of the solvents and their density values⁴.

The dielectric constants for dmf + water mixtures and formamide + water mixtures were taken from the literature^{5,6}. The optical density readings were recorded with a Beckman DU-2 spectrophotometer maintained at 298K. The pH-meter readings were noted with a ECIL expanded scale pH-meter (having an accuracy of ± 0.01) and used the glass and the calomel electrode.

Determination of H^+ ion in dmf + water and formamide + water mixtures

For the determination of H^+ ion concentrations in mixed solvents, the glass and the Calomel electrodes should be properly calibrated in the solvent in question and the appropriate correction factors are to be determined. Due to moderately large dielectric constants homoconjugation and ion-pairing are extensive in dmf-medium which can be avoided only at very low concentrations of salts and acids. However, it is always preferable to determine the dissociation constants of acids and bases at very low ionic strengths and in absence of inert electrolytes so that the thermodynamic dissociation constants could be determined.

The glass electrode is known to function satisfactorily in dmf. Kolthoff and co-workers⁷ used 4-chloro-2,6-dinitrophenol and

2,6-dinitrophenol as standard acids and used buffer mixtures of these acids and their tetramethylammonium salts for calibration of glass electrodes. However, there is almost no report of the used of glass electrodes in formamide solutions.

We, however, used the glass and the Calomel electrodes both in dmf + H₂O and formamide + H₂O mixtures. For calibration of electrodes, the same procedure suggested by Van Uitert⁸ and extensively used by Lahiri, Aditya and co-workers^{9,10} was followed. The instrument was first standardized with potassium-hydrogen phthalate (0.05 mol dm⁻³) buffer and then with 10⁻⁴ mol dm⁻³ HClO₄ acid solution. The glass electrode was then kept immersed in the appropriate solvent medium for equilibration the meter readings of 10⁻⁴ mol dm⁻³ HClO₄ and other solutions with unknown H⁺ ion concentrations were taken. The process was repeated to examine the reproducibility of the results. The calibration is to be performed in each solvent composition and for each set of measurement.

After the measurement, the glass electrode was dipped in 1N HCl for ten minutes and then kept in distilled water. The correction factors (log U_H) determined in the way described previously, are given in the Table 1.

Results :

The thermodynamic dissociation constants for the reaction(1) is represented by

$$K_T = \frac{a_A \cdot x \cdot a_{H^+}}{a_{AH^+}} = \frac{c_A \cdot x \cdot c_{H^+}}{c_{AB^+}} \cdot x \frac{f_A \cdot x \cdot f_{H^+}}{f_{AH^+}} \approx \frac{c_A \cdot x \cdot c_{H^+}}{c_{AH^+}} \dots (2)$$

(In very dilute solutions)

$$\text{Thus, } pK_T = pH + \log \frac{[AH^+]}{[A]} \quad \dots (3)$$

$$= B + \log U_H + \log \frac{[AH^+]}{[A]} \quad \dots (4)$$

$$= B + \log U_H + \log \frac{d - d_M}{d_1 - d} \quad \dots (5)$$

the terms have the usual significance as described previously^{2,3}

$$\text{Moreover, } [H^+]_{\text{Total}} = [H^+] + [AH^+] \quad \dots (6)$$

$$\text{and } [A]_{\text{Total}} = [A] + [AH^+] \quad \dots (7)$$

Thus, with the use of the appropriate values, pK-values could be determined. Tables 2 - 6 gives the result of dissociation constants in the mixed solvents. The average of pK-values are recorded in Table 7.

The ionic strength of the solutions range between 1.5 - 3.5 x 10⁻³ mol dm⁻³.

Discussions :

Since the pK-values are determined at low concentrations of acid and ionic strengths, these are regarded to be thermodynamic values. Furthermore, since the solutions are dilute, the "medium effect" could be easily determined as $\gamma_{\pm} \rightarrow 1$ and $\gamma_i = \gamma_{\pm} \cdot \nu_i \approx \gamma_{\pm}$. This is particularly important to elucidate the role of the solvents.

The results (Table 7) show that the pK-values of 2,2-bipyridine and 1,10-phenanthroline decrease with the addition of organic solvents but the change is appreciable in formamide + water mixtures

at the beginning but the subsequent changes are small.

It is obvious that the greater solubility of the ligands in organic solvents and the solvational properties of bipy H^+ , phen H^+ and H^+ ions are responsible for the changes in pK-values² but the solubility of bipy is probably much higher than phen at higher percentages of dmf + water mixtures. Moreover, the pK of 1,10-phenanthroline decreases, reaches a maximum at about 80 wt% of organic solvents and then decreases. No such behaviour is observed in case of 2,2'-bipyridine.

However, the pK-values decrease, reach minimum at about 40 wt% and then increase again in case of formamide + water mixture (Figs. 1,2).

The pK-values when plotted against mole-fraction or $\frac{1}{D}$ show linearity at best upto 50 wt% beyond which considerable deviations occur (Figs 3 & 6). This is particularly surprising in case of formamide + water mixtures when the dielectric constants are higher than 78.5. It is obvious that the specific solute-solvent interactions are of great importance in determining the pK-values.

The ligands are expected to be more basic in these basic solvents and basically should be greater in formamide + water mixtures which is not actually observed.

The changed behaviour of the ligands are due to differences in the characters of the solvents.

Formamide is highly basic hydrogen-bonding solvent ($\mu = 3.75D$) with high dielectric constant (109.5) and whereas dmf is weakly basic dipolar aprotic solvent with low dielectric constant. Though the dielectric constant of dmf is comparable to that of methanol but the changes in pK-values are different in these two solvents due to differences in solute-solvent interactions. The bipy H^+ and phen H^+ are likely to be stabilised by hydrogen bonding in these solvents. The probability of hydrogen-bond formation by bipy or phen will diminish with increasing concentrations of dmf (but not in case of formamide). In both cases, however, solute-solvent interactions and dispersion forces would be high but dipole-dipole interactions are greater in cases of phen ($\mu = 4.11D$)^{11,12} than that of trans bipy ($\mu = 0.91D$)^{11,12}. Thus, the total effects of ion-dipole interactions and dipole-dipole interactions would determine the 'medium effects'¹³.

In order to throw light on solvent basicity and ion-solvent interactions, it is necessary to dissect ΔG_t° into $\Delta G_{t(e1)}^\circ$ and $\Delta G_{t(none1)}^\circ$. In spite of the limitations, the simple Born equation¹⁴ can be utilised to calculate the $\Delta G_{t(e1)}^\circ$ for the reaction (1) using the relation

$$\Delta G_{t(e1)}^\circ = 166 \times 4.184 \left(\frac{1}{D} - 0.0127 \right) \left(\frac{1}{r_{H^+}} - \frac{1}{r_{AH^+}} \right)$$

r_{H^+} has been taken equal to 0.86 \AA ^{15,16} and $r_{phen H^+}$ or $r_{bipy H^+}$ has been calculated to be 3.70 \AA . It is apparent that the electrostatic contributions are considerable even in case of isoelectric reaction(1) due to the differences in radii of ions.

In view of the limitations of Born equation, one layer solvation model was also utilised¹⁷

$$\Delta G_{t(\text{el})}^{\circ} = \frac{NZ^2}{2} \left(\frac{1}{\epsilon_1} - 1 \right) \left(\frac{1}{a} - \frac{1}{b} \right) + \frac{NZ^2}{2} \left(\frac{1}{\epsilon_0} - 1 \right) \left(\frac{1}{b} \right)$$

$\epsilon_1 = 2$; a = crystallographic radii of ions

$b = a + \text{solvent radius.}$

ϵ_0 = bulk dielectric constant,

$r_{\text{H}_2\text{O}}$, r_{dmf} and $r_{\text{formamide}}$ have been taken from the literature.

$r_{\text{dmf} + \text{H}_2\text{O}}$ and $r_{\text{formamide} + \text{H}_2\text{O}}$ have been assumed to vary with solvent composition.

The Born equation and one layer model, however, give widely divergent results and we prefer simple Born equation.

It has been suggested that greater negative values of $\Delta G_{t(\text{nonel})}^{\circ}$ indicate increased basicity of the mixed solvents compared to water¹⁸. The $\Delta G_{t(\text{nonel})}^{\circ} = \left[\Delta G_{t}^{\circ} - \Delta G_{t(\text{el})}^{\circ} \right]$ values have been found to be increasingly negative in $\text{dmf} + \text{H}_2\text{O}$ mixtures indicating that the basicity increases with increasing dmf content. But in case of $\text{formamide} + \text{H}_2\text{O}$ mixtures, $-\Delta G_{t(\text{nonel})}^{\circ}$ is maximum at about 40 wt%, and then decreases which means that the basicity is maximum at about 40 wt%. The values of $-\Delta G_{t(\text{nonel})}^{\circ}$ is not consistent with the correction factors $\log U_{\text{H}}$ values. The $\log U_{\text{H}}$ values indicate that the basicity increases upto 80 wt% of dmf and then decreases in case of $\text{dmf} + \text{H}_2\text{O}$ mixtures whereas the basicity continually increases in case of $\text{formamide} + \text{H}_2\text{O}$ mixtures. The $\text{formamide} + \text{water}$ mixtures are much more basic than

those of the corresponding dmf + H₂O mixtures as well as alcohol + water mixtures.

In order to have better insight regarding the basicity of the solvent mixtures and ion-solvent interactions, attempts have been made to determine the free energies of transfer of hydrogen ions $\Delta G_t^{\circ}(\text{H}^+)$.

For the reaction (1) we have,

$$\begin{aligned} \Delta \Delta G_t^{\circ}(1) &= \Delta G_s^{\circ}(1) - \Delta G_w^{\circ}(1) \\ &= \Delta G_t^{\circ}(\text{A}) + \Delta G_t^{\circ}(\text{H}^+) - \Delta G_t^{\circ}(\text{AH}^+) \\ &= \Delta G_t^{\circ}(\text{H}^+) - \Delta G_t^{\circ}(\text{el})(\text{AH}^+) \\ \Delta G_t^{\circ}(\text{AH}^+) &= \Delta G_t^{\circ}(\text{A}) + \Delta G_t^{\circ}(\text{el})(\text{AH}^+) \\ \text{Thus, } \Delta G_t^{\circ}(\text{H}^+) &= \Delta \Delta G_t^{\circ}(1) + \Delta G_t^{\circ}(\text{el})(\text{AH}^+) \end{aligned}$$

From the experimental $\Delta \Delta G_t^{\circ}(1)$ and calculated $\Delta G_t^{\circ}(\text{el})(\text{AH}^+)$ (Born) values, the $\Delta G_t^{\circ}(\text{H}^+)$ values in different solvents have been calculated. The results are recorded in tables 8 and 9. Since the ΔG_t° value have been determined in very dilute solutions, the solutions may be regarded to be in their respective standard states.

The Born equation or other modified equations are strictly applicable to spherical ions. Thus, the use of Born equation in case of flat molecular ions like Phen H⁺ or bipy H⁺ may introduce some error. However, the limitations of Born equation or other

equations with adjusted radii or dielectric constant values are well-known¹⁹⁻²¹. The uncertainties in the radii values of spherically symmetrical ions are also known.

In spite of the limitations of calculating $\Delta G_{t(eL)}^{\circ}(AH^+)$, $\Delta G_{t(H^+)}^{\circ}$ values calculated using bipy or phen are in good agreement qualitatively and almost quantitatively in formamide + water and dmf + H₂O mixtures.

It is to be noted that deviations arising from an error in pK-values (± 0.02 pK units at low percentages to ± 0.05 pK units at high percentages) would account for a change in about ± 0.5 KJ in $\Delta G_{t(H^+)}^{\circ}$ values. The deviations are rather high in case of formamide + water mixtures and at higher percentages of dmf + water mixtures. The differences in $\Delta G_{t(H^+)}^{\circ}$ values in these solvents may be due to differences in solute-solvent interactions.

The comparison of $\Delta G_{t(H^+)}^{\circ}$ values however, are not possible due to lack of data.

The $\Delta G_{t(H^+)}^{\circ}$ values are negative indicating the spontaneity of transfer of H⁺ ions from water to mixed solvents. This is reasonable in view of the known basicities of dmf and formamide. However, $-\Delta G_{t(H^+)}^{\circ}$ increases with increase in dmf becomes maximum in the region 80 - 90 wt% but $-\Delta G_{t(H^+)}^{\circ}$ is maximum at about 40 wt% of formamide indicating that the basicity

is maximum in this region.

It is, however, difficult to correlate the "medium effects" with the solvent structure. In general, the addition of organic solvent to water first causes the enhancement of three-dimensional polymeric structure of water. Next, disruption of solvent structures (water, dmf etc.) and formation of H_2O -formamide or H_2O -dmf molecules take place and ultimately at higher percentages (above 70% by wt% of formamide and 80% by wt. of dmf) disruption of H_2O -organic solvent bond takes place. Thus the marked changes in the solvent structures take place at about 20 - 30 wt% and 75 - 90 wt% of organic solvents. Therefore, the solute-solvent interactions and basicity maximum would probably be observed in these regions.

Table - 1

Correction factors at various organic solvent

dmf				Formamide			
Wt%	Mole-Fraction	$\frac{1}{D} \times 10^2$	Correction factor	Wt%	Mole-Fraction	$\frac{1}{D} \times 10^2$	Correction factor
0	0	1.27	-	0	0	1.27	-
9.52	0.025	1.31	- 0.13	11.17	0.048	1.21	- 1.52
19.14	0.055	1.34	- 0.29	22.06	0.103	1.14	- 1.88
28.87	0.091	1.38	- 0.46	32.67	0.163	1.08	- 2.20
38.64	0.135	1.45	- 0.75	43.01	0.232	1.04	- 2.42
48.64	0.180	1.52	- 0.95	53.10	0.312	0.99	- 2.64
58.68	0.259	1.63	- 1.13	62.94	0.405	0.95	- 2.80
68.84	0.352	1.76	- 1.35	72.54	0.513	0.92	- 3.01
79.11	0.483	1.96	- 1.52	81.91	0.644	0.90	- 3.19
89.58	0.675	2.24	- 1.36	91.06	0.801	0.89	- 3.40

Table - 2

Dissociation constants of 2,2'-bipyridine at 48.64% by wt of dmf

Concentration of 2,2'-bipyridine soln. = 5×10^{-3} mol dm⁻³

Temp = 298K

Fractions of the ligand neutrali- sed (10^{-3} mol dm ⁻³)	Meter readings	pH after correction	pK	Average pK
1	2	3	4	5
1.5	3.96	3.01	2.64	
2.0	3.78	2.83	2.65	2.64
2.5	3.59	2.64	2.64	
3.0	3.40	2.45	2.63	
3.5	3.22	2.27	2.64	

Table - 3

Dissociation constants of 1,10-phenanthroline at 38.64% by wt% of dmf.

(pH-metric)

Concentration of 1,10-phenanthroline soln = 5×10^{-3} mol dm⁻³

Fraction of the ligand neutralised (10^{-3} mol dm ⁻³)	Meter readings	pH after correction	pK	Average pK
1.5	4.64	3.89	3.52	
2.0	4.46	3.71	3.53	3.53
2.5	4.29	3.54	3.54	
3.0	4.10	3.35	3.53	
3.5	3.89	3.14	3.51	

Table - 4

Dissociation constants of 2,2'-bipyridine at 53.10% by wt. of Formamide

Concentration of 2,2'-bipyridine soln = 5×10^{-3} mol dm⁻³

Temp = 298K

Fraction of the ligand neutralised (10^{-3} mol dm ⁻³)	Meter readings	pH after correction	pK	Average pK
1	2	3	4	5
1.5	6.15	3.51	3.14	
2.0	5.97	3.33	3.15	
2.5	5.80	3.16	3.16	3.15
3.0	5.61	2.97	3.15	
3.5	5.43	2.79	3.16	

Table - 5

Dissociation constants of 1,10-phenanthroline at 53.10%^{wt} of formamide

Concentration of 1,10-phenanthroline soln. = 5×10^{-3} mol dm⁻³

Fraction of the liquid neutralised (10 ⁻³ mol dm ⁻³)	Meter readings	pH after correction	pK	Average pK
1	2	3	4	5
1.5	6.33	3.69	3.32	
2.0	6.14	3.50	3.32	
2.5	5.96	3.32	3.32	3.32
3.0	5.78	3.14	3.32	
3.5	5.60	2.96	3.33	

Dissociation constants of 1,10-phenanthroline at 38.64% by wt% of dmf

(Spectrophotometrically)

Temp = 298K

Cell length = 1 cm.

Analytical wavelength = 310 nm.

O.d. of the molecular form (d_M) = 0.210

O.d. of the ionic form (d_I) = 1.17

Meter reading	pH after correction	observed d	$d - d_M$	$d_I - d$	$\log \frac{d - d_M}{d_I - d}$	pK
1	2	3	4	5	6	7
4.52	3.77	0.535	0.325	0.635	- 0.29	3.48
4.45	3.70	0.580	0.370	0.590	- 0.20	3.50
4.37	3.62	0.615	0.405	0.555	- 0.14	3.48
4.24	3.49	0.690	0.480	0.475	+ 0.01	3.50
4.19	3.44	0.716	0.506	0.454	+ 0.05	3.49
4.14	3.39	0.750	0.540	0.420	+ 0.11	3.50

Average pK value from O.d. reading = 3.49 ± 0.01

Table - 7

Wt% of dmf	pK _T of 2,2'-bipy			pK _T of 1,10-phen			Wt% of Forma- mide	pK _T of bipy (pH-met- ric)	pK _T of 1,10-phen (pH-metric)
	pH- metric	Spectro- photo- metric	Average	pH- metric	Spectro- photo- metric	Average			
0	4.47		4.47	5.05		5.05	0	4.47	5.05
9.52	4.07	4.03	4.05	4.48	4.45	4.47	11.17	3.23	3.69
19.14	3.75	3.71	3.73	4.17	4.14	4.16	22.06	3.13	3.50
28.87	3.42	3.36	3.39	3.91	3.87	3.89	32.67	3.09	3.31
38.64	2.98	2.92	2.95	3.53	3.49	3.51	43.01	3.08	3.26
48.64	2.64	2.60	2.62	3.30	3.25	3.28	53.10	3.15	3.32
58.68	2.34	2.27	2.31	3.03	2.97	3.00	62.94	3.25	3.41
68.84	1.82	1.74	1.78	2.81	2.75	2.78	72.54	3.32	3.44
79.11	1.46	1.38	1.42	2.50	2.42	2.46	81.91	3.43	3.49
89.58	1.28	1.18	1.23	2.66	2.58	2.62	91.06	3.49	3.54

Table - 8

Free-energy of transfer of Protons and related properties in dmf + H₂O mixture
Temp. = 298K

Wt% of dmf	ΔG_t° (kJoules)		$\Delta G_t^{\circ}(\text{el})$ (kJoules)				$\Delta G_t^{\circ}(\text{H}^+)$ (kJoules)						
	Bipy	Phen	r = (A)		r = (B)		Bipy	(A)		Average	(B)		Average
			0.86	3.70	0.86	3.70		Phen	Phen		Phen	Phen	
9.52	- 2.40	- 3.31	0.32	0.06	5.55	1.08	- 2.32	- 3.23	- 2.78	- 1.32	- 1.23	- 1.28	
19.14	- 4.22	- 5.08	0.57	0.13	10.93	3.25	- 4.09	- 4.95	- 4.52	- 1.97	- 1.83	- 1.90	
28.87	- 6.16	- 6.62	0.89	0.21	15.59	3.62	- 5.95	- 6.41	- 6.18	- 2.64	- 3.10	- 2.87	
38.70	- 8.67	- 8.79	1.45	0.34	20.02	4.58	- 8.33	- 8.45	- 8.39	- 4.09	- 4.21	- 4.15	
48.64	-10.56	-10.10	2.02	0.47	24.20	5.72	-10.09	- 9.63	- 9.86	- 4.84	- 4.38	- 4.61	
58.68	-12.32	-11.70	2.91	0.67	28.28	6.86	-11.65	-11.03	-11.34	- 5.46	- 4.84	- 5.15	
68.84	-15.35	-12.95	3.96	0.92	31.91	8.23	-14.43	-12.03	-13.23	- 7.12	- 4.72	- 5.92	
79.11	-17.40	-14.78	5.57	1.29	35.94	9.26	-16.11	-13.49	-14.80	- 8.14	- 5.52	- 6.83	
89.58	-18.49	-13.86	7.91	1.84	39.36	10.32	-16.65	-13.02	-14.83	- 8.17	- 3.54	- 5.86	

A = Calculated using Born Equation.

B = Calculated using one layer continuum model.

Table - 9

Free-energy of transfer of Protone and related properties in Formamide + H₂O mixtures

Temp. 298K

Wt% of Formamide	ΔG_{t}° (kJoules)		ΔG_{t}° (el) (kJoules)				ΔG_{t}° (H ⁺) (kJoules)					
	Bipy	Phen	A		B		A			B		
			r = 0.86	r = 3.70	r = 0.86	r = 3.70	Bipy	Phen	Average	Bipy	Phen	Average
11.17	-7.07	- 7.75	-0.48	-0.11	-6.31	-0.38	-7.18	-7.86	-7.52	-7.45	- 8.13	- 7.79
22.06	-7.65	- 8.84	-1.05	-0.24	-5.10	-1.09	-7.89	-9.08	-8.48	-8.75	- 9.93	- 9.34
32.67	-7.87	- 9.93	-1.53	-0.36	-7.53	-1.39	-8.23	-10.24	-9.26	-9.26	-11.32	-10.29
43.01	-7.93	-10.21	-1.86	-0.43	-9.52	-1.79	-8.36	-10.64	-9.50	-9.72	-12.00	-10.86
53.00	-7.53	- 9.87	-2.26	-0.52	-11.90	-2.46	-8.05	-10.39	-9.17	-9.99	-12.33	-11.16
62.94	-6.96	- 9.36	-2.58	-0.60	-13.98	-2.78	-7.56	- 9.96	-8.76	-9.74	-12.14	-10.94
72.54	-6.56	- 9.19	-2.82	-0.66	-16.20	-3.44	-7.22	- 9.85	-8.54	-9.90	-12.63	-11.27
91.91	-5.93	- 8.90	-2.98	-0.69	-18.29	-3.74	-6.62	- 9.59	-8.10	-9.67	-12.64	-11.16
91.06	-5.59	- 8.62	-3.06	-0.71	-20.28	-4.40	-6.30	- 9.33	-9.82	-9.99	-13.02	-11.51

A = Calculated using Born Equation

B = Calculated using one layer continuum model.

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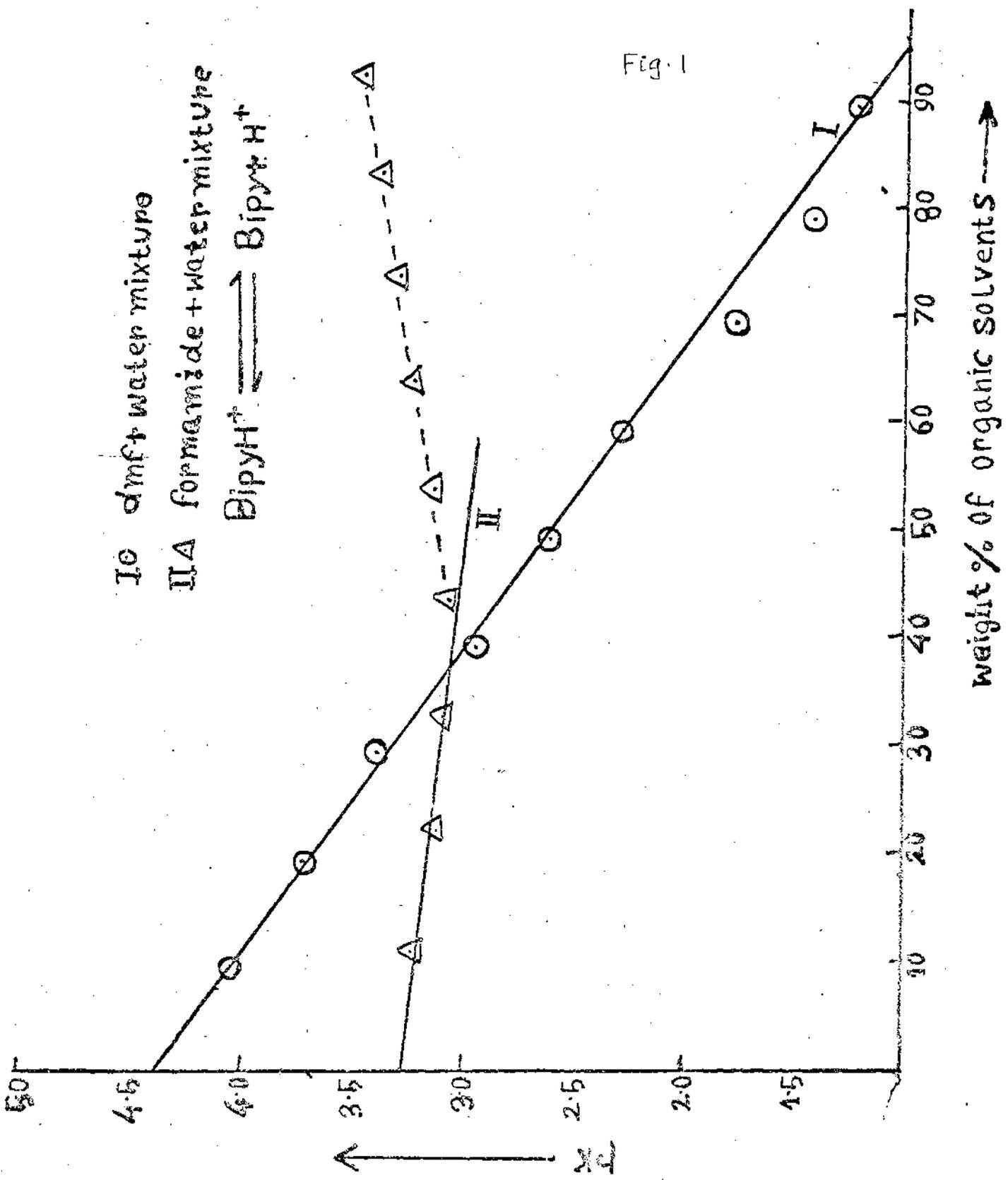
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Ic dmf + water mixture

IIa formamide + water mixture



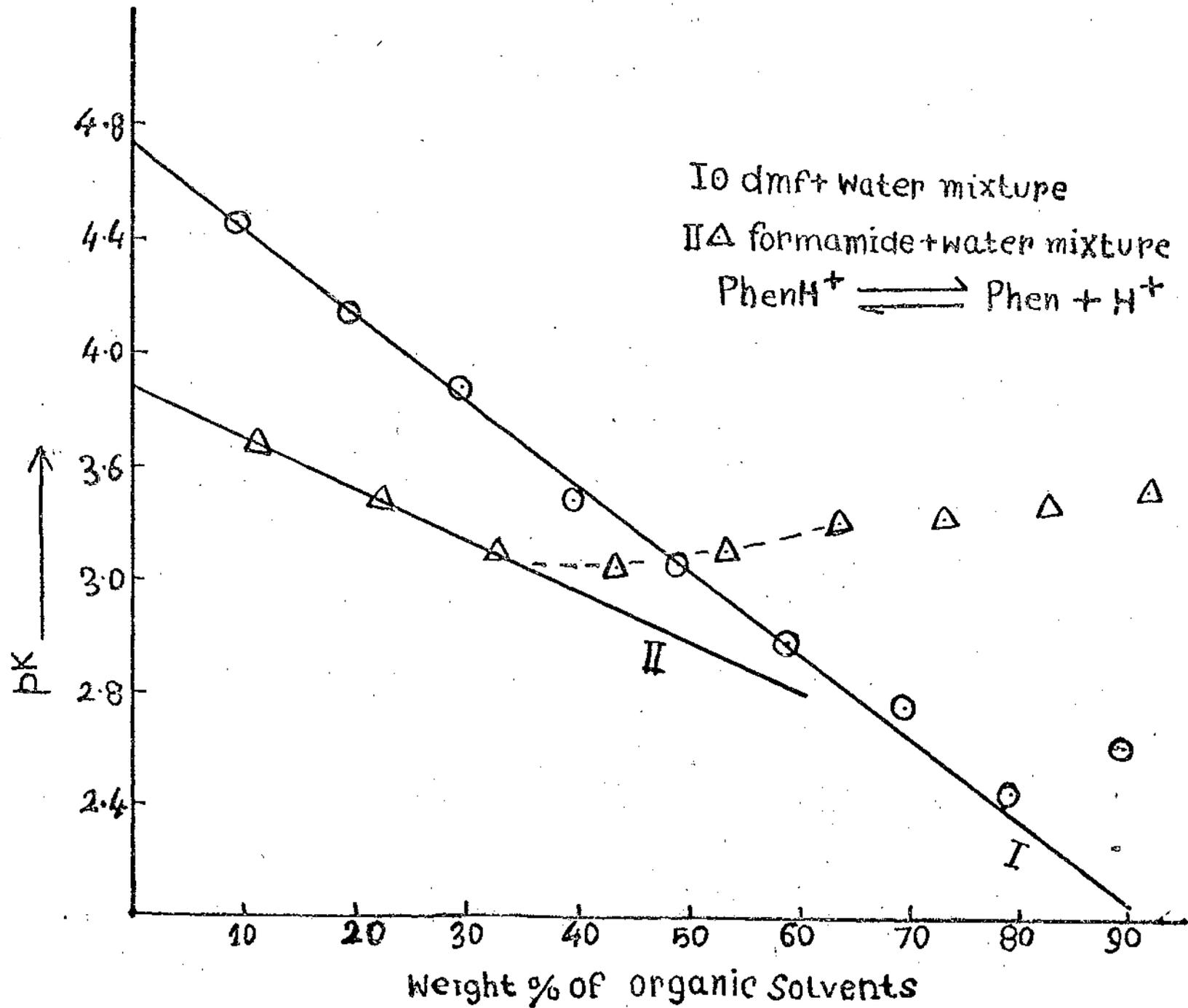
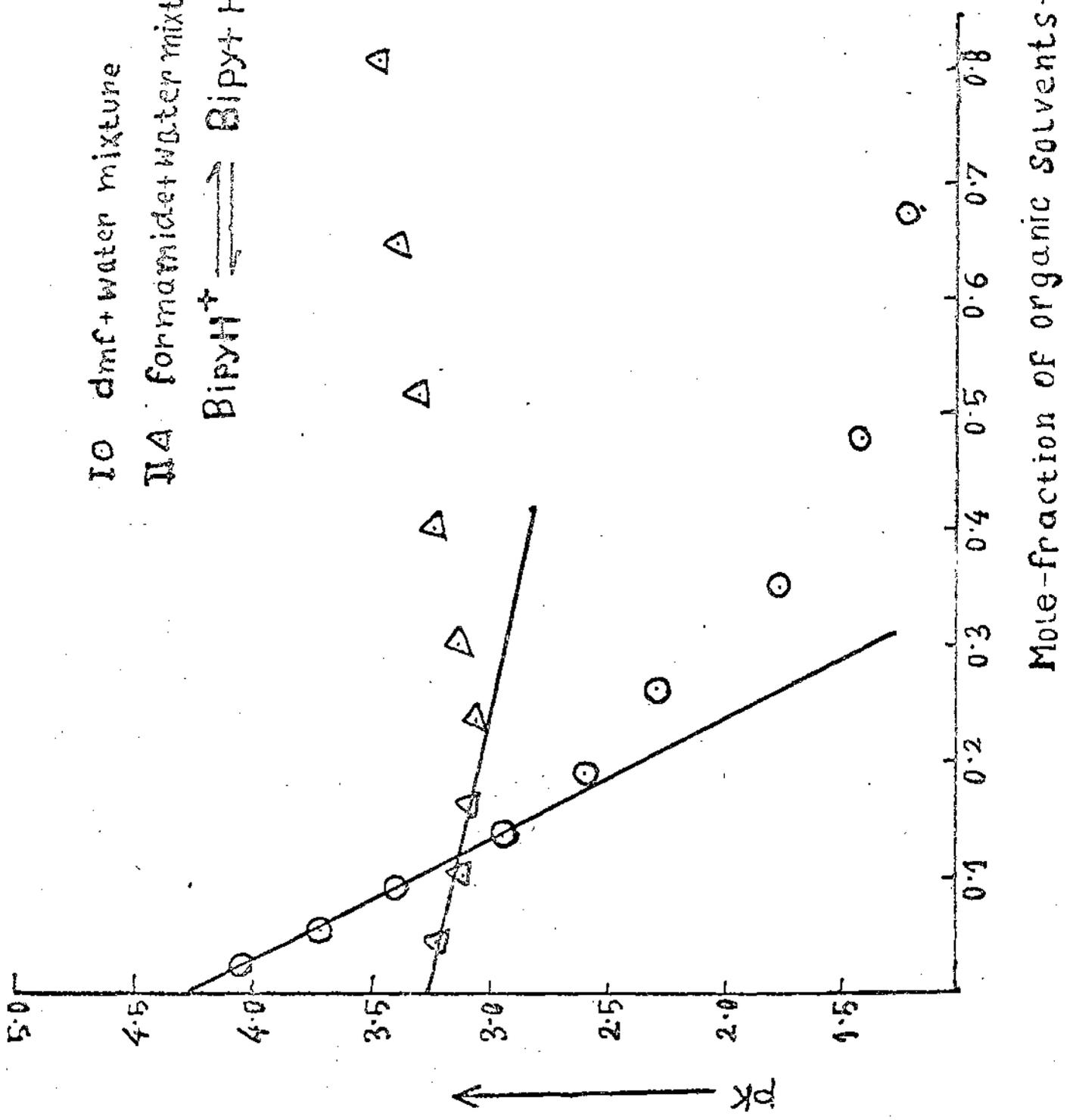


Fig. 2

IO dmf+water mixture
 II A formamide+water mixture
 $\text{BipyH}^+ \rightleftharpoons \text{Bipy} + \text{H}^+$

Fig. 3



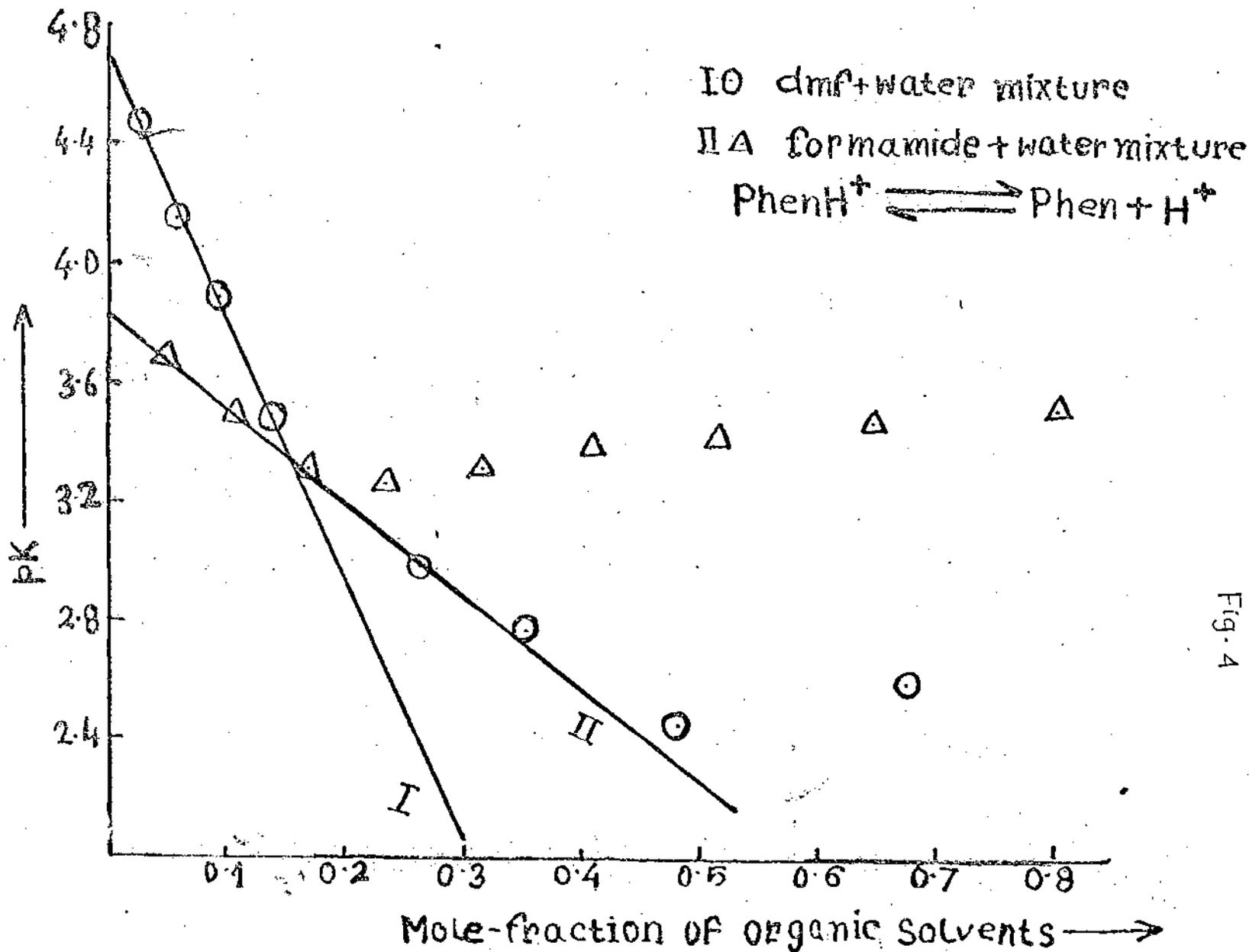
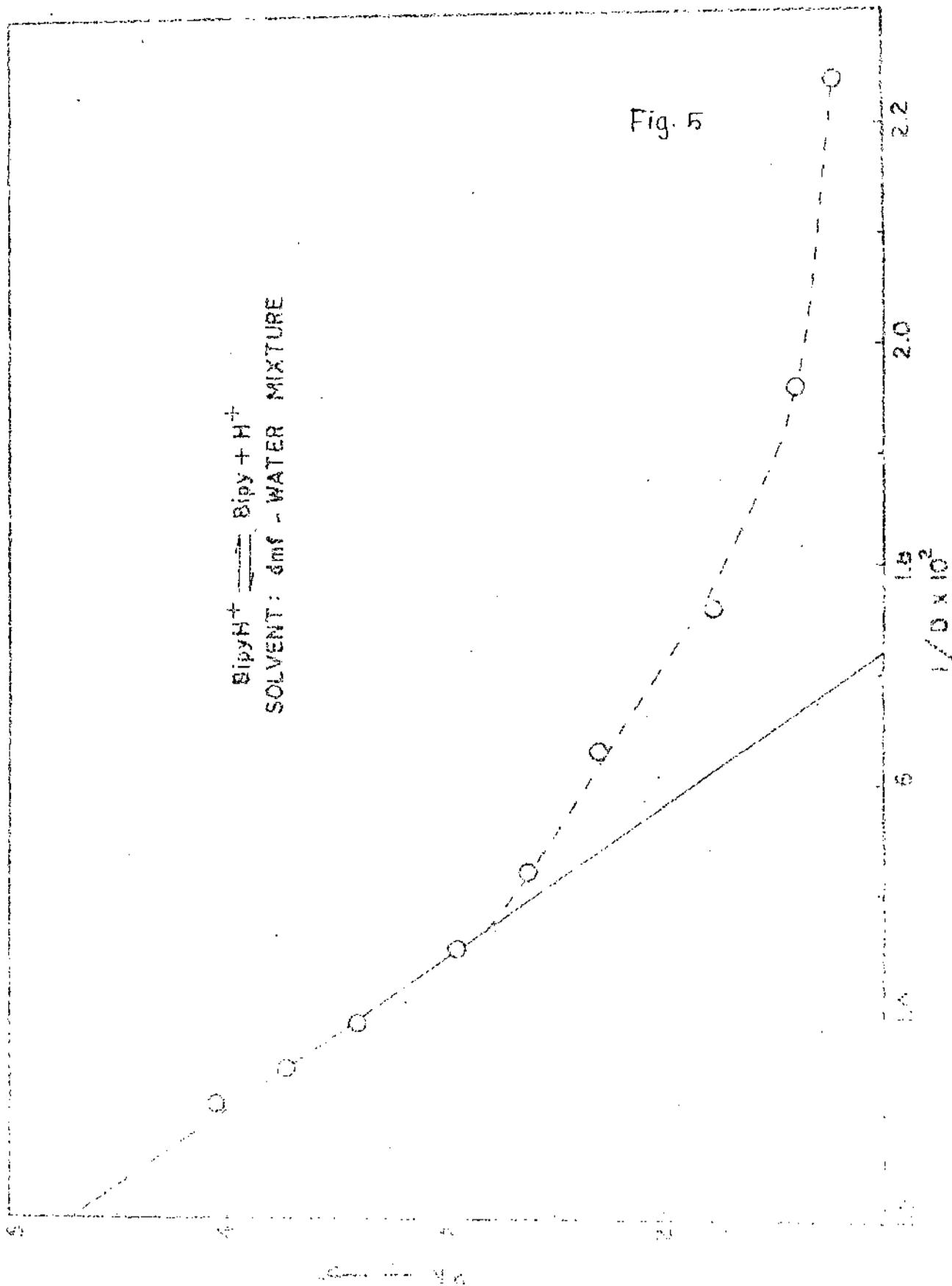
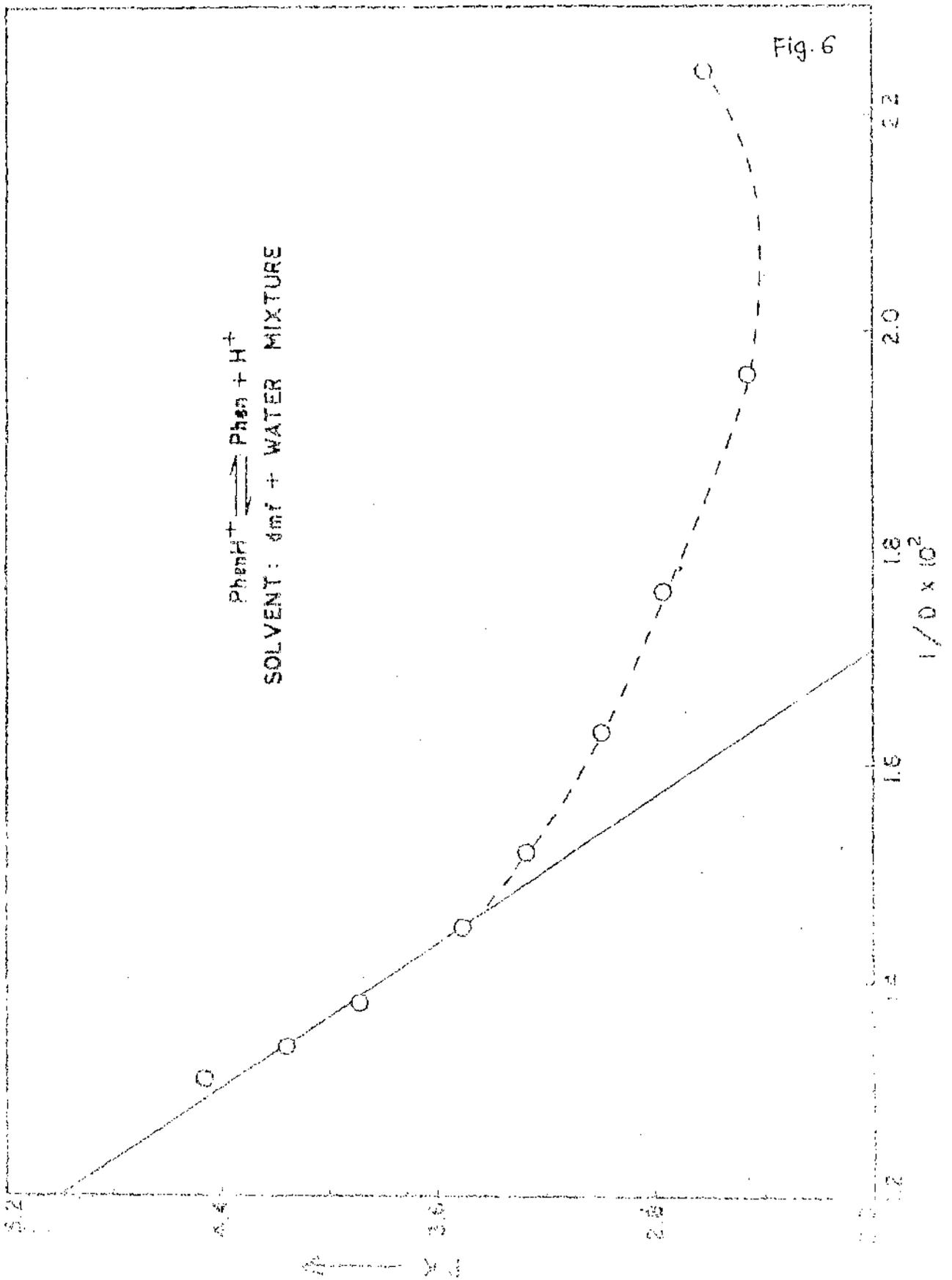


Fig. 4

$\text{BipyH}^+ \rightleftharpoons \text{Bipy} + \text{H}^+$
SOLVENT: dmf - WATER MIXTURE

Fig. 5

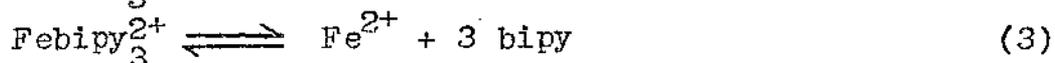
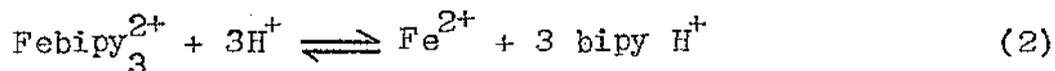
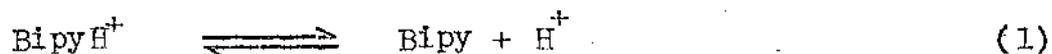




Section - IV

The role of solvents on the dissociation constants of the weak acids are widely studied and relatively known, though clear picture is yet to come. But comparatively little is known about the effect of solvents on the dissociation constants of metal complexes. In order to explore the role of solvents on the dissociation constants of metal chelates, Pal and Lahiri¹ studied the equilibrium constants of ferric salicylate and ferric sulphosalicylate in a number of equidielectric mixtures of different solvent compositions. But owing to lack of fundamental data on dissociation constants of phenolic groups, the effect of solvents could not be predicted.

Hazra, Lahiri and others²⁻⁵ studied the dissociation constants of ferrous-tris-bipyridine complex (ferrodiin) and ferroin in different mixed solvents so as to get informations and insight regarding the effect of solvents on the equilibrium constants of



Their works gave us the impetus to study the effect of other solvents on the reaction (1), (2) and (3) so that comparative study can be made regarding the behaviour of different solvents on the reaction (1) to (3).

In the present section, we describe the results of our studies

on the dissociation constants for the reactions (1) to (3) in different dmsc. + water and formamide + water mixtures.

Experimental

Dimethylsulphoxide (Baker analyzed) and formamide (G.R.E. Merck) were purified in the same way as described in the previous sections. All the reagents were G.R.E. Merck grade. Ferrous ammonium sulphate (G.R.E. Merck) was dissolved in known quantity of HClO_4 . The purity was checked by estimation of the iron-content analytically with standard potassium dichromate in the usual way. The solution was utilized within several hours. For each set of measurement freshly prepared solution was used. 2,2'-bipyridine solution was prepared by directly weighing bipyridine (G.R.E. Merck) and dissolving it in the appropriate solvent.

The addition of Fe^{2+} ion to bipyridine gives an intense red colouration with an absorption maximum at 524 nm (absorption maxima changes to 522 nm in mixed solvents having high percentages of organic solvents). The absorption maxima remained unchanged with change in pH, but the o.d. of the solution (same Fe^{2+} and ligand) was found to decrease with increasing H^+ ion concentrations. However, due to basicity of the solvent mixtures relatively high concentrations of acid are necessary to study the complexes. It has been assumed that under the experimental conditions used, Febipy_2^{2+} and Febipy_2^{2+} were not formed as suggested by Kolthoff et.al.⁶, Febipy_3^{2+} alone was formed in aqueous and mixed solvents. We have also observed that mono complex is formed only when Fe^{2+}

is present in large excess compared to bipy. The complex is rapidly converted to $\text{Fe}(\text{bipy})_3^{2+}$ but no $\text{Fe}(\text{bipy})_2^{2+}$ could be detected.

The extinction co-efficients (ϵ) of ferrodian were determined from the measurements of O.d.'s of solutions containing 10 - 20 fold excess of ligand to different concentrations of Fe^{2+} ion at wave lengths 520 nm, 522 nm and 530 nm. Under the condition, the concentration of the complex could be taken equal to ferrous ion. This is confirmed by the fact that for the same concentration of ferrous ion and different concentration of bipyridine, the O.d. readings were same. The extinction co-efficients (ϵ) in different percentages of mixed solvents are given in tables 1 - 3.

For the determination of the stability constants, O.d.'s of solutions containing different concentrations of ferrous ion and bipyridine were measured (ferrous ion was added to bipyridine) at 520 nm, 522 nm and 530 nm. Measurements were made at 298K.

The concentrations of the complex were calculated from O.d. readings and extinction co-efficient values at these wave lengths. The concentrations of the complex came out to be almost equal at these wave lengths. For the calculation of equilibrium constant for the reaction (2), the average values of the complex obtained from measurements at three wavelengths were taken.

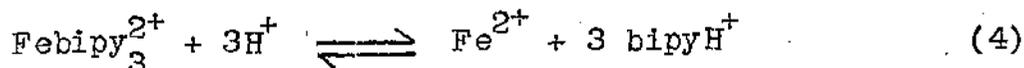
Optical density values were taken with a Beckman DU 2

spectrophotometer maintained at 298K. Other experimental details are the same as described in the previous section.

Results

Dissociation constant of ferrodin

The equilibrium between ferrodin and a strong acid may be represented as



Thus

$$\begin{aligned} k_a &= \frac{c_{\text{Fe}^{2+}} \times c_{\text{bipyH}^+}^3}{c_{\text{Fe}(\text{bipy})_3^{2+}} \times c_{\text{H}^+}^3} \times \frac{f_{\text{Fe}^{2+}} \times f_{\text{bipyH}^+}^3}{f_{\text{Fe}(\text{bipy})_3^{2+}} \times f_{\text{H}^+}^3} \\ &= k_c \times \frac{f_{\text{Fe}^{2+}} \times f_{\text{bipyH}^+}^3}{f_{\text{Fe}(\text{bipy})_3^{2+}} \times f_{\text{H}^+}^3} \end{aligned} \quad (5)$$

if $f_{\text{Fe}^{2+}} = f_{\text{Fe}(\text{bipy})_3^{2+}}$ and $f_{\text{bipyH}^+} = f_{\text{H}^+}$, k_c becomes equal to k_a . But since bipyH^+ is likely to have much larger size, it may that $f_{\text{bipyH}^+} \neq f_{\text{H}^+}$, which would need an accurate determination of f_{bipyH^+} .

Accurate determination of thermodynamic dissociation constants are possible only in dilute solutions where activity co-efficients are unity. In concentrated solutions the determination of activity co-efficients are difficult. Theoretical equations like Debye - Hückel equation or semi-empirical equations like Davies⁷ equations are limited use and these equations are applicable only in dilute solutions. Deviations are appreciable

in concentrated solutions. The complexity increases much more in mixed solvents. The orientation of solvent molecules around the ions are not known and it is difficult to know the extent of solute-solvent interactions in mixed solvents.

In mixed solvent it is convenient to separate activity co-efficients of the *i*-th species into factors

$$\gamma_i = m\gamma_i \cdot s\gamma_i^8 \quad (6)$$

The 'salt-effect' $s\gamma_i$ varies with the solute concentration. Simple Debye-Hückel equation with appropriate allowances for the effect of altering the dielectric constant of the medium *s* can be used to estimate $s\gamma_i$ when the ionic species are involved. The limitations which affect the actual determination of activity co-efficients in aqueous solutions would be much more in mixed or non-aqueous solutions. In dilute solutions $s\gamma_i \rightarrow 1$ and thus only the 'medium effects' with which we are concerned in the study of dissociation constants will be involved.

In view of the above facts the present work has been carried out in solutions of μ of the order of 10^{-3} mol dm⁻³ (ionic strengths were of order 1.4×10^{-3} to 3.3×10^{-3} mol dm⁻³) where it is reasonable to assume $f_{Fe^{2+}} = f_{Fe(bipy)_3^{2+}}$ and $f_{bipyH^+} = f_{H^+}$ (slight discrepancy, if any, may be neglected). Thus k_c becomes equal to thermodynamic equilibrium constant k_a .

Now

$$(\text{bipy H}^+) = (\text{bipy}) - 3(\text{Fe bipy}_3^{2+}) - (\text{bipy}) \quad (7)$$

Total

(bipyH⁺) is calculated where necessary from previous section taking appropriate pK values.

The concentration Fe²⁺ is calculated from the relation

$$[\text{Fe}^{2+}]_{\text{free}} = [\text{Fe}^{2+}]_{\text{Total}} - [\text{Fe bipy}_3^{2+}] \quad (8)$$

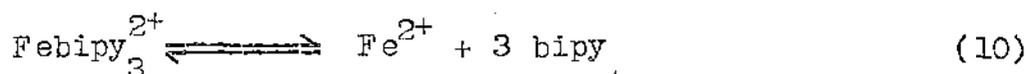
The measurement of the hydrogen ion concentrations of the solutions containing the complexes and bipyH⁺ are difficult. However, we have calculated H⁺ ion concentrations in the solutions from meter-readings after appropriate corrections.

The equilibrium constants for the reaction (2) in dmsO + H₂O and in formamide + H₂O mixtures are given in table 4 - 5.

The equilibrium constants

$$K = \frac{[\text{Fe}^{2+}] [\text{bipy}]^3}{[\text{Fe bipy}_3^{2+}]} \quad (9)$$

for the reaction



in different solvents are given by

$$K_{\text{dissn.}} \text{Fe bipy}_3^{2+} = k_a \times k_T^3$$

The results are given in Table - 6.

Discussions :-

It has been found that extinction coefficient of the complexes are higher in mixed solvents and the trend is quite regular in dmsO + water mixtures. The extinction coefficient increases reaches a maximum at about 72 wt% but decreases from about 82% and onwards. The trend, however, is some what different in formamide + water mixtures where maxima are observed at about 63 wt% and 82 wt% (Table - 3). These results cannot be correlated with the solvent dielectric constant or other known solvent properties. However, since the extinction coefficients are related to the oscillator strengths, it is expected that oscillator strengths would change with change in solvent compositions obviously due to change in solute-solvent interactions.

The results show that pK-value for reaction(2) slightly decreases with the introduction of organic solvents but increases with increase in organic component. In case of dmsO + water mixtures, pK-value reaches a minimum at about 30 wt% and then increases continuously but the pK-jump is very much conspicuous at about 82 wt% dmsO. In case of formamide + water mixtures, the pK-value increases, reaches a maximum at about 53 wt% of formamide, then decreases but increases again at 82 wt% formamide. This is shown in Fig. 1. Thus, we find that ΔG_t° in most cases are positive i.e. the reaction is non-spontaneous in organic solvent mixtures. However, ΔG_t° values for the reaction (3) are increasingly negative in dmsO + water mixtures indicating

that the reaction (3) is spontaneous i.e. the dissociation of Febipy_3^{2+} is favoured in mixed solvents. Similar conclusions may be derived in case of formamide + water mixtures. As in case of reaction (2), significant changes are also observed between 20 - 30 wt% of dmsO and in the region 43 to 53 wt% and 82 wt% of formamide. The results indicate that Febipy_3^{2+} is less stable in these organic solvent mixtures but the stability is less in formamide + water mixtures.

The reasons may be

- 1) Increase in basicity of the solvent mixtures and consequent removal of H^+ ions by the solvents.
- 2) Increase in solubility of bipyridine in the solvent mixtures.
- 3) The competition of the solvents to form complexes with Fe^{2+} and the consequent displacement of bipy by the solvents from Febipy_3^{2+} particularly when the dmsO or formamide concentrations are high.

All these reactions are isoelectric in character. Thus the decrease in dielectric constant should have slight effect on the dissociation constants, the change in pK-values must be due to solute-solvent interactions which is likely to be high in the solvent mixtures. The solvation of Febipy_3^{2+} and bipyH^+ should be less compared to those of Fe^{2+} and H^+ ions.

It is seen that the pK values for reaction (2) is a linear function of $\frac{1}{D}$ at best upto 50 wt% beyond which considerable

deviations arise. (Fig - 2). But it is impossible to get a clear idea of the solute-solvent interactions of the different ions in solutions.

These data however, could be utilised to have quantitative idea of $\Delta G_t^{\circ}(\text{Fe}^{2+})$ and $\Delta G_t^{\circ}(\text{Fe}(\text{bipy})_3^{2+})$ provided we know the solubility values of $\text{Fe}(\text{bipy})_3(\text{ClO}_4)_3$ and bipyridine and $\Delta G_t^{\circ}(\text{ClO}_4^-)$ in these solvent mixtures. For the reaction (3), we have

$$\Delta \Delta G_t^{\circ} (3) = \Delta G_t^{\circ}(\text{Fe}^{2+}) + 3 \Delta G_t^{\circ}(\text{bipy}) - \Delta G_t^{\circ}(\text{Fe}(\text{bipy})_3^{2+})$$

$$\Delta G_t^{\circ}(\text{Fe}(\text{bipy})_3^{2+}) = \Delta G_t^{\circ}[\text{Fe}(\text{bipy})_3(\text{ClO}_4)_2] - 2 \Delta G_t^{\circ}(\text{ClO}_4^-)$$

$$\text{and } \Delta G_t^{\circ}(\text{Fe}^{2+}) = \Delta \Delta G_t^{\circ}(3) - 3 \Delta G_t^{\circ}(\text{bipy}) + \Delta G_t^{\circ}(\text{Fe}(\text{bipy})_3^{2+})$$

It is thus apparent that the proper understanding of the role of the solvents on the dissociation constants and their successful utilization necessitate systematic investigations of the different aspects of the solution chemistry.

Table - 1

Media - 52.35% by weight of dmso

Temp. = 298K

Total Molar concentration of		pH	Optical density at 520nm	Extinction co-efficient at 520 nm	Optical density at 522nm	Extinction co-efficient at 522 nm	Optical density at 530nm	Extinction co-efficient at 530 nm
$Fe^{++} \times 10^5$	2,2'-bipyridine $\times 10^5$							
1	2	3	4	5	6	7	8	9
2.00	40.00	4.29	0.175	8750	0.177	8850	0.173	8650
3.00	60.00	4.18	0.267	8900	0.271	9030	0.262	8730
4.00	80.00	4.13	0.352	8800	0.355	8875	0.346	8650
5.00	100.00	4.09	0.442	8840	0.449	8980	0.435	8700
6.00	120.00	4.06	0.528	8800	0.532	8866	0.521	8683
7.00	140.00	4.03	0.612	8742	0.618	8820	0.608	8685
8.00	160.00	4.00	0.705	8812	0.705	8812	0.695	8687

Table - 2

Media - 43.01% by weight of formamide

Temp = 298K

Total Molar concentration of		Optical density at 520 nm	Extinction co-efficient at 520 nm	Optical density at 522nm	Extinction co-efficient at 522 nm	Optical density at 530nm	Extinction co-efficient at 530 nm
Fe ⁺⁺ X 10 ⁵	2,2'-bipyridine X 10 ⁵						
1	2	3	4	5	6	7	8
2.00	20.00	0.173	8650	0.175	8750	0.172	8600
3.00	30.00	0.261	8700	0.263	8766	0.258	8600
4.00	40.00	0.346	8650	0.348	8700	0.342	8550
5.00	50.00	0.430	8600	0.432	8640	0.427	8540
6.00	60.00	0.518	8633	0.520	8666	0.514	8566
7.00	70.00	0.604	8633	0.607	8671	0.600	8571
8.00	80.00	0.695	8687	0.697	8712	0.691	8637

Table - 3

Extinction co-efficient of tris-(2,2'-bipyridine)-Fe(II) complex at different percentage of aqueous dimethylsulphoxide and formamide solution.

Percentage of dmsO by wt	Extinction co-efficient at 520nm	Extinction co-efficient at 522 nm	Extinction co-efficient at 530 nm	Percentage of formamide by wt	Extinction co-efficient at 520 nm	Extinction co-efficient at 522 nm	Extinction co-efficient at 530 nm
1	2	3	4	5	6	7	8
10.87	8490	8553	8401	11.17	8400	8456	8333
21.53	8563	8633	8513	22 .06	8490	8553	8401
32.02	8654	8671	8581	32.67	8560	8610	8513
42.28	8716	8800	8685	43.01	8650	8700	8581
52.35	8827	8862	8734	53.10	8733	8833	8633
62.24	8873	8933	8827	62.94	8800	8880	8671
71.94	8969	9018	8873	72.54	8563	8600	8490
81.46	8843	8911	8800	81.91	8843	9000	8827
90.81	8761	8830	8734	91.06	8761	8850	8761

Temp = 298K

Table - 4

Media - 42.28% by weight of dmso.

Total concentration of $\text{Fe}^{2+} \times 10^5$	2,2'-bipyridine $\times 10^5$	pH after proper correction	Concentration of tris-(2,2'-bipyridine)- Fe(II) complex taking average from the three wavelengths. $\text{mol dm}^{-3} \times 10^5$	Concentration of free Fe^{2+} $\text{mol dm}^{-3} \times 10^5$	Concentration of bi- pyridine as Bipy H^+ $\text{mol dm}^{-3} \times 10^5$	$K_a \times 10^5$
1	2	3	4	5	6	7
10.00	12.00	3.35	3.550	6.450	0.940	1.70
10.00	15.00	3.36	4.467	5.533	1.105	2.01
12.00	10.00	3.27	2.863	9.137	1.035	2.29
12.00	13.00	3.27	3.779	8.221	1.220	2.56
14.00	15.00	3.14	4.352	9.648	1.532	2.10
16.00	14.00	3.11	4.065	11.935	1.443	1.89
16.00	18.00	3.11	5.223	10.337	1.862	1.47
18.00	20.00	3.08	5.841	12.159	2.007	2.93

Average = 2.13

Table - 5

Dissociation constants of tris-(2,2'-bipyridine)-Fe(II) complex in aqueous dimethylsulphoxide and Formamide solutions.

Wt% of dmso	K_a	pK	Wt% of Formamide	K_a	pK
1	2	3	4	5	6
0	7.56×10^{-5}		0	7.56×10^{-5}	
10.87	10.60×10^{-5}	3.97	11.17	9.34×10^{-6}	5.03
21.53	7.58×10^{-5}	4.12	22.06	8.96×10^{-6}	5.05
32.02	11.00×10^{-5}	3.93	32.67	7.63×10^{-6}	5.11
42.28	2.13×10^{-5}	4.67	43.01	5.01×10^{-6}	5.30
52.35	1.50×10^{-5}	4.82	53.10	2.75×10^{-6}	5.56
62.24	8.55×10^{-6}	5.07	62.94	5.67×10^{-6}	5.24
71.94	7.69×10^{-6}	6.11	72.54	1.42×10^{-5}	4.85
81.46	9.76×10^{-8}	7.01	81.91	1.21×10^{-5}	4.92
90.81	3.87×10^{-8}	7.41	91.06	2.53×10^{-5}	4.60

Table - 6

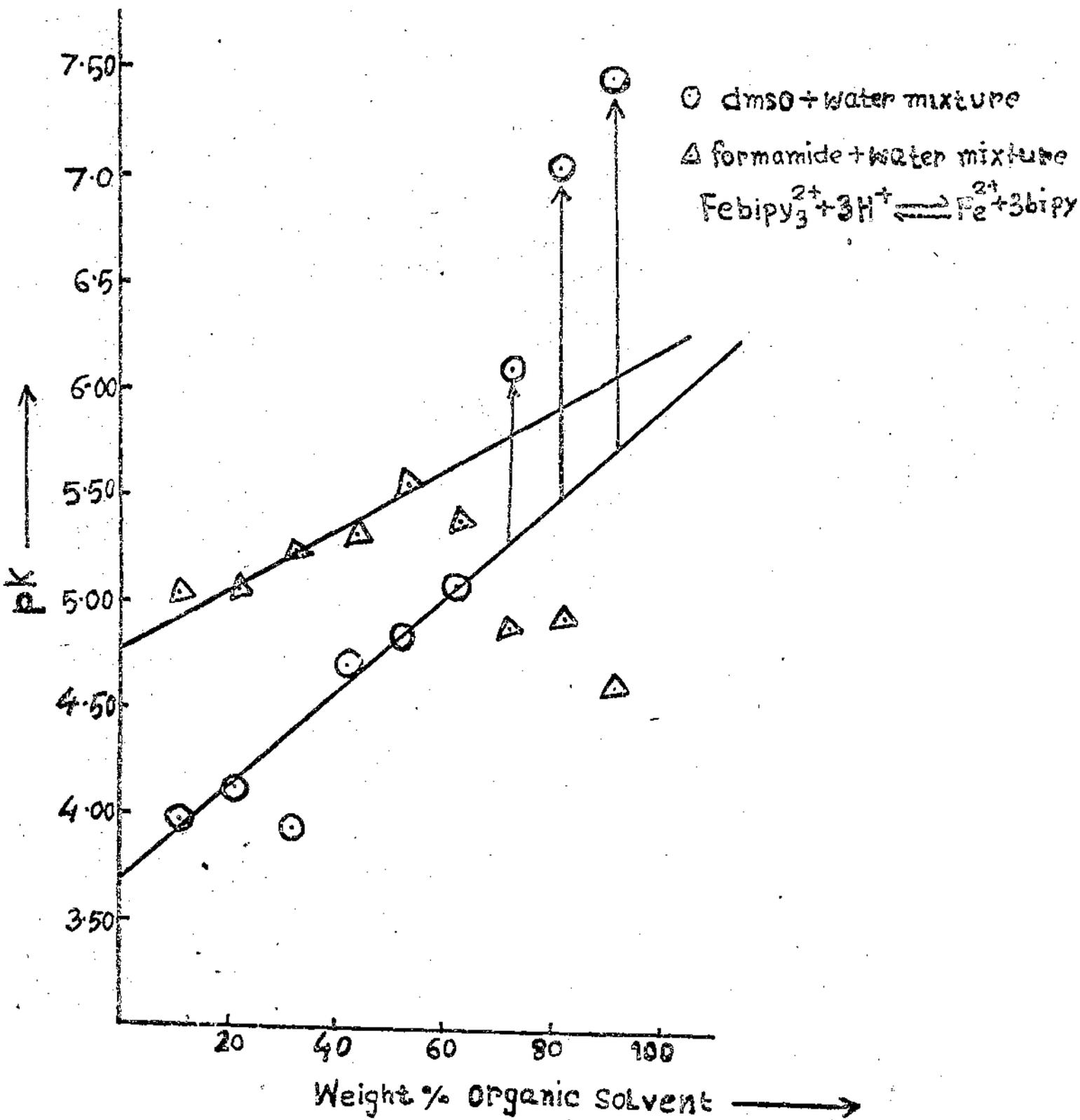
Values of $K_{\text{dissn.}} \text{Febipy}_3^{2+}$ in aqueous dimethyl sulphoxide and formamide solutions

Wt% of dmsO	$k_a \times k_T^3$	wt% of Formamide	$k_a \times k_T^3$
0	2.94×10^{-18}	0	2.94×10^{-18}
10.87	2.85×10^{-17}	11.17	1.91×10^{-15}
21.53	7.07×10^{-17}	22.06	3.65×10^{-15}
32.02	3.52×10^{-16}	32.67	4.10×10^{-15}
42.28	1.58×10^{-16}	43.01	2.88×10^{-15}
52.35	8.24×10^{-16}	53.10	9.76×10^{-16}
62.24	3.52×10^{-15}	62.94	1.01×10^{-15}
71.94	6.54×10^{-15}	72.54	1.56×10^{-15}
81.46	1.51×10^{-14}	81.91	8.21×10^{-16}
90.81	1.04×10^{-14}	91.06	8.57×10^{-16}

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Fig. 1



CHAPTER - I I

Section - I

One of the important aspects of Chemical Kinetics is the determination of the rates of Chemical reactions, which in turn, is capable of unfolding the various path-ways or mechanisms by which a chemical reaction actually takes place. The rates of reaction and reaction mechanisms can be suitably altered by the change in the conditions i.e. a reaction rate can be changed by several powers of ten in magnitude by merely changing the solvent medium in which the reactions occur.

Some of the manifestations of solvent effects have been satisfactorily explained on the basis of electrostatics ion-ion, ion-dipole, ion-induced-dipole interactions, hydrogen-bonding, (i.e. solvation of solute) internal cohesions of the solvent, protic or dipolar aprotic nature of solvents, viscosity and other understandable properties of solvents and solutes! But most of the behaviours of solutes in solution still elude our grasp. The elucidation of solvent influence on solutes is difficult in view of the obscurity as to the causes of such effects and enormity of the problems.

There has recently been considerable activity in the field of inorganic reaction kinetics, especially in the area involving the reaction of metal ions. With the development of fast-reaction techniques, it has become possible to examine in detail systems which had been outside the scope of the investigators. Thus the studies of the fast-reactions coupled with the traditional slow

reactions have helped us to understand the effects on reaction rates, the changes in the overall charge of the metal complex, of other ligands in solution, of the nature of the central metal ion and of solvent².

In view of the diverse nature of the subject and enormity of the works done in this field, it is difficult to give a satisfactory account of the kinetics in a very short review. Various kinetic aspects and solvent effects on the reaction rates and mechanisms have been elegantly put forward by Amis³, Amis and Hinton⁴, Bosolo and Pearson^{4,5}, Parker^{6,7} & others⁸⁻¹².

We do not intend to give detailed accounts of the various physico-chemical theories but we want to outline only a few salient features which would form the basis of our studies i.e. solvent effects on the rates and mechanisms of Inorganic complexes. Generally solvents can be classified into three broad headings :

- 1) Non-polar and weakly polar solvents
- 2) Dipolar aprotic solvents
- 3) Protic solvents

Of these dipolar aprotic and polar protic solvents are marked by the similarities of their physico-chemical properties

and also dissimilarities in their ability to solvate anions, particularly anions of high charge and small radii¹². These differences are manifested in profound rate effects particularly in bimolecular reactions involving anionic nucleophiles.

The contrasting response of anions and cations makes difficult the direct, simple interpretations of solvent changes in terms of mechanism of the reactions of cationic co-ordination compounds with anions. It is the counteraction of increased anion activity by decreased cation activity on transfer from protic to dipolar aprotic solvents that cause such reactions to be insensitive to solvent transfer¹².

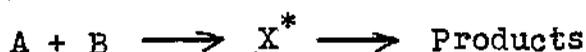
Parker and Co-workers^{6,7} have found bimolecular reactions between anions and polar molecules, especially bimolecular nucleophilic substitution reactions (SN_2 reactions) at saturated carbon atoms, to be much faster in dipolar aprotic solvents than in polar solvents.

Dipolar aprotic and polar protic solvent effects on rates have been the key phenomena which led Parker to the concept of solvent activity coefficients of an ionic solute. The aspects have been treated elsewhere.

It is well-known that the influence of solvent on reaction

rates is determined by the difference in free-energies, enthalpies and entropies of solvations of the reactants and the transition states.

From the absolute rate theory the equation for the reaction is



in which the rate constant in solution in general can be related to that in the ideal solutions by the equation

$$k' = k'_0 \frac{\gamma_A \cdot \gamma_B}{\gamma^*}$$

The activity coefficient γ relates the behaviour of a solute species to its behaviour of a solute species to its behaviour in ideal solutions and k'_0 is the specific velocity constant for the reaction in ideal solution.

It is apparent that the rates of reaction is pronouncedly influenced by the degree of solvation of the reactants and activated complex. If the activated complex is relatively much more solvated than the reactants the activity co-efficient of the complex is much less than in solvents in which it is not solvated and the rate of the reaction is much greater in the former solvents. For a solvent which solvates reactants to a higher degree than it solvates activated complex, the reactions will take more slowly than in a solvent that does not solvate the reactants. The generalisation is valid for reactions in an

inert solvent which has little effect on kinetic behaviour. However, ionizing power of the solvent, electrostatic forces and other solvent influences may predominate in solvent influences on the reaction rates¹³.

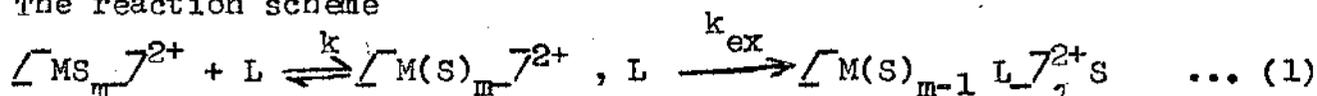
Perker^{6,7} however, explains the solvent effect in terms of solvent activity co-efficients ${}^{\circ}\gamma^s$.

$$\text{Thus } k^s = k^{\circ} \frac{{}^{\circ}\gamma_A^s + {}^{\circ}\gamma_{B^-}^s}{{}^{\circ}\gamma_{X^*}^s}$$

However, in view of the difficulties of calculating or determining the solvent activity co-efficient of ions etc. quantitative application is possible only in limited cases.

Solvent effects on the kinetics of the reactions of metal ions(II) with bidentate ligands in water and other mixed solvents have been extensively studied by Caldin and Co-workers^{14,15}, Wilkins¹⁶. They postulate that the substitution of a ligand (L) in the first hydration sphere of a metal cation (M^{2+}) is the rate determining step involving the loss of a solvent molecule(s) from the sphere. This is thought to be preceded by the rapid formation of an outer sphere complex as in equation

The reaction scheme



predicts the correct rate law, first order in M^{2+} and L. k_{ex} is the first order rate constant for exchange of a solvent molecule

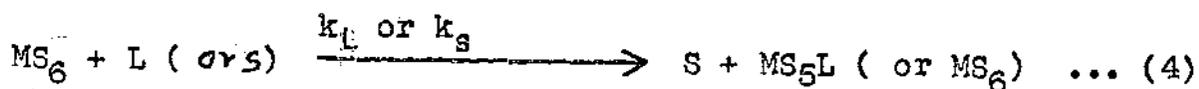
between the first hydration sphere of the bulk solvent, k_f is the second order rate constant for the overall forward reaction and k_o is the equilibrium constant for the formation of the outer sphere complex, then the kinetic behaviour is the simplest one, with M^{2+} ion in large excess should be governed by reaction (2) $k_f = k_o k_{ex} (2)$. Even in aqueous solution, the equation is obeyed much less accurately than is often supposed.

The outer sphere complex treatment leads to the same transition state as the interchange mechanism

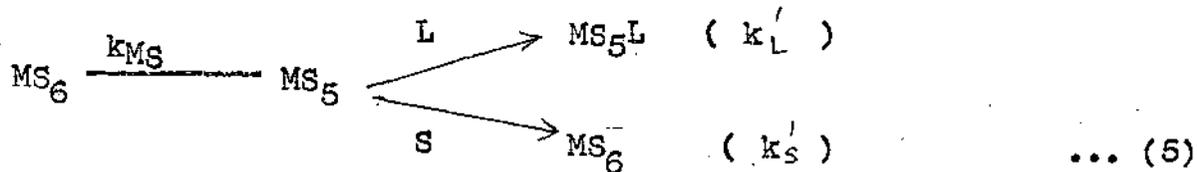


The processes of ligand substitution and solvent exchange are similar; solvent exchange is simply a particular kind of ligand substitution. The mechanisms (dissociative or interchange models) can be regarded to be similar.

Interchange Mechanism :-



Dissociative Mechanism :-



For the solvent water, the rate determining processes are dominated by the displacement of a water molecule from the first solvation shell. The behaviour is somewhat modified in non-aqueous media where a dependence on the structural properties of the solvent is observed.

The change from a single to a two - component solvent increases the number of factors which may affect a substitution reaction. These are : -

- a) The break down of an ion-solvent bond would be the dominant feature of the reaction but there is uncertainty as to the nature of the leaving molecule. The question of selective solvation is also of importance but in general, except at extreme ends, both solvent molecules must be in the first co-ordination shell and only the determination of solvent to metal bonding could conclude conclusively the stronger solvent-metal interactions.
- b) The rates of solvent exchange for each component will inevitably vary with the character of the solvent mixture beyond the first solvation shell and the changes will depend on the solvent composition. The properties of the bulk liquid will also determine the rates of reaction. It is usually observed that the solvent molecule which leaves an ion in an exchange or substitution reaction may be expected to be usually first solvent in

the first-solvent rich region and second solvent from the second-solvent rich region. On the other hand, the type of molecule entering the first solvation shell may well be strongly influenced by the stoichiometric composition of the bulk mixture. The relative importance of these entering and leaving processes in determining the exchange rate will vary over the solvent range. The consequence is that the exchange process for the mixed solvent should depend on both the electron-donating properties of the particular mixture.

The enormity and complexity of the reaction kinetics or even the solvent effects on rates and mechanisms of inorganic reactions are thus obvious. We, therefore, confined our studies on the rates of formation and dissociation of ferrous-tris-bipyridine (ferrodiin) and ferrous-tris-phenanthroline(ferroin) in water, dmf and water-dmf mixtures which are described in subsequent chapters.

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Section II

The kinetics of formation and dissociation of metal complexes have been well studied. However, the kinetics in different mixed and non-aqueous solvents are yet to be properly understood. Such studies are useful and interesting in view of complex physico-chemical processes associated with them though relatively little is known regarding the effects of solvents on the reaction mechanism. The reaction rate is affected not only due to the change in the dielectric constant of the medium as the second solvent is introduced but also due to the change in non-electrostatic part arising from solute-solvent interactions and acid-base character of diversing characteristics. It is to be noted in this connection that the metal ions are solvated by the most predominant solvent water in their first co-ordination shell. The reaction on addition of a ligand means the displacement of water molecules by ligand molecules. In mixed solvents preferably in presence of high percentage of the second solvent the displacement of water molecules by the second solvent in the first co-ordination shell becomes a distinct probability.¹

Moreover, the reaction kinetics would be influenced by the bulk properties of the solvent mixtures.

In order to study the solvent effect on the reaction

rates, the rates of formation and dissociation of the complex, $\text{Fe}(\text{bipy})_3^{2+}$ have been determined in water, dmf + water mixtures and dmf. Studies on the dmf exchange^{2,3} in co-ordinated complexes are useful in elucidating the mechanism of simple ligand substitution in solutions⁴. Furthermore, studies on equilibrium and kinetics in mixed solvents may be of great assistance in interpreting the role of solvents in inorganic reactions⁵.

The rates of formation and dissociation of the red complex, $\text{Fe}(\text{bipy})_3^{2+}$ in water have been extensively studied by Baxendale and George⁶ and Krumholtz⁷. It is well known that the tris-complex is very stable in aqueous medium and when ferrous ion is mixed with 2,2'-bipyridine in the ratio 1 : 6, the complete complex formation $\text{Fe}(\text{bipy})_3^{2+}$ takes place at $\text{pH} \approx 4.0$ having λ_{max} at 524 nm. The maximum changes to 522 nm in mixed solvents⁸. Ferrous ion also forms complex with dmf (which is light greenish in colour) having an absorption maximum at 375 nm. Thus, both 2,2'-bipyridine and dmf have capacity to act as ligand and both should compete to form complexes with ferrous ion. It is, therefore, interesting to study the rates of reaction in dmf + water mixtures and dmf where dmf exchange and complex formation appears to be reasonable.

We present in this section the study of rates of formation and dissociation of ferrodin⁸ $[\text{Fe}(\text{bipy})_3^{2+}]$ and their thermodynamics in dmf + water mixtures (0 - 100%).

Experimental:

The dark-red coloured complex tris (2,2'-bipyridine) iron(II) perchlorate $[\text{Fe}(\text{bipy})_3]^{2+}[\text{ClO}_4]^{-2}$ was prepared following Dwyer and McKenzie⁹ and its purity was checked by micro analysis.

(Found : Fe 7.8%, N 11.82%, Theo: Fe 7.72%, N 11.61%)

Mohr salt (G.R.E. Merck) was dissolved in known amount of HClO_4 acid. Iron content was estimated in the usual way 2,2'-bipyridine (G.R.E. Merck) was used. N,N^1 -dimethyl-formamide (E. Merck) was dried over freshly ignited quicklime for several hours. It was finally purified by fractional distillation under reduced pressure. The dielectric constant values in mixed solvents were calculated using the dielectric constant values of pure solvents from the literature¹⁰ in the usual way using the law of mixtures and comparing the dielectric constant values given in the literature¹¹.

Both the solvents and the solutions of Mohr salt were kept in nitrogen atmosphere and utilized within 24 hours. Perchloric acid (70% G.R.E. Merck) was used to vary H^+ ion concentration. Double distilled water from all glass distilling set was used.

The rates of formation and dissociation of ferrodiin were followed spectrophotometrically in the way described by Baxendale and George with the help of DU 2 spectrophotometer maintained at 298K.

Measurement of the rate of formation of ferrodiin

The solutions containing (a) a definite concentration of Mohr salt in known excess of acid and (b) an acidified solution of bipyridine (both in dmf + water mixtures or in pure solvents as the case may be) were brought to the desired temperature in a thermostat(± 0.01), mixed and stirred well. The colour changes at different intervals of time (A_t) at 522 nm were noted till the constancy in absorbance (A_∞) was observed. The rates of formation of ferrodiin was measured throughout the whole composition range at 293 K. The rates of formation were measured at three different temperatures namely. 293, 300.5 and 308 K in 20-80% (v/v) dmf-water mixtures. The change of O.D readings with time at 40% v/v dmf + water mixture were recorded in Table 1.

Rates of dissociation of ferrodiin

The dissociation reaction was initiated by the addition of a definite amount of ferrodiin (in the desired solvent) to water or dmf + water mixtures in absence or in presence of definite amount of acid. Both the solutions were brought to the desired temperature before mixing. In absence of the acid, the complex was found to be stable up to 60%(v/v) of dmf beyond which the rate of decomposition was found to be appreciable. The rate of decomposition of ferrodiin in dmf + water mixtures becomes measurable only in presence of high concentration of acid and the

decomposition was measured at an optimum concentration of $\text{HClO}_4 = 0.22 \text{ mol dm}^{-3}$ throughout the whole composition range. For measurement at 100% dmf, water is replaced by dmf.

The dissociation reaction was monitored spectrophotometrically by following the decrease in absorbance (A_t) at 522 nm. The reaction was allowed to proceed to completion as observed from the experimental optical density (A_∞) values.

The change of O.d readings with time at 90 and 80% v/v of dmf + water mixtures were recorded in Table 2.

The reactions were studied in the dark and the readings at different interval of times were taken using aliquots from the original reaction mixtures. The rate constants were found to be reproducible to within $\pm 5\%$ from several sets of experiments.

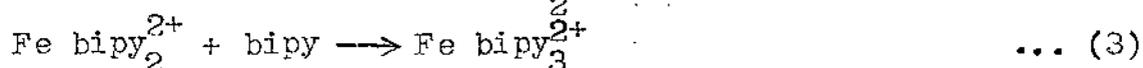
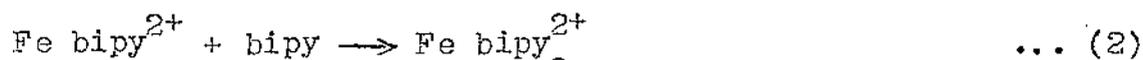
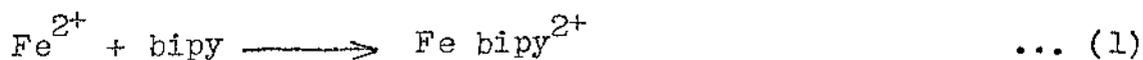
The rates of dissociation were measured at 291 K over the whole composition range.

The activation parameters of the decomposition were determined from the measurements of the rate constants at three different temperatures namely at 293, 298 and 303 K.

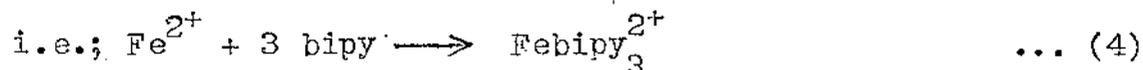
Results and Discussion :

The rates of formation of ferrodin in water were extensively

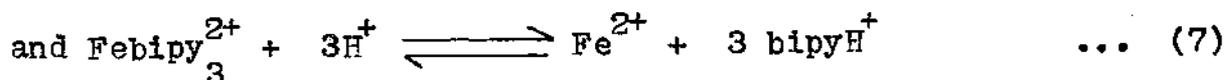
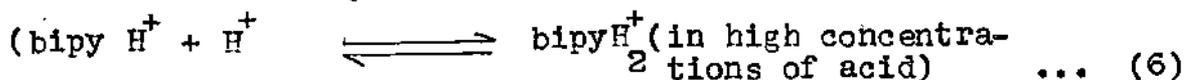
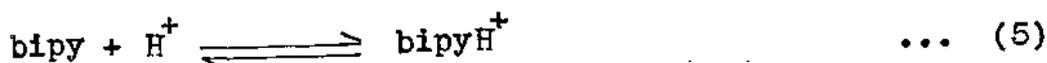
studied by Baxendale and George⁶. Though we are particularly interested in the study of the rates of formation of ferrodiin in dmf + H₂O mixtures but some preliminary works in water have also been done. Our studies indicate that the pseudo-first order rate of formation of ferrodiin for a fixed Fe²⁺ ion concentration is dependent on the concentration of the acid, ligand as well as ionic strength as would be apparent from the values of the first order rate constants obtained from the plots of $\log \frac{A_{\infty} - A_0}{A_{\infty} - A_t}$ against time (Table 2). However, the values of rate constants differ considerably from those reported by George et.al.⁶ in view of changed reaction conditions. But the trend appears to be similar. The formation of ferrodiin involves the following steps :-



The overall reaction has been suggested to one of the fourth order



Thus when the concentration of bipy is very high, the rate is dependent only on Fe²⁺ concentration. Apparently, the reaction is independent of pH. However, the addition of acid is found to affect the rate constants markedly due to the reactions



At higher pHs, hydrolysis of Fe^{2+} ion and subsequent conversion to Fe^{3+} ion takes place.

All the steps (1) to (3) are fast but the step (1) appears to be rate determining though Baxendale and George⁶ consider the step (3) to be rate determining. But the works of Irving and co-workers¹² show conclusively that "orbital stabilization" does not take place in the (1) or (2) step but only in the (3) step as the reaction is accompanied by the greater ease in the free-energy change. The electronic rearrangement is manifested in the unusual heat and entropy changes and $k_3 \gg k_2$ and k_1 .

The linearity of plot (Fig 1) of the first order rate constants at a constant H^+ ion and Fe^{2+} concentrations against bipyridine concentrations suggest that the reaction is of the second order and the rate determining step is bimolecular in nature. However, we are interested in the kinetic studies in dmf + water mixtures or in dmf. These are associated with the following difficulties :

- 1) The rate of formation of ferrodin in dmf + water

mixtures or dmf is very fast in neutral solutions or in solutions of low H^+ ion concentrations, but the rate is found to be measurable in presence of high concentrations of H^+ ions. This is natural as dmf is basic in character and the addition of large excess of acid is necessary to make the dmf + water mixture sufficiently acidic. The optimum concentration of H^+ ions were kept to be 0.9 mol dm^{-3} in all measurements in dmf + water mixtures or dmf but this concentration is too high for the formation of Febipy_3^{2+} ion in aqueous solutions. In presence of high concentration of H^+ ions, the decomposition of Febipy_3^{2+} also takes place (reaction 6).

ii) The pK-values for the reaction (5) decreases with increasing percentages of dmf¹³ and the exact concentration of H^+ ion is difficult to determine in mixed solvents or non-aqueous solvents.

From the measurements of rate of formation in dmf + water mixtures or dmf, it has been found that the increase in H^+ ion concentration decreases the rate of formation of Febipy_3^{2+} whereas increase in ligand concentration increases the rate as would be apparent from the rate constant values from the plots of $\log \frac{A_\infty - A_0}{A_\infty - A_t}$ against time (Figs. 2 and 3 ; Table 4).

The rate constants as obtained from the plot of $\log \frac{A_\infty - A_0}{A_\infty - A_t}$ (Fig. 4) were found to increase with increase in concentration of dmf at a fixed H^+ ion concentration. The rate constant values at different percentage of dmf and at different temperatures are recorded in Table - 3. The increase in rate constants can be attributed to the decrease in the effective concentration of H^+ ions and lowering of pK_a -values for the reaction (5) with increase in dmf concentrations, thereby increasing the concentration of bipy. The increase in k-values further suggests that dmf, inspite of being a strong co-ordinating ligand, is not capable of competing with bipy at least up to 80% (v/v) of dmf, beyond which the rate drops sharply as shown in fig. 5 and Table 5.

An analysis of the rate of formation of the complex in terms of free-base as done by Baxendale and George⁶ is given below :

$$\text{Rate} = k_f [\text{bipy}]^3 [\text{Fe}^{2+}] = k_f [\text{bipy}]_T^3 [\text{Fe}^{2+}] \cdot \frac{k_a^3}{(k_a + [H^+])^3}$$

$$= k_{obs} [\text{bipy}]^3 [\text{Fe}^{2+}] \quad \dots (8)$$

$$\text{or } k_{obs} = k_f \frac{k_a^3}{(k_a + [H^+])^3} \quad \dots (9)$$

Thus, for the same concentrations of bipy, Fe^{2+} and H^+

ions, we have calculated k_f -values of the reaction at various dmf concentrations using K_a -values determined in this laboratory¹³. The values of $k_a^3 / (k_a + [H^+])^3$ increase (i.e. the concentration of bipy decrease) enormously with increase in dmf leading to a decrease in k_f -values as would be apparent from Table - 6.

It is apparent that the rates of formation of ferrodin decreases rapidly with increase in dmf concentration, though the apparent first order rate constant for the formation increases with solvent composition.

The change in k obs. values cannot be correlated with the change in $\frac{1}{D}$ values as in the case of "isoelectric reactions" (Fig. 6). The effect of D is probably insignificant, non-electrostatic contributions and the changes in acid-base character being important. However, at high concentrations of dmf, complexation of Fe^{2+} with dmf is a probability due to mass-effect i.e., Fe^{2+} will be solvated by dmf. ^{This results} in the sharp drop in the values of the rates of formation beyond 80% (v/v) dmf.

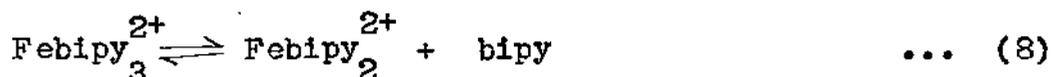
Comparison of our results with those of Baxendale and George⁶ in aqueous solutions is not possible due to changed experimental conditions. However, the energies of activation for the formation of ferrodin in different dmf + water mixtures have been found to be almost zero as would be apparent from fig. 4 and Table 5 similar to the observation of Baxendale and George. This is due to ligand

field stabilizations associated with the favourable enthalpy and particularly entropy effects arising from the displacement of six solvent molecules by three bipy molecules.

Rates of dissociation or exchange reactions :

The rates of dissociation of ferrodin complex follow first order kinetics in presence or in absence of perchloric acid. This is apparent from the linear plot of $-\log(A_t - A_\infty)$ against time (Fig. 7 and 8). The dissociation reactions as apparent from the equations (1-4) are independent of pH but the dependency on pH arises from the equations (5),(6) and (7). It has been found that the specific rate constant is dependent on H^+ ion concentration but when the acid concentration exceeds 0.5 mol dm^{-3} it does not affect the rate significantly as the dissociation would be completed due to formation of bipy to $bipH^+$ and subsequently to $bipy \text{ H}_2^{+8}$ (at high acidities).

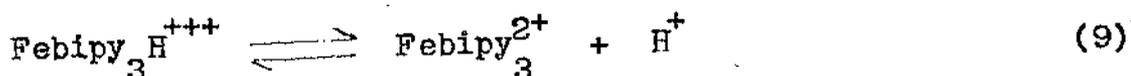
Following the same arguments as before the rate determining step for the dissociation of $Fe bipy_3^{2+}$ can be represented as



but the predominant reaction for the decomposition in presence of acid being reaction(7). At low pH's (2.2 - 2.8) studied by Baxendale and George⁶, more than 95% of bipy is in the form of $bipy \text{ H}^+$. Therefore, the rate seems to be unaffected.

At very high acid concentration, the forward reaction(7)

is complete and the rate would be independent of H^+ ion concentration. The postulation



seems to have no significance as the equation(9) does not hold good over the whole range of H^+ ion which the authors⁶ themselves admit.

The rate of dissociation or exchange is independent of bipy even upto 100-fold concentrations. The reaction is found to be independent of total ionic strength of the solution.

The rate of dissociation or exchange in presence or absence of acid at constant H^+ ion concentration can be represented as

$$-\frac{d[Fe(bipy)_3^{2+}]}{dt} = k_d [Fe(bipy)_3^{2+}]$$

But the values of k_d are lower in presence of acid.

The values of k_d at various percentage of dmf + water mixtures are recorded in Table - 7. Since the reaction becomes fast at 298K the reaction was carried out at 291K to study the dissociation reaction over the whole range of composition (0-100%). The rate constants for the dissociation of ferrodin in presence of acid at high percentages of dmf at different temperatures have been recorded in table 8. The thermodynamic parameters as obtained from the plot of $\log k$ against T have also been included in Table 8. In absence of acid (or at low acidities), the complex is highly stable up to 60% (v/v) percentage of dmf beyond

which the rate constant is measurable. The first order rate constant increases rapidly afterwards with increase in dmf concentration.

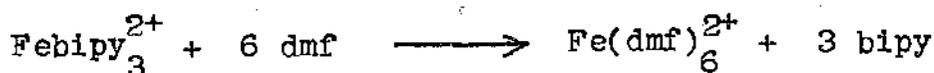
This may be due either to

i) dissociation of the complex due to decrease in acidity and conversion of Fe^{2+} to Fe^{+3} ion with subsequent hydrolysis.

ii) Exchange of bipy by dmf. The plot of k_d vs $\frac{1}{D}$ (fig-9) show linearity in the region 70 - 100% dmf.

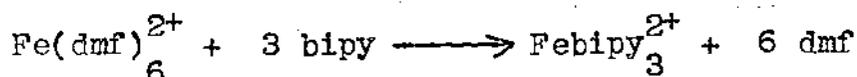
The increase in k_d with increasing dmf at a particular H^+ ion concentration can be explained by the fact that dmf is highly co-ordinating ligand capable of combining with acid reducing the co-ordinating capability of ligand and acidity of the medium. This also explains why we have to choose a high concentration of acid to determine k_d in dmf + water media.

A plot of k_d against volume percentage of dmf in acidic solution (Fig. 10) shows that k_d drops with addition of dmf remains nearly constant upto 50% v/v, then increases linearly up to 90% v/v of dmf. The change is conspicuous at 100% of dmf. The result suggests that the exchange of bipy by dmf probably takes place at high percentage of dmf and the rate of exchange is particularly high at 100% dmf medium. Since $\text{Fe}(\text{bipy})_3^{2+}$ is highly stable compared to weak $\text{Fe}(\text{dmf})_6^{2+}$, the exchange reaction



is possible only under favourable conditions.

But the reverse reaction

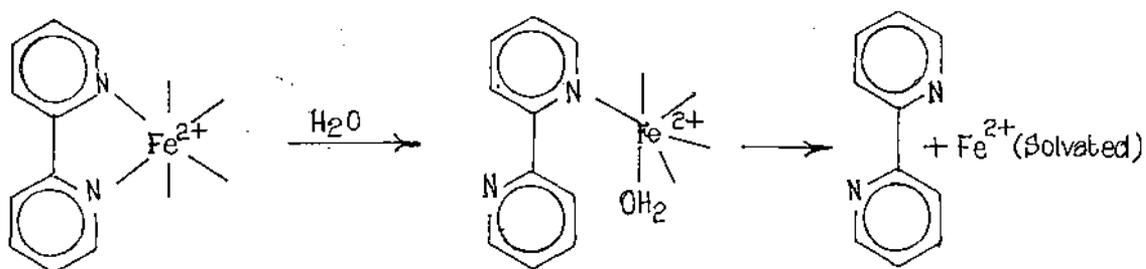


should be easier to follow.

But unfortunately the reaction is difficult to study as $\text{Fe}(\text{dmf})_6^{2+}$ is formed in nearly neutral or alkaline medium. Addition of bipy probably brings about of the reaction but at this high pH, $\text{Fe}(\text{bipy})_3^{2+}$ is unstable and immediate decomposition takes place. The results indicate that the change in dielectric constant has no specific contribution in the decomposition.

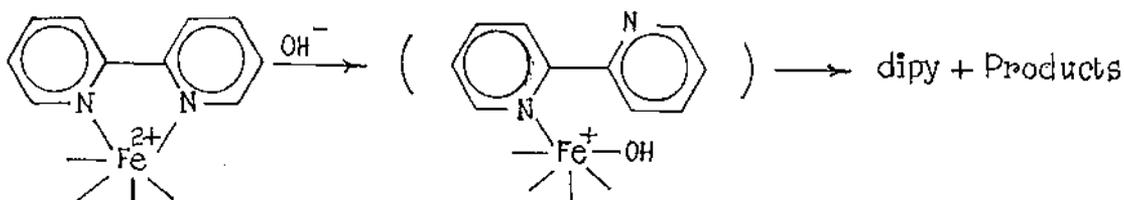
The observed dissociation or exchange kinetics follow either a dissociative or interchange mechanism. The mechanism of dissociation under various conditions can be given as follows¹⁴ :

a) In neutral or slightly acid solution in water and water - dmf mixtures:

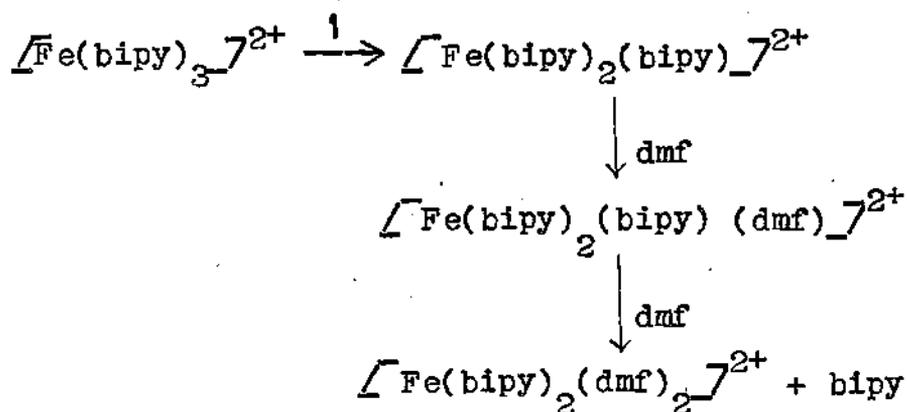


In highly acidic solution, H^+ may be attached to the N-atom and ultimate conversion of trans bipy to cis - bipy H^+ would take place.

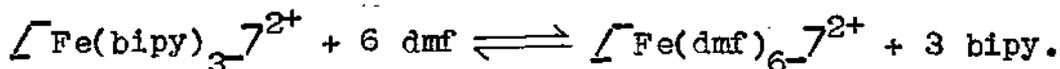
b) In alkaline solution or in dmf + water mixture :



c) In dmf - medium



Total reactions :



It is apparent that in all the cases the bond-repture is the major process in the formation of transition state¹⁵.

It is apparent that the dissociation or exchange proceeds through a nucleophilic attack on the six-co-ordinated complex to form an intermediate transition state, where the metal is assumed to be co-ordinated both by the leaving and incoming ligands¹⁶. The complex subsequently decomposes with the rupture of the metal-ligand bond. The high electronegative co-group in dmf may increase the rate at which the metal - nitrogen bonds are broken.

The attack of H_2O or dmf would depend on the composition of the solvent. The chances of the complex capturing a dmf or a water molecule are in direct-proportion to their numbers in their solvation shell. Naturally, as the percentages of dmf increases exchange process may predominate.

The ΔH^\ddagger values of the rates of decomposition are highly endothermic implying that the rupture of the metal-ligand bond is difficult. The observed variation of k_d , ΔH^\ddagger and ΔS^\ddagger with $[dmf]$ indicates that the environment external to the first co-ordination sphere is not significantly medified and the observed enthalpy changes arise mainly from the structure forming entropy effect. The formation of transition state should accompany a decrease in entropy whether the transition complex includes water or dmf.

The entropy decrease as observed may be due to decrease of the total number solvent molecules as the concentration of dmf increases as well as structural changes associated with the changes in solvent compositions.

The decrease in the enthalpy values are directly proportional to the decrease in entropy values as apparent from the linear plots of ΔH^\ddagger vs ΔS^\ddagger (fig 11) indicating that the structural factors associated with ΔH^\ddagger and ΔS^\ddagger arising from the changes in solvent environment compensate each other to give a simple linear free-energy relationship with changes in solvent composition. The fact suggests that in every case the rupture of the metal-N-bond is rate determining step and the successive addition of the organic solvent alters the rate without influencing the mechanism so that the mechanism is the same for the different solvent compositions.

It is, however, very difficult to correlate the rates of formation or dissociation of ferrodin with the structure of the solvent mixtures.

Dimethylformamide is a highly associated liquid whereas water is a highly structural solvent. Addition of dmf to water strengthens the water-structure, but at the same time strong interactions of water with dmf leads to the formation of the hydrogen-bonded solvent system associated with a slight entropy

increase. With further addition of dmf, extensive depolymerisation of dmf takes place to form hydrogen-bonded dmf-water system at least up to about 80% (v/v) of dmf assuming 1 : 1 interaction between the solvent molecules. Beyond this region, disruption of dmf-water may occur and solvation of Fe^{2+} by dmf or exchange of bipy by dmf may take place.

Thus up to at least 80% (v/v) dmf, there is only marginal changes in the secondary solvation shell arising from disruption of water and dmf structures with concomitant formation of dmf-water structure. This may lead to slight decrease in entropy values which would be totally reflected in ΔH^\ddagger values. Beyond this region primary solvation is likely to be affected and exchange of water by dmf from the solvation sphere of Fe^{2+} and finally displacement of solvent by bipy may take place. Similarly, exchange of bipy by dmf from ferrodin also takes place in this region with changes in entropy and enthalpy values.

However, the study of the exchange kinetics by stopped flow technique probably would give more insight regarding the mechanism of the rate process.

Table - 1

Bipy. concn. = 7.5×10^{-3} mol dm⁻³; $[Fe^{2+}] = 1.5 \times 10^{-4}$ mol dm⁻³;

$[H^+] = 0.9$ mol dm⁻³. Solvent = 60% v/v of dmf.

Wave length = 522 nm; $A_\alpha = 1.38$

Temperature = 293K

Time (mins)	o.d.	$\log \frac{A_\alpha - A_0}{A_\alpha - A_t}$	$K_{obs} \times 10^5$ sec.
7	0.120	0.039	
17.5	0.200	0.068	15.35
25	0.285	0.100	
32	0.350	0.127	

Temperature = 300.5K

Time(mins)	o.d.	$\log \frac{A_\alpha - A_0}{A_\alpha - A_t}$	$K_{obs} \times 10^5$ sec.
7	0.115	0.038	
17.5	0.200	0.068	14.77
25	0.280	0.098	
32.5	0.340	0.123	

Temperature = 308K

Time (mins)	o.d.	$\log \frac{A_\alpha - A_0}{A_\alpha - A_t}$	$K_{obs} \times 10^5$ sec.
7	0.118	0.039	
17	0.205	0.070	15.73
25	0.290	0.102	
32	0.360	0.130	

Table - 2

Dissociation of ferrodin

a. Solvent = 90%(v/v) dmf + water. Complex Conc = $4 \times 10^{-5} \text{ moldm}^{-3}$
 $[H^+] = 0 \text{ moldm}^{-3}$ Temp = 291 K

A_∞ (Absorbance of at infinite time) ≈ 0.00

Time (min)	$O.d$	$-\log (A_t - A_\infty)$	kobs $\times 10^4$
5	0.238	0.623	
10	0.185	0.733	
15	0.138	0.860	7.39
20	0.108	0.966	
25	0.088	1.055	
30	0.075	1.125	
35	0.055	1.259	

b. solvent 80% (v/v) dmf+water

Time(min)	$O.d$	$-\log (A_t - A_\infty)$	kobs $\times 10^4$
10	0.247	0.608	
20	0.186	0.730	
30	0.144	0.842	4.39
40	0.126	0.906	
50	0.106	0.975	
60	0.095	1.022	

Table - 3

A. Effect of H^+ ion concentration on the rate of formation of ferrodiin in water media.

$$[Fe^{2+}] = 4 \times 10^{-5} \text{ mol dm}^{-3}, \text{ Bipy. Conc.} = 1 \times 10^{-3} \text{ mol dm}^{-3}$$

Temp=298K.

$[H^+] \text{ mol}^{-1}\text{dm}^3$	$k_{\text{obs}} \times 10^4 \text{ sec}$	$\left(\frac{K_a}{K_a + H^+} \right)^3$	k_f
0.198	13.19	5×10^{-12}	2.64×10^8
0.206	11.11	4.4×10^{-12}	2.52×10^8
0.218	7.67	3.5×10^{-12}	2.20×10^8

B. Effect of Bipy. Conc. on the rate of formation of ferrodiin in water medium.

$$[Fe^{2+}] = 4 \times 10^{-5} \text{ mol dm}^{-3}; [H^+] = 0.198; \text{Temp} = 298 \text{ K}$$

$$[Bipy] \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \qquad k_{\text{obs}} \times 10^4 \text{ sec}$$

4	5.11
6	6.52
7	7.80
8	9.78
9	11.13

C. Effect of ionic strength on the reaction rate in water medium

$$[Fe^{2+}] = 4 \times 10^{-5} \text{ mol dm}^{-3}; \text{ Bipy. Conc.} = 1 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[H^+] = 0.206 \text{ mol dm}^{-3}$$

$$[NaClO_4] \text{ mol}^{-1}\text{dm}^3 \qquad k_{\text{obs}} \times 10^4 \text{ sec}$$

0.04	10.55
0.06	10.15
0.08	9.21

Table - 4

Effect of variation of Bipyridine and H^+ ion concentrations on the rate of formation of ferrodian.

a. $[Fe^{2+}] = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$; $[H^+] = 0.9 \text{ mol dm}^{-3}$

Temp = 300.5K

% v/v of dmf	$[bipy] 10^3 \text{ mol}^{-1} \text{ dm}^3$	kobs x 10^5 sec.
	6.5	13.81
80	7.0	18.04
	7.5	26.35

b. $[Fe^{2+}] = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$; $[bipy] = 7.5 \times 10^{-3} \text{ mol dm}^{-3}$

Temp = 298 K

% (v/v) of dmf	$[H^+] \text{ mol}^{-1} \text{ dm}^3$	kobs X 10^5 sec
	0.8	36.85
80	0.9	26.35
	1.0	18.42

Table - 5

Pseudo-first order rate constants k_{obs} of formation
of ferrodin complex in dmf+water media.

$$[Bipy] = 7.5 \times 10^{-3} \text{ mol dm}^{-3}, [Fe^{2+}] = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[H^+] = 0.9 \text{ mol dm}^{-3}$$

% v/v of dmf	Temp(°K)	$k_{obs} \times 10^5 \text{ sec}$
0		No formation
	293	0.999
20	300.5	1.07
	308	1.92
	293	5.11
40	300.5	5.24
	308	5.50
	293	15.35
60	300.5	14.77
	308	15.73
	293	24.75
80	300.5	26.35
	308	27.17
	293	2.78
90		
	293	1.92
100		

Table - 6

Calculation of k_f from k_{obs} . at various percentage of
dmf + water media.

% (v/v) of dmf	k_a (at 298K)	$(\frac{k_a}{k_a + [H^+]})^3$	$k_{obs} \times 10^5$ (at 300.5 K)	$k_f \times \text{sec.}$
0	3.38×10^{-5}	5.0×10^{-12}	131.9	2.64×10^8
20	2.09×10^{-4}	12.49×10^{-12}	1.07	8.57×10^5
40	1.41×10^{-3}	3.87×10^{-9}	5.24	1.35×10^4
60	5.89×10^{-3}	2.75×10^{-7}	14.77	5.37×10^2
80	4.79×10^{-2}	1.28×10^{-4}	26.35	2.06

Table - 7

Pseudo-first order rate constants of dissociation of Ferrodin
Complex in dmf + water media.

Complex Conc = $4 \times 10^{-5} \text{ mol dm}^{-3}$ Temp = 291 K

% v/v of dmf	[HClO ₄] mol dm ³	k _{obs} × 10 ⁴ sec
100	0	16.12
	0.22	5.29
90	0	8.16
	0.22	2.64
80	0	4.28
	0.22	1.98
70	0	2.52
	0.22	1.58
60	0	-
	0.22	1.21
50	0	-
	0.22	1.02
40	0	-
	0.22	1.02
30	0	-
	0.22	1.02
20	0	-
	0.22	1.02

CONTD FROM PAGE - 36.

% v/v dmf	$\overline{[HClO_4]}$ mol dm ³	k _{obs} X 10 ⁴ sec
10	0	-
	0.22	1.02
0	0	-
	0.22	1.53

Table - 8

The activation parameters for the dissociation of ferrodin complex in
dmf + water media

$$[\text{Complex}] = 8 \times 10^{-5} \text{ mol dm}^{-3}; [\text{HClO}_4] = 0.22 \text{ mol dm}^{-3}$$

% (v/v) of dmf	Temp (Kelvin)	k _{obs} X 10 ⁻⁴ Sec	log ₁₀ A	ΔH^\ddagger (kJ K ⁻¹ mol ⁻¹)	ΔS^\ddagger (JK ⁻¹ mol ⁻¹)
	293	3.17			
90	298	5.91	14.19	99.27	26.92
	303	12.08			
	293	2.71			
80	298	4.56	14.66	102.27	35.82
	303	9.20			
	293	1.84			
70	298	3.91	14.87	104.38	40.13
	303	7.85			
	293	1.39			
60	298	3.05	14.45	108.36	51.00
	303	6.25			

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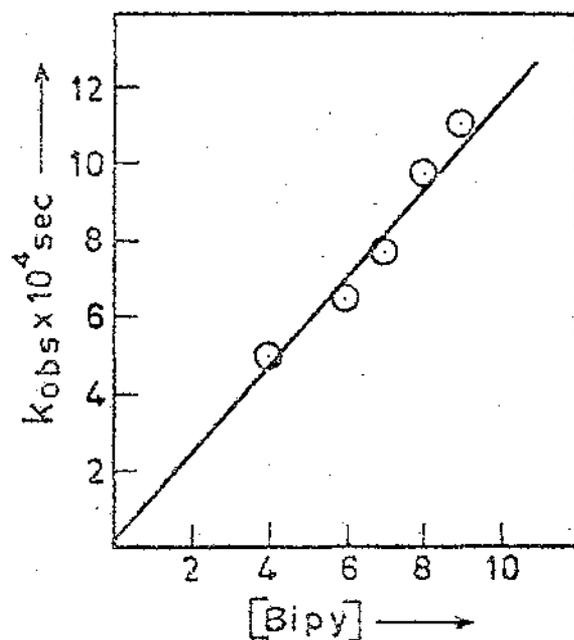


Fig.1 Plot of k_{obs} vs $[Bipy]$

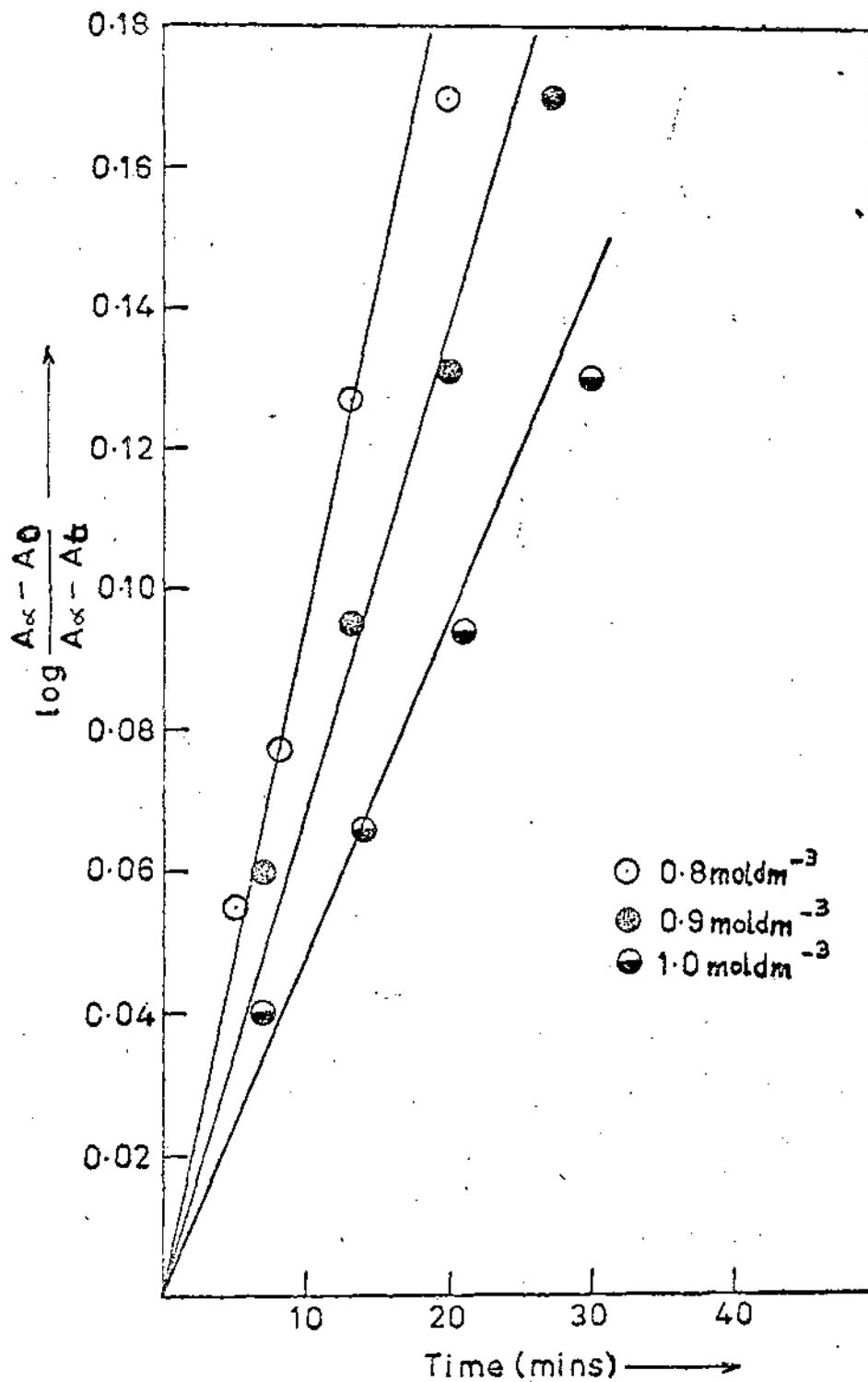


Fig.2 Effect of $[H^+]$ on reaction rate at 300.5K.
Solvent: 80% (v/v) dmf-water.

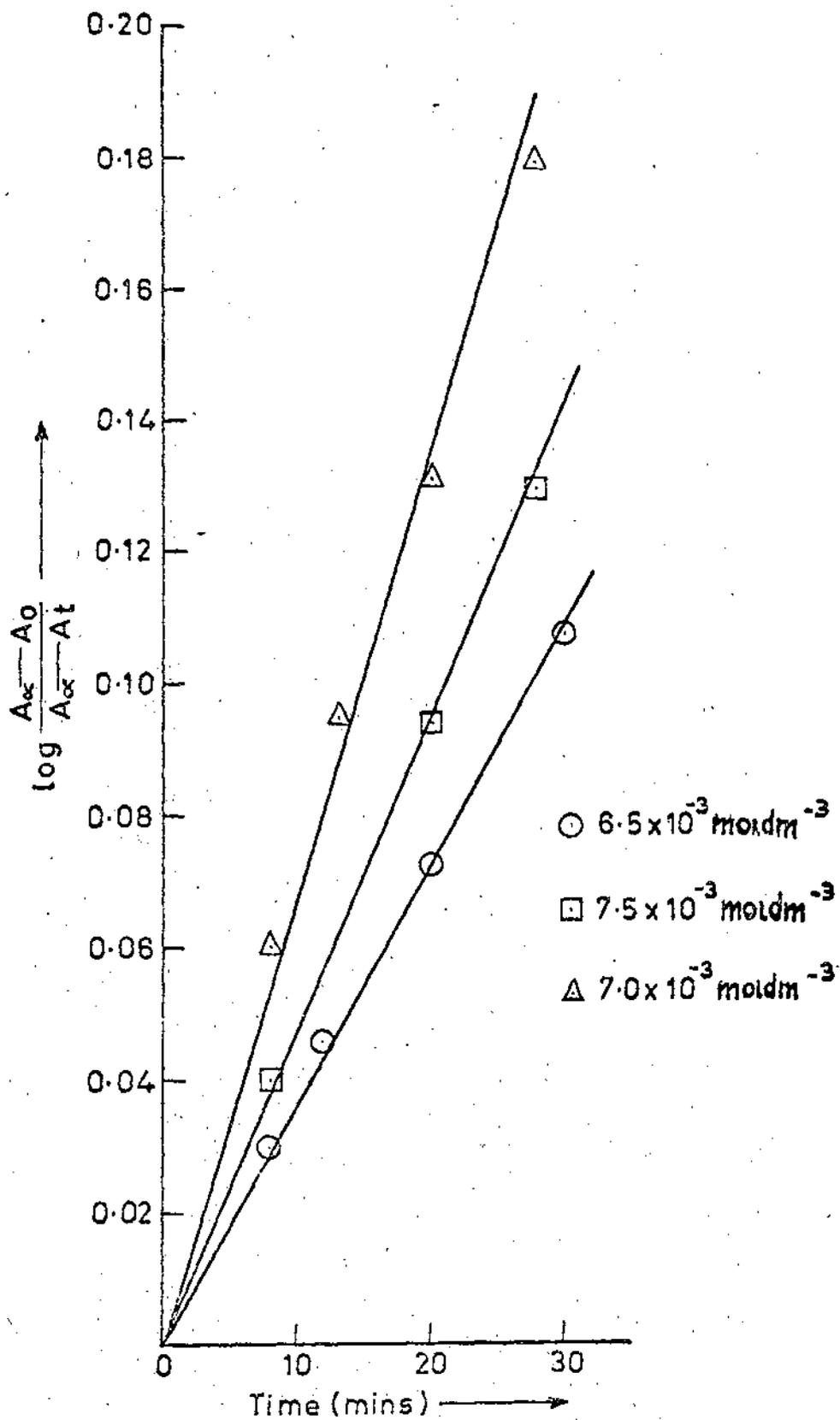


Fig. 3 Effect of [BIPY] on reaction rate at 300.5K
 Solvent : 80% (v/v) dmf-water.

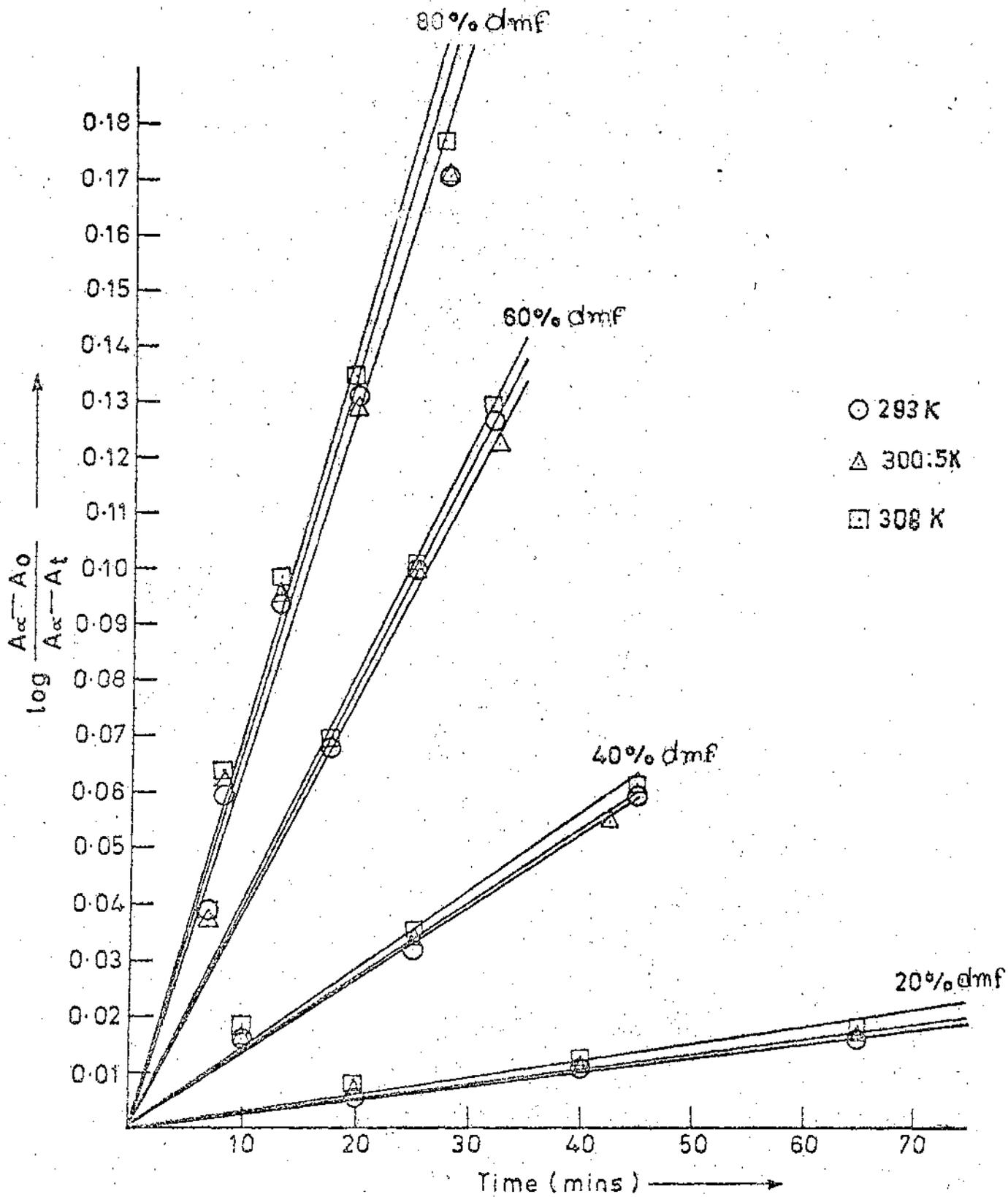


Fig. 4 Effect of temperature on the reaction rate at different percentage of mixed solvents.

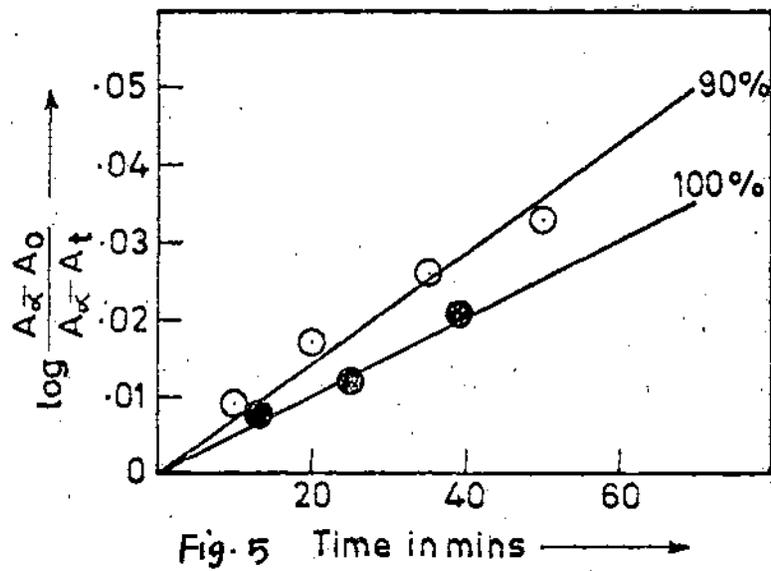


Fig. 5 Time in mins →

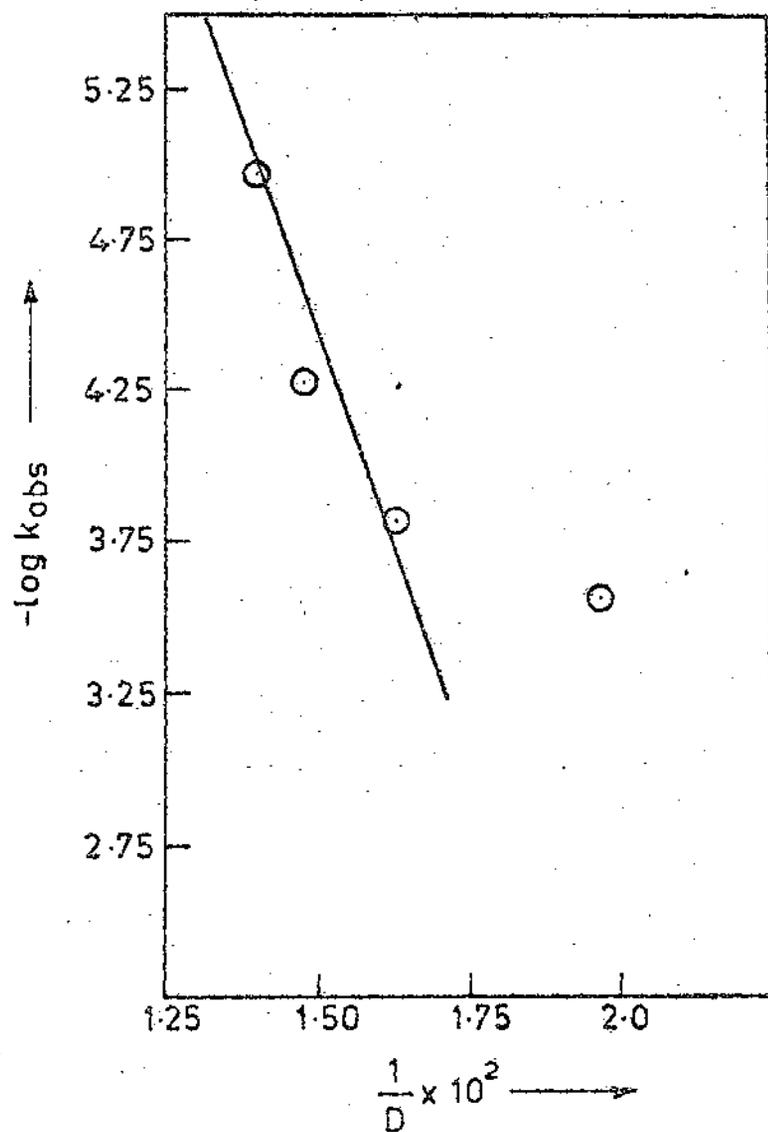


Fig. 6 Effect of dielectric constant on the reaction rate of formation of Ferrodiin.

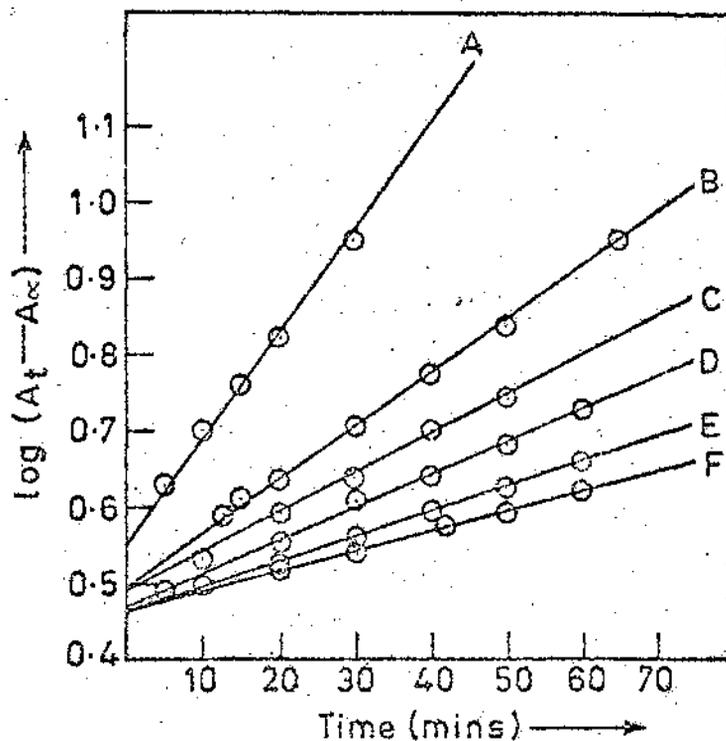


Fig.7 Plot of $[-\log (A_t - A_\infty)]$ vs time for the dissociation of ferriodin complex at different percentage of mixed solvents.

Complex concentration = $4.0 \times 10^{-5} \text{ mol dm}^{-3}$

Added acid concentration = 0.22 mol dm^{-3}

A 100%; B 90%; C 80%; D 70%;

E 60%; F 50% v/v dmf+water mixtures.

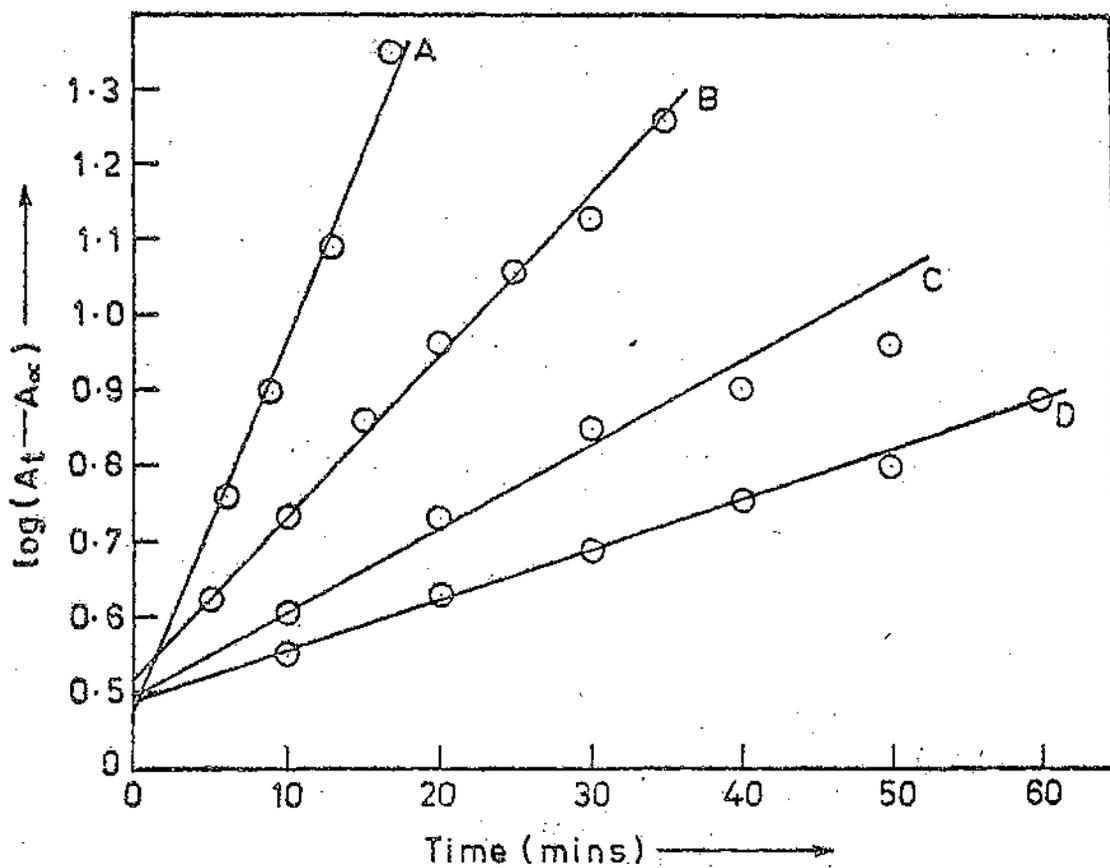


Fig. 8 Plots of $[\log (A_t - A_\infty)]$ vs time for the dissociation of Ferrodin complex at different percentage of mixed solvents without any added acid and at 291K.

(Initial concentration of ferrodin complex = $4.0 \times 10^{-5} \text{ mol dm}^{-3}$ [A 10%, B 90%, C 80%, D 70% v/v dmf + water mixtures])

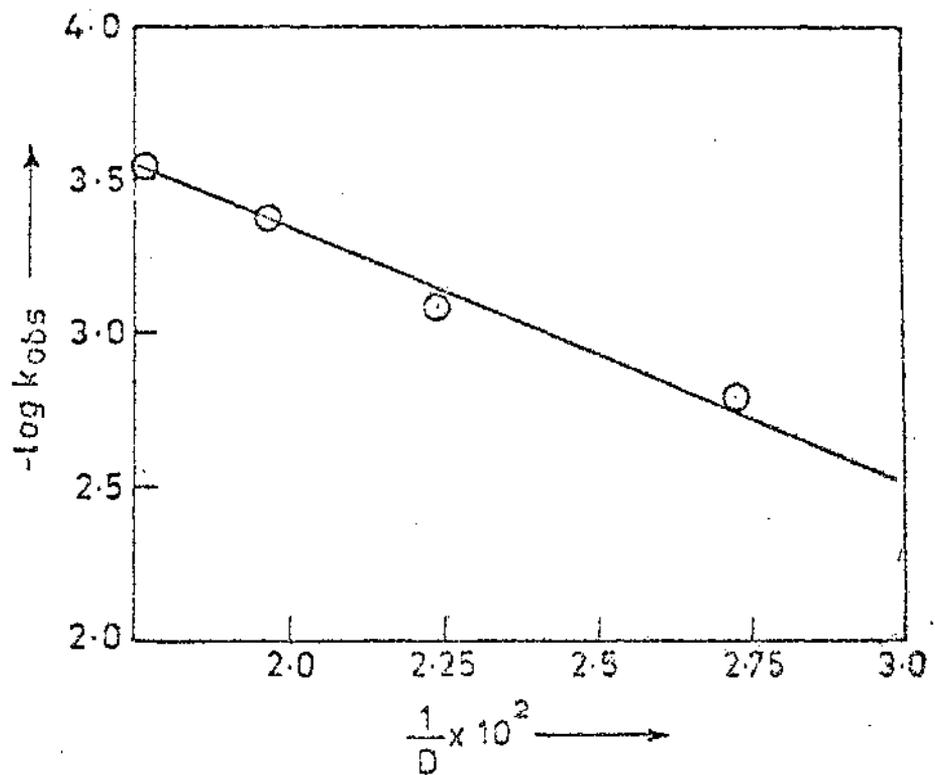


Fig.9 Variation of rate constants with the dielectric constant of the medium.

Fig. 10

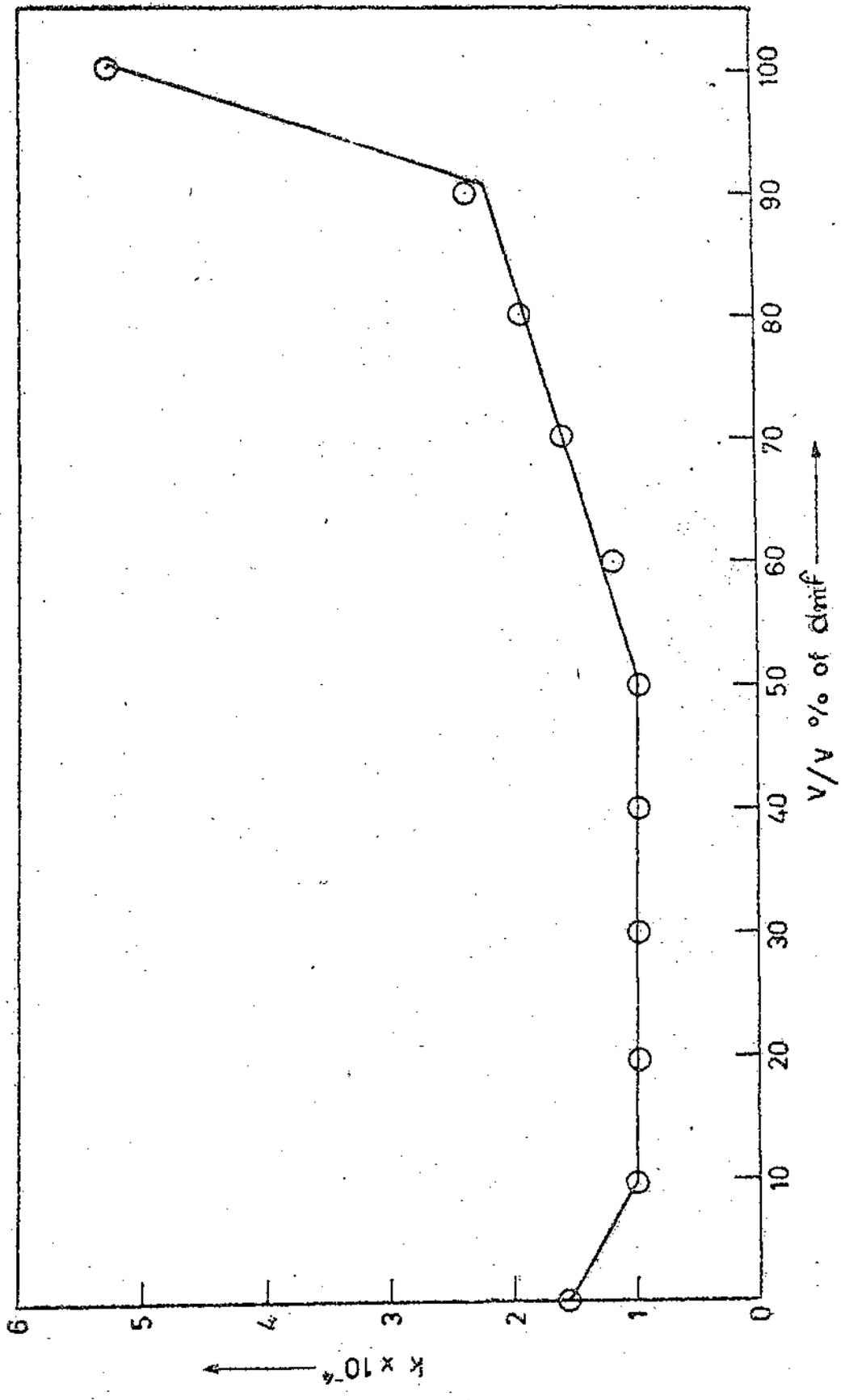


Fig.

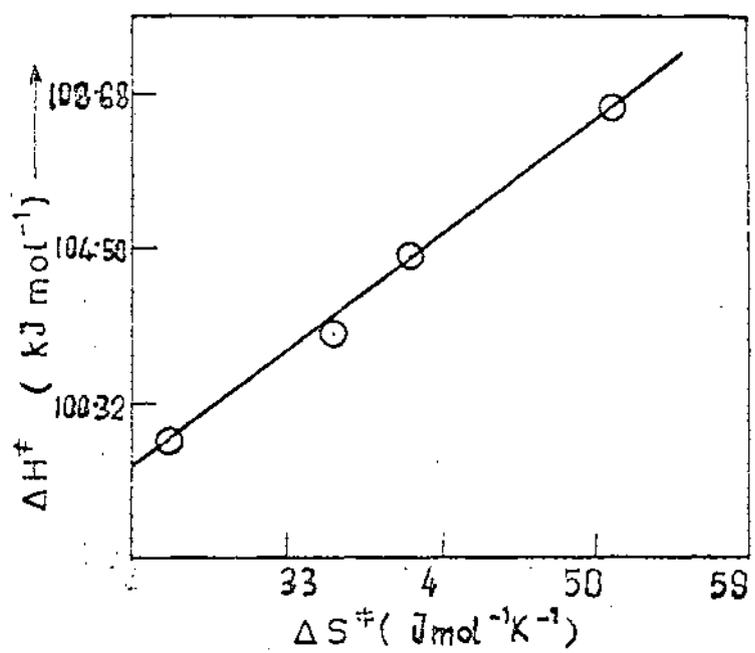


Fig. II Plot of ΔH^\ddagger vs ΔS^\ddagger for the dissociation of Ferrodim

Section - III

The kinetics of formation and dissociation of the tris (2,2'-bipyridine) and tris (1,10-phenanthroline) iron(II) [ferrodiin and ferroin] are of great importance in view of the peculiarity and exceptional stability of the complexes and particularly because of the fact that these reactions involve no separation of formal charge. The kinetics of formation and particularly of dissociation have been extensively studied by Baxendale and George¹, Kolthoff et.al.², Krumholtz³, Bosolo et.al.^{4,5}, Twigg⁶ and Raman⁷. However, the solvent effects on the rates of formation and dissociation in different mixed and non-aqueous solvents have been relatively little studied. Though the effects of variation of solvents are known to have profound effects on the rates and mechanism of reactions, Van Meter and Neumann⁸, however, studied the rates of dissociation of ferroin and particularly the rates of racemization of ferroin in various solvents.

We present in this section the results of our study on the rates of formation and dissociation of ferroin in water + dmf mixtures (0 - 100%) in presence and absence of HClO_4 . Since the rates of dissociation of ferroin in water by acids and anions have been studied by different workers only some preliminary measurements were made in water.

Experimental

The tris (1,10-phenanthroline) Iron(II) perchlorate was

prepared following Dwyer and McKenzie⁹ and its purity was checked by microanalysis.

Mohr salt (G.R.E. Merck) was dissolved in known amount of HClO_4 and was estimated in the usual way. 1,10-phenanthroline (G.R.E. Merck) was used as such. $\text{N,N}'$ -dimethylformamide (E. Merck) was dried over freshly ignited quicklime for several hours. It was finally purified by fractional distillation under reduced pressure.

The dielectric constant values of dmf + water mixtures were obtained from the literature¹⁰.

Both the solvents and the solutions of Mohr salt were kept in nitrogen atmosphere and utilized within 24 hours. Perchloric acid (70%, G.R.E. Merck) was used to vary H^+ ion concentration. Double distilled water from all glass distilling set was used.

The measurements were made with the help of DU 2 spectrophotometer maintained at 298°K . The rates of formation in water and mixed solvents was measured spectrophotometrically by noting the optical density changes at different intervals of time (A_t) at 510 nm till the constancy (A_∞) in o.d. reading is observed. The optical density changes at different intervals of time are recorded in Table - 1.

The rates of formation at 293 K and the other thermodynamic parameters were also measured.

The rate of formation of ferroin in dmf + water mixtures

or dmf is very fast in neutral solutions or in solutions of low H^+ ion concentrations. The rates however, are measurable in presence of high concentrations of H^+ ions. This is due to basic nature of dmf + H_2O mixtures. The optimum concentrations of H^+ ions were kept at 0.9 mol dm^{-3} throughout the composition range and this concentration is too high for the formation of $FePhen_3^{2+}$ ion in aqueous solutions. In presence of high concentrations of H^+ ions the decomposition of $FePhen_3^{2+}$ also takes place. For proper comparison of reaction rates in different solvent compositions, the concentrations of Fe^{2+} ($1.5 \times 10^{-4} \text{ mol dm}^{-3}$) and 1,10-phenanthroline ($7.5 \times 10^{-3} \text{ mol dm}^{-3}$) were kept constant.

The dissociation of ferroin was initiated by the addition of a definite amount of ferroin in absence and in presence of definite amount of acid. In absence of the acid and light, ferroin was stable upto 60%(v/v) of dmf beyond which the rate of dissociation is appreciable. The dissociation in dmf + water mixtures becomes measurable only in presence of high concentrations of acid and an optimum concentrations of 0.22 mol dm^{-3} of H^+ was maintained throughout.

The decrease in absorbance (A_t) at 510 nm was followed till completion as determined from A_∞ -values. The O.d readings at different intervals of time are recorded in Table - 2.

The reactions were studied in the dark and the readings at

different interval of time were taken using aliquot from the original reaction mixtures. The rate constants were found to be reproducible to within $\pm 5\%$ from several sets of measurements. The thermodynamic parameters were determined from the measurements of rate constants at three different temperatures.

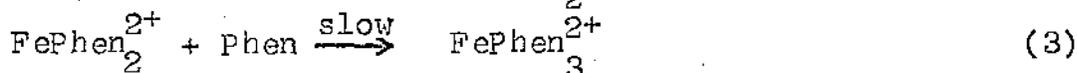
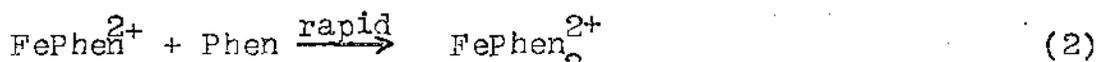
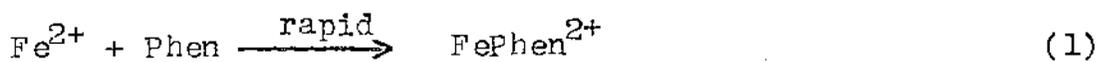
Results and Discussion :

Since the rates of formation in aqueous solutions was studied by Kolthoff et.al.², we made only some preliminary studies in aqueous solution. The results in mixed solvent indicate that the pseudo-first order rate of formation of ferroin for a fixed Fe^{2+} ion concentration is dependent on the concentration of the acid and ligand as well as ionic strength as would be apparent from the values of the first order rate constants obtained from the plots of $\log \frac{A_{\infty} - A_0}{A_{\infty} - A_t}$ against time (Table 3). In these measurements, concentration of H^+ ion and ligands are very large compared to the concentration of Fe^{2+} ion so that they can be regarded to be effectively constant in a particular measurement. Kolthoff et.al.² formulated a rate equation considering a zero-order rate of formation and first order rate of dissociation of ferroin which is inconsistent with our data.

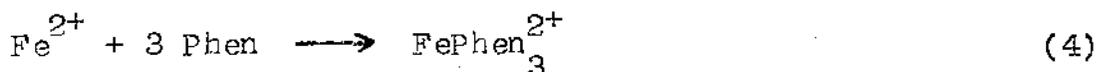
The zero-order rate constant had been reported to be dependent on the concentration of the reactants. Moreover, the rates of formation as well as rate of dissociation are very much

dependent on acid. The activity coefficients of PhenH^+ used in the calculation are erroneous. They have performed the reactions under conditions where complete conversion of Fe^{2+} to ferroin is not possible.

The rates of formation of ferroin has been formulated by them as



so that the overall reaction



seemed to be one of the fourth order similar to the formulation given by George and Baxendale¹ in case of Fe hipy_3^{2+} .

In presence of high concentrations of Phen or bipy, the reaction is independent only on Fe^{2+} concentrations. But marked changes in the reaction rate occurs in presence of acid due to the reactions.



All the steps (1) to (3) are fast, Kolthoff et.al.² like Baxendale et.al.¹ consider the step (3) to be rate-determining as it is the stage where the high spin \longrightarrow low spin occurs but we consider the step (1) to be rate determining due to the following

reasons :

1) In the dissociation of $\text{Fe}(\text{bipy})_3^{2+}$ or $\text{Fe}(\text{Phen})_3^{2+}$ the step low spin state \longrightarrow high spin state ($\text{Fe}(\text{bipy})_3^{2+} \longrightarrow \text{Fe}(\text{bipy})_2^{2+} + \text{bipy}$) is rate determining. The reverse should be true in case of forward process.

2) The rate law

$$\frac{d [\text{Fe}(\text{bipy})_3^{2+}]}{dt} = k_f \cdot [\text{Fe}^{2+}] [\text{bipy}]^3$$

With zero activation enthalpy (as reported)¹ is unacceptable in view of the fact that the apparent activation enthalpy is composite containing three ΔH^\ddagger values for successive equilibria as well as ΔH^\ddagger for the rate determining addition of the third bipy. molecule. This should be true in case of Ferriin complex also.

3) The change in electron configuration (high spin state \longrightarrow low spin state) should be fast compared to the rate process we measure. The works of Irving and co-workers¹¹ show conclusively that "orbital stabilization" does not take place in the first or the second step but only in the third step as the reaction is accompanied by the greater ease in the free-energy change. The electronic rearrangement is manifested in the unusual heat and entropy changes and $K_3 \gg K_2$ and K_1 .

- 4) The addition of Phen to a large excess of Fe(II) salt results the complex FePhen^{2+} (with a broad maximum in the region 450 nm) which is rapidly converted to FePhen_3^{2+} . The first order rate constant was obtained for the formation of Ni^{2+} reaction when Ni^{2+} ion concentration is fairly large compared to Phen (50 : 1)¹².
- 5) Fe^{2+} is octahedrally co-ordinated with H_2O molecules. Thus an attack of Phen and consequent replacement of two molecules of water from the co-ordination sphere should be the slow process but after the formation of FePhen_2^{2+} , the addition of third molecule of Phen and consequent removal of two molecules of water should be a fast process from symmetric and energetic considerations.

The linearity of the plot of the first order rate constants at a constant H^+ ion and Fe^{2+} concentrations against (Phen) suggest that the reaction is of second order and the rate-determining step is bimolecular in nature in water as well as in mixed solvents. However, the rates of formation in dmf + water or in dmf decrease with the increase in H^+ ion concentrations whereas increase with increasing $[\text{Phen}]$ as is apparent from the plots of $\log \frac{A_\infty - A_0}{A_\infty - A_t}$ against time [Figures 1(a) and 1(b)].

The rate constants (Table 4) were found to increase with increase in concentration of dmf at a fixed H^+ ion concentrations. This is apparent from the figures(2(a - 2d)). This is due to the decrease in the effective concentration of H^+ ion and lowering of

pK_a of 1,10-phenanthroline and consequent increase in the free [Phen] . The k -values suggest that dmf is incapable of competing with Phen at least up to 80% (v/v) beyond which the rate drops sharply. The overall rate of formation k_f of the complex in terms of equation (4) is

$$k_{\text{obs}} = k_f \frac{K_a^3}{(K_a + H^+)^3}$$

where K_a (the dissociation constant in mixed solvents for the reaction $\text{PhenH}^+ \rightleftharpoons \text{Phen} + \text{H}^+$)¹² has been determined by us. The overall rate constant determined for the same concentrations of Phen, Fe^{2+} and H^+ decreases with increase in concentration of dmf. Some uncertainty exists, however, due to the use of concentration terms instead of activity terms. Still the values indicate that the overall rate constant of formation of ferriin decreases rapidly with increase in dmf concentration (Table 5) in spite of the fact that the apparent rate constant increases with solvent composition.

The changes in $\log k_{\text{obs}}$ are well-correlated with the change in $1/D$ values up to about 60% v/v (Fig. 3). The effect of D is probably insignificant, the changes in acid-base character being important. But when the percentage of dmf is high, there must be a competition of Phen and dmf to enter into the co-ordination sphere of Fe^{2+} and Fe^{2+} - dmf complexation is a distinct reality which makes k_{obs} to drop sharply above 80% (v/v).

It is not possible to compare our results with those

of Kolthoff² in view of different experimental conditions and the formulations suggested by them are defective.

Experimental activation energies could not be compared due to lack of data. However, the ΔH^\ddagger values are considerable (about $42.03 \text{ kJ K}^{-1} \text{ mol}^{-1}$) which does not compare favourably with zero activation enthalpies for the formation of ferrodiin.

The formation of the activation complex involves the approach of the ligands trans-bipy, Phen, H_2O , loosening H_2O molecules, formation of Fe - N bonds. However, formation of $\text{Fe}(\text{bipy})_3^{2+}$ involves the conversion^{of} trans bipy to cis bipy (an exothermic process)¹³ whereas the formation of $\text{Fe}(\text{Phen})_3^{2+}$ involves the detachment of H_2O molecules from Phen. This accounts for the difference in activation enthalpies and larger negative entropy for the formation of ferroin.

The enthalpy of activation drops at 20% v/v of organic solvent, then increases. However, we are unable to measure the enthalpy values above 80% v/v organic solvents due to instant dissociation of the complex at the higher temperatures. The entropy value increases with the percentage of organic solvent. The 10-30^{wt%} and about 75-90 wt% organic component in mixed organic component + water media are critical with respect to replacement of water by organic component in the solvent sheath¹⁴. This is probably reflected in the enthalpy values at 20% and the k_{obs} values above 80% v/v.

$$k = k_1 \frac{k_1 + k_4 [\text{H}^+]}{k_2 + k_3 + k_4 [\text{H}^+]}$$

Bosolo et.al. and Baxendale et.al. observed only qualitative but no quantitative agreement which is attributed to activity effects.

In view of the elaborate works of Bosolo et.al., we studied the dissociation reactions in mixed or dmf media though some preliminary measurements have been made in water.

The rates of dissociation of ferroin follow first order kinetics in presence or absence of acid as observed from the plots of $-\log (A_t - A_\infty)$ against time (Fig 4).

The specific rate constant has been found to be dependent on $[\text{H}^+]$ ion concentrations (in addition to ferroin) which is also corroborated from the extensive studies of Bosolo et.al.^{4,5,15} (and Raman⁷ in case of dissociation of Febipy_3^{2+}) who noted that in addition to H^+ ions, anions and cations^{5,17,18} also have significant influence on reaction rates. The equations (1 - 4) indicate that the dissociation is independent of pH but the dependency on pH arises from the equations (5) and (6). The rate reaches almost limiting value when the acid concentration exceeds 0.5 mol dm^{-3} , it does not affect the rate significantly due to the conversion of Phen to Phen H^+ .

The rates of dissociation or exchange in presence or absence of acid at constant pH can be represented as

$$-\frac{d[\text{Fe Phen}_3^{2+}]}{dt} = k_d [\text{Fe Phen}_3^{2+}]$$

But the values of k_d are lower in presence of acid.

The values of k_d at 291 K at various percentage of dmf + water mixtures are recorded in table 6. The rate constants for the dissociation of ferroin in presence of acid and the other thermodynamic parameters in the solvent range (60 to 100% v/v dmf) are included in table 7.

The rate of dissociation in presence of acid increases with addition of dmf and remains effectively constant upto 50% v/v. The rate increases afterwards. However, the rate constant increases much more rapidly in neutral solutions. The results may be explained in the following way.

1) dissociation of the complex due to increase in basicity with the addition of basic solvent dmf and the conversion of Fe^{2+} to Fe^{3+} ion with subsequent hydrolysis.

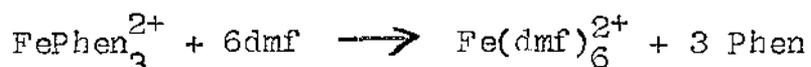
2) exchange of Phen by dmf.

The plot of k_d vs 1/D show linearity in the region 70-100% dmf. Slight deviation is observed at 90% (Fig 5).

The increase in k_d with increasing dmf at a particular H^+ ion concentration is due to the probable combination of H^+ ion with the highly co-ordinating dmf reducing the acidity of the

medium and also capability of H^+ ion to combine with Phen. This also explains why we have to chose a high concentrations of acid to determine the k_d in dmf + water mixtures.

The values of k_d suggest that no exchange of Phen with dmf takes place at low percentages of dmf but only at very high percentages (above 80%) the exchange of Phen with dmf is a distinct reality and possibly high at 100% dmf. Since $FePhen_3^{2+}$ is highly stable compared to $Fe(dmf)_6$, the exchange reaction



is possible only under favourable condition. The results indicate that the change in dielectric constant has no specific contribution in the decomposition.

The comparison of the rates of dissociation is not possible as we have not determined the rates under comparable conditions. The value of k_d given by Kolthoff et.al. is $4.5 \times 10^{-3} \text{ min}^{-1}$ or $7.5 \times 10^{-5} \text{ sec}^{-1}$ for in 0.005, 0.05 and 0.5 mol dm^{-3} H_2SO_4 whereas the value reported by Bosolo et.al. is $7.0 \times 10^{-5} \text{ sec}^{-1}$ in 1 mol dm^{-3} HCl at 298 K which compares very well with our value, $1.79 \times 10^{-4} \text{ sec}^{-1}$ in 0.22 mol dm^{-3} $HClO_4$ at 303 K, the reported activation energy (water) in 1 mol dm^{-3} HCl is $134.2 \pm 2.1 \text{ kJ}$ could not compared. The activation energy in neutral solution at 70% dmf is 109.00 kJ.

Similarly the comparison of the dissociation constant values

in non-aqueous media is not possible due to lack of data. The rate of dissociation was measured by Van Meter and Neumann⁸ using $1.5 \times 10^{-4} \text{ mol dm}^{-3} \text{ Fe(Phen)}_3^{2+}$ in $1.5 \times 10^{-2} \text{ mol dm}^{-3} \text{ Ni}^{2+}$ (as perchlorate) ion. Though the k_d value $7.7 \times 10^{-5} \text{ sec}^{-1}$ at 298K compare very favourably with the value reported by Bosolo et.al. under widely different conditions, we feel it useless to compare our result with those reported by Van Meter et.al.⁸

The observed dissociations or exchange kinetics follow either a dissociative or interchange mechanism similar to those suggested by Gillard et.al.¹⁹

The approach of solvents and bond-rupture is the major process in the formation of transition state. The dissociation or exchange proceeds through a nucleophilic attack on the six co-ordinated complex to form an intermediate transition state where the metal is assumed to be co-ordinated both by the leaving and incoming ligands. The activated complex then decomposes with the rupture of the metal-ligand bond. The high electronegative C=O -group in dmf may increase the rate at which the metal-nitrogen bonds are broken.

The attack by H_2O or dmf would depend on the composition of the solvent. The changes of the complex capturing a dmf or a water molecules are in direct proportion to their numbers in the bulk medium. Thus, exchange by dmf may increase as the percentage of dmf increases.

The ΔH^\ddagger values for dissociation are highly endothermic indicating the rupture of metal-ligand bond and subsequent replacement of Phen by H_2O or dmf is difficult though the attachment of Fe with highly electronegative co-group of dmf may decrease the enthalpy of activation. However, the observed variation of k_d , ΔH^\ddagger and ΔS^\ddagger with [dmf] indicate that the environment external to the first co-ordination sphere is not significantly modified and observed enthalpy changes arise mainly from the structure forming entropy effect. The formation of transition state should accompany a decrease in entropy whether the activated complex includes water or dmf. The entropy decrease may be due to decrease in the total number of solvent molecules with increasing dmf concentration as well as structural changes associated with the changes in solvent compositions.

The proportional decrease in the enthalpy and entropy values indicate that the structural factors associated with ΔH^\ddagger and ΔS^\ddagger arising from the changes in solvent environment compensate each other. The fact also suggests that in every case the rupture of metal-N-bond is rate determining step and the successive addition of the organic solvent alters the rate without influencing the mechanism.

The correlation of rates of formation or dissociation of ferroin with the structures of the solvent mixtures is difficult. Addition of dmf to water first enhances the water-structure (between 20-30% dmf), further addition of dmf leads

to extensive depolymerisation of water molecules and dissociation of dmf and consequent formation of hydrogen-bonded dmf-water system which goes upto about 80% v/v. Beyond this region, disruption of dmf-water may occur and solvation of Fe^{2+} by dmf or exchange of Phen by dmf may take place.

Thus, up to at least 80% (v/v) of dmf there is only marginal changes in the secondary solvation shell arising from the disruption of water and dmf structures with concomittant formation of dmf-water structure. This may lead to decrease in entropy and enthalpy values. Beyond this region, primary solvation is likely to be affected and exchange of Phen by dmf from ferroin also takes place in this region with changes in entropy and enthalpy values.

It is clear that the study of the exchange kinetics by stopped-flow technique would provide better insight regarding the mechanism of formation and dissociation of Ferroin.

Table - 1

Formation of ferriin

a. Solvent = 40% v/v dmf + water. Complex concentration =
 $6 \times 10^{-5} \text{ mol dm}^{-3}$

$$[\text{H}^+] = 0.22 \text{ mol dm}^{-3}$$

Temp = 293 K

$$A_{\infty} (0. \text{d at infinite time}) = 1.25$$

Time (mins)	o.d	$\log \frac{A_{\infty} - A_0}{A_{\infty} - A_t}$	$k_{\text{obs}} \times 10^4 \text{ sec}$
9	0.300	0.119	
16	0.450	0.194	
24	0.620	0.298	3.85
30	0.710	0.365	

b. Solvent = 40% v/v dmf + water. Complex concentration =
 $6 \times 10^{-5} \text{ mol dm}^{-3}$

$$[\text{H}^+] = 0.22 \text{ mol dm}^{-3}$$

Temp = 300.5 K

$$A_{\infty} = 1.25$$

Time (mins)	o.d.	$\log \frac{A_{\infty} - A_0}{A_{\infty} - A_t}$	$k_{\text{obs}} \times 10^4 \text{ sec}$
9	0.335	0.136	
16	0.510	0.228	
24	0.670	0.334	6.00
30	0.770	0.416	

Table - 2

Dissociation of ferroin

a. Solvent = 100% dmf. Complex concentration = $6 \times 10^{-5} \text{ mol dm}^{-3}$

$$[\text{H}^+] = 0.00 \text{ mol dm}^{-3}$$

Temp = 303 K

$$A_{\infty} (\text{O.d at infinite time}) = 0.00$$

Time (mins)	O.d	$-\log (A_t - A_{\infty})$	$k_{\text{obs}} \times 10^4 \text{ sec}$
5	0.275	0.56	
10	0.225	0.65	
15	0.150	0.83	13.80
20	0.100	1.00	
25	0.065	1.19	

b. Solvent = 100% dmf ; Complex concentration = $6 \times 10^{-5} \text{ mol dm}^{-3}$

$$[\text{H}^+] = 0.00 \text{ mol dm}^{-3}$$

Temp = 308 K

$$A_{\infty} = 0.00$$

Time(mins)	O.d	$-\log (A_t - A_{\infty})$	$k_{\text{obs}} \times 10^4 \text{ sec}$
3	0.250	0.60	
6	0.150	0.82	24.80
10	0.080	1.09	
15	0.040	1.39	

Table - 3

Effect of variation of phenanthroline concentration, H^+ ion concentration and ionic strength on the rate of formation of ferroin.

a. $[Fe^{2+}] = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$, $[H^+] = 0.9 \text{ mol dm}^{-3}$; Temp = 300.5 K

% (v/v) of dmf	$[Phen] \times 10^3 \text{ mol}^{-1} \text{ dm}^3$	$k_{obs} \times 10^4 \text{ sec}$
	6.5	10.29
80	7.0	18.42
	7.5	34.54

b. $[Fe^{2+}] = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$; $[Phen] = 7.5 \times 10^{-3} \text{ mol dm}^{-3}$

Temp = 300.5 K

% (v/v) of dmf	$[H^+] \text{ mol}^{-1} \text{ dm}^3$	$k_{obs} \times 10^4 \text{ sec}$
	0.9	34.54
80	1.01	15.35
	1.12	8.82

c. $[Fe^{2+}] = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$; $[Phen] = 7.5 \times 10^{-3} \text{ mol dm}^{-3}$;

$[H^+] = 0.9 \text{ mol dm}^{-3}$

Temp = 300.5 K

% (v/v) of dmf	$[NaClO_4] \text{ mol}^{-1} \text{ dm}^3$	$k_{obs} \times 10^4 \text{ sec}$
	0.06	8.57
80	0.08	7.38
	0.10	6.42

Table - 4

Pseudo-first order rate constants and activation parameters for the formation of ferroin complex in dmf-water media.

$$[\text{Fe}^{2+}] = 1.5 \times 10^{-4} \text{ mol dm}^{-3}; \text{Phenanthroline Conc}^n = 7.5 \times 10^{-3} \text{ mol dm}^{-3}, [\text{H}^+] = 0.9 \text{ mol dm}^{-3}$$

% V/V of dmf	Temp(K)	$k_{\text{obs}} \times 10^4 \text{ sec}$	$\log_{10} A$	$\Delta H^\ddagger (\text{kJK}^{-1} \text{mol}^{-1})$	$\Delta S^\ddagger (\text{JK}^{-1} \text{mol}^{-1})$ at 300.5 K
0	293	0.294	3.11	42.93	-185.60
	300.5	0.460			
	308	0.690			
20	293	1.10	3.41	30.00	-178.90
	300.5	1.72			
	308	2.55			
40	293	3.85	4.52	43.72	-159.90
	300.5	6.00			
	308	8.92			
60	293	11.51	5.21	45.98	-145.30
	300.5	16.88			
	308	25.71			
80	293	23.03	5.79	47.53	-134.30
	300.5	34.54			
	308	57.57			
90	293	6.23	-	-	-
100	293	4.51	-	-	-

Table - 5

k_f values for the formation of Ferriin Complex at various percentage of dmf + water media.

%(v/v) of dmf	pK _a (at 298K)	K _a	$\left(\frac{K_a}{K_a/[H^+]}\right)^3$	k _{obs} x 10 ⁴ (at 300.5 K)	k _f x sec
0	5.05	8.9 x 10 ⁻⁶	9.67 x 10 ⁻¹⁶	0.460	4.75 x 10 ¹⁰
20	4.10	7.94 x 10 ⁻⁵	6.86 x 10 ⁻¹³	1.72	2.51 x 10 ⁸
40	3.44	3.63 x 10 ⁻⁴	6.54 x 10 ⁻¹¹	6.00	9.17 x 10 ⁶
60	2.95	1.12 x 10 ⁻³	1.90 x 10 ⁻⁹	16.86	8.87 x 10 ⁵
80	2.39	4.07 x 10 ⁻³	9.1 x 10 ⁻⁸	34.54	3.79 x 10 ⁴

Table - 6

Pseudo-first order rate constant of dissociation of ferrioxalate complex in dmf-water media in absence and in presence of acid.

Complex Concⁿ = 6 x 10⁻⁵ mol dm⁻³ Temp = 303 K

% v/v of dmf	[H ⁺] mol ⁻¹ dm ³	k _{obs} x 10 ⁴ sec
100	0	13.80
	0.22	10.89
90	0	8.67
	0.22	7.02
80	0	7.01
	0.22	5.68
70	0	5.00
	0.22	3.70
60	0	-
	0.22	3.19
50	0	-
	0.22	2.17
40	0	-
	0.22	2.17
30	0	-
	0.22	2.17
20	0	-
	0.22	2.17
10	0	-
	0.22	2.17
0	0	-
	0.22	1.79

Table - 7

Pseudo-first order rate constants and the activation parameters for the dissociation of ferroin complex in dmf+water Media.

Complex Concⁿ = 6×10^{-5} mol dm⁻³; [HClO₄] = 0.0 mol dm⁻³

% (v/v) of dmf	Temp (K)	k _{obs} x 10 ⁴ sec	log ₁₀ A	ΔH [‡] (kJK ⁻¹ mol ⁻¹)	ΔS [‡] (JK ⁻¹ mol ⁻¹) at 303 K
100	303	13.80	11.82	37.18	-1900
	308	24.80			
	313	45.00			
90	303	8.67	13.44	95.85	12.26
	308	16.46			
	313	30.60			
80	303	7.01	14.08	100.10	24.73
	308	13.34			
	313	24.33			
70	303	5.00	15.03	109.00	42.81
	308	8.62			
	313	16.10			

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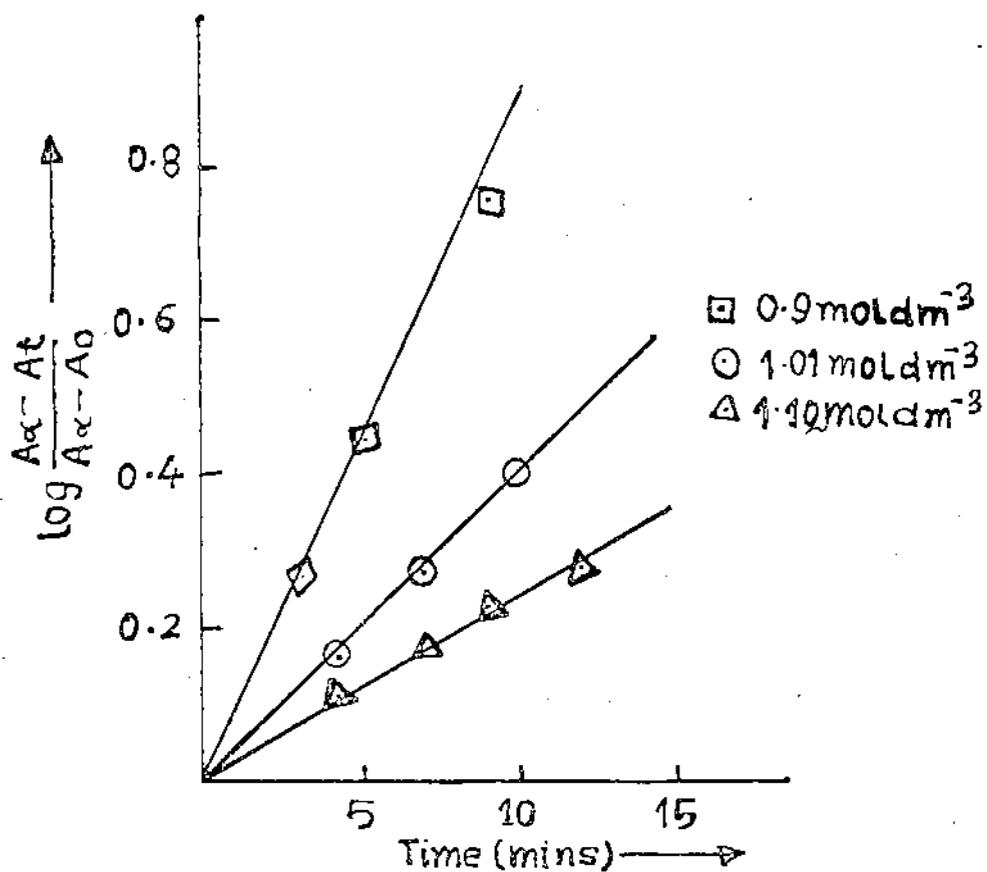


Fig. 1(a) Effect of $[H^+]$ on reaction rate at 300.5K
 Solvent: 80% (v/v) dmf-water.

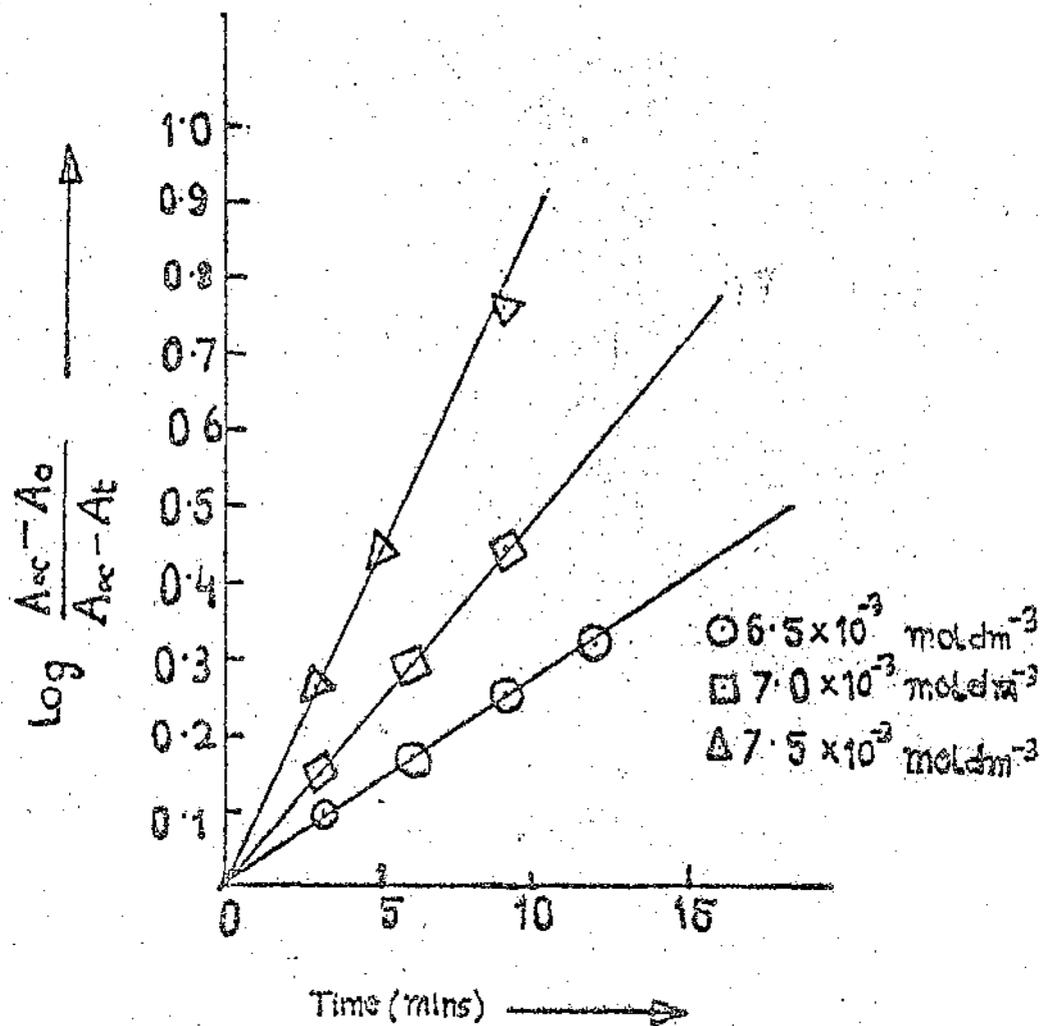


Fig. (b) Effect of [Phen] on reaction rate at 300.5K
 Solvent : 80% (v/v) dmf-water.

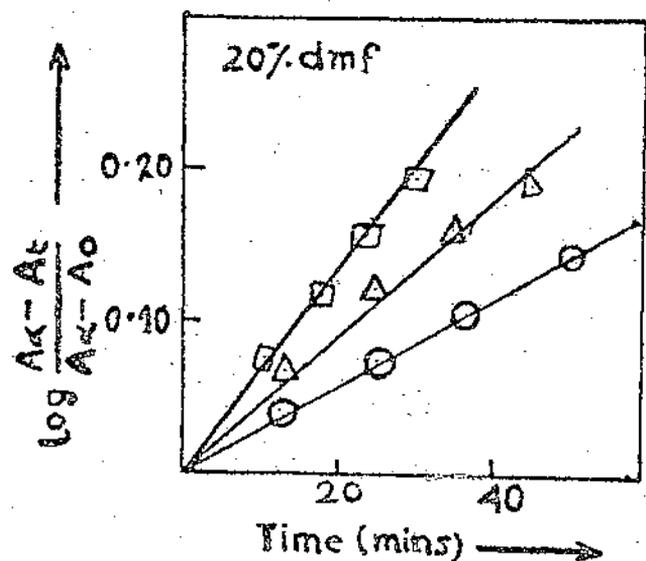


Fig. 2a

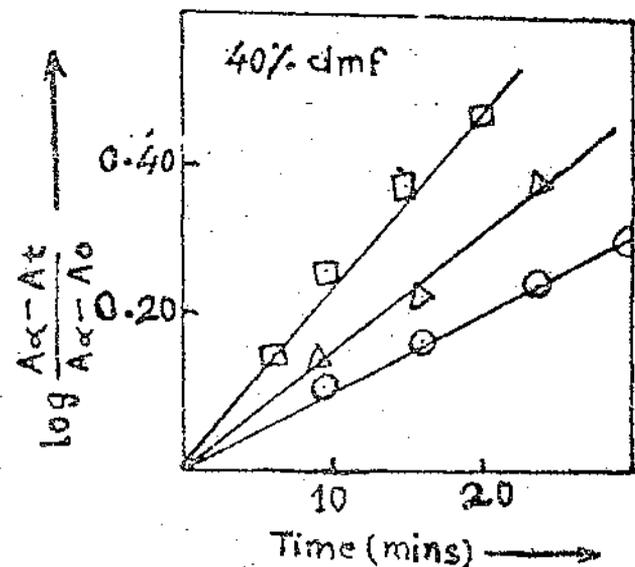


Fig. 2b

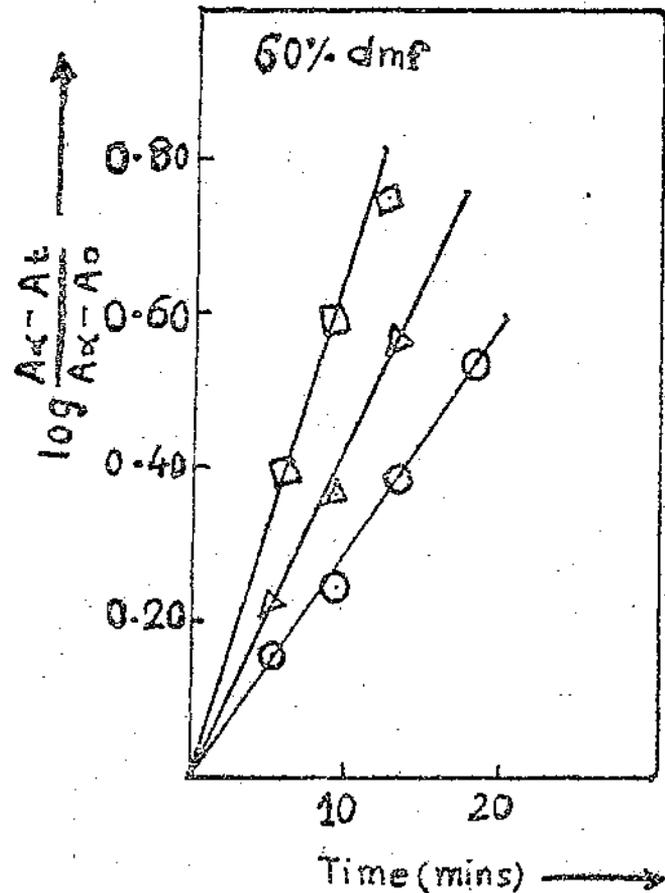


Fig. 2c

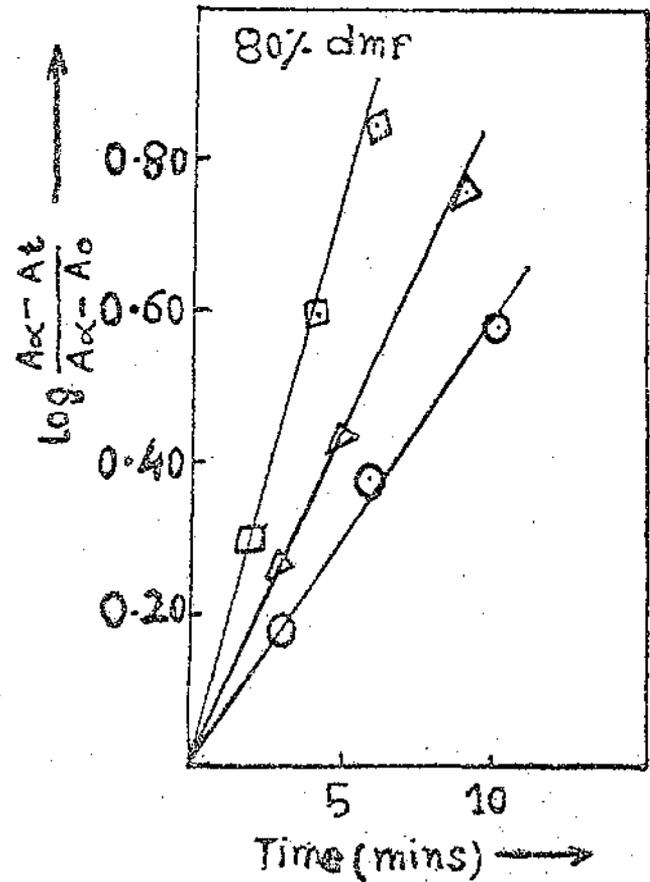


Fig. 2d

○ 293K ; △ 300.5K ; □ 308K

Rate of Formation of Ferrioin

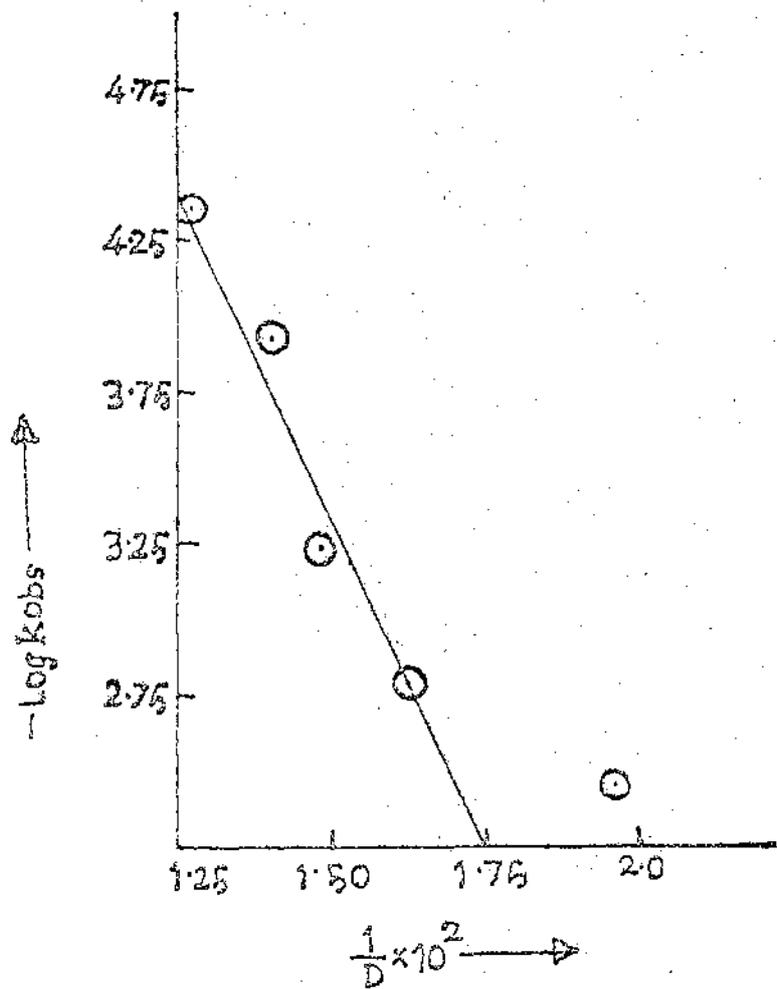


Fig. 3 Effect of dielectric constant on the reaction rate of formation of Ferriin.

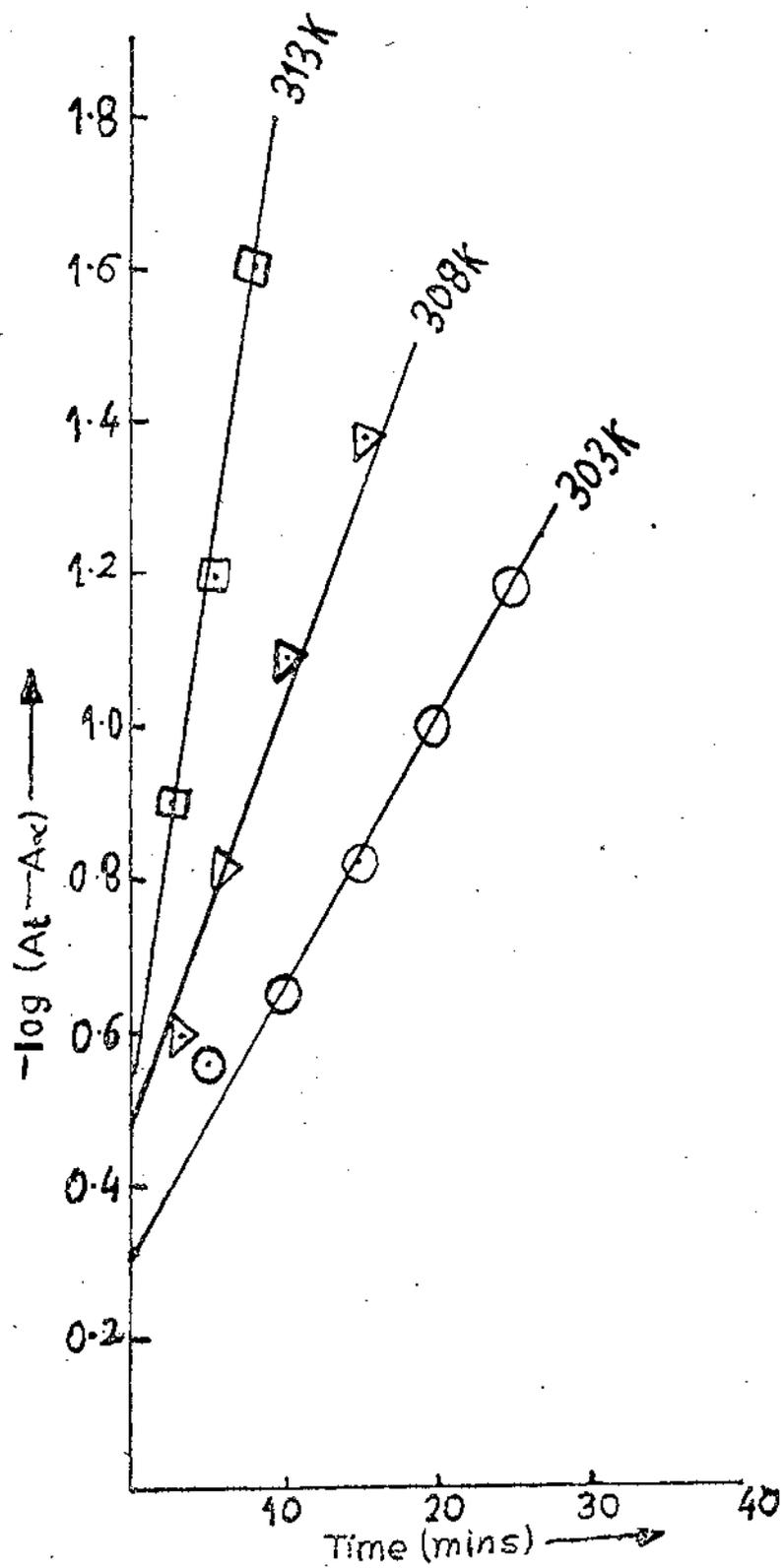


Fig.4 dissociation of ferriin in 100% DMF

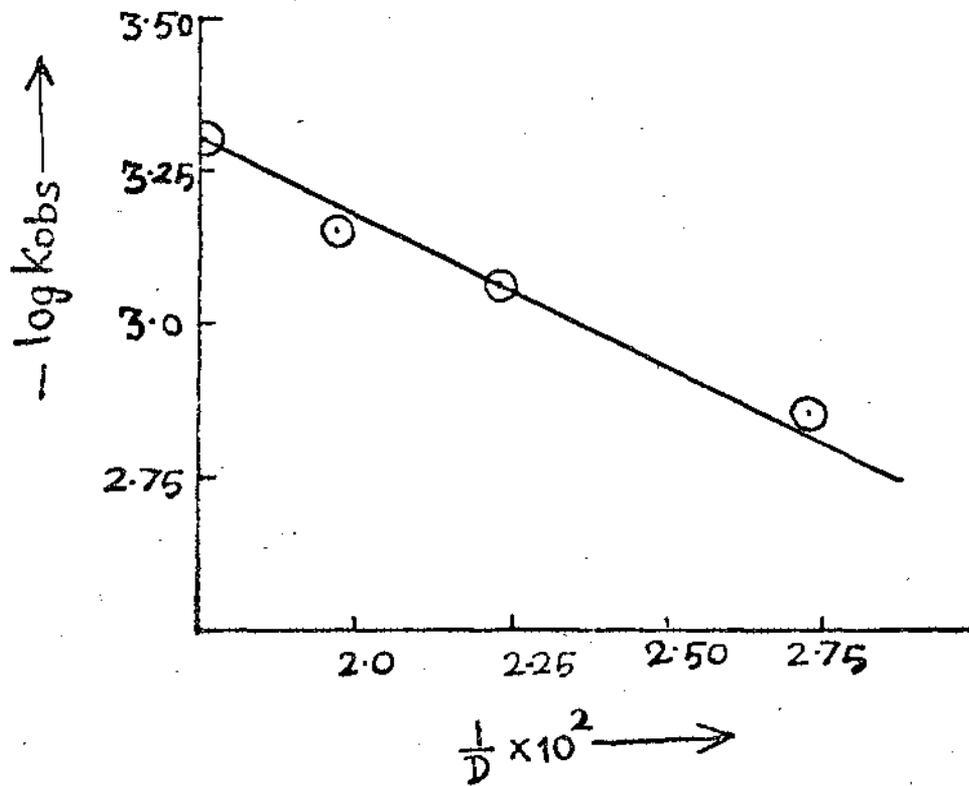


Fig. 5 Plot of $-\log k_{obs}$ vs $\frac{1}{D}$

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

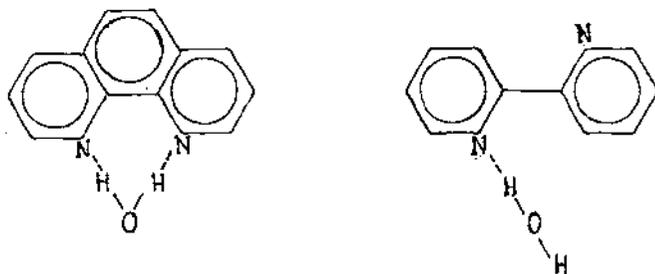
All the ligands have two very intense bands in the U.V.

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 $Ph.H_2O$ though Ph is known to retain water tenaciously. Spectra of Ph and $Ph.H_2O$ 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).



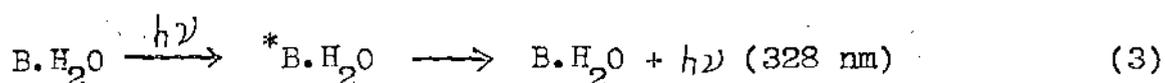
We found no band for B corresponding to α or ρ - band observed in case of Ph. However, no question of obtaining pure B spectra arise in solutions of pH 4.5 ($pK_B = 4.48$)¹² or even at higher pHs as it would be the result of the combined spectra of B and BH^+ , BH^+ having much higher ϵ than B and at 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.

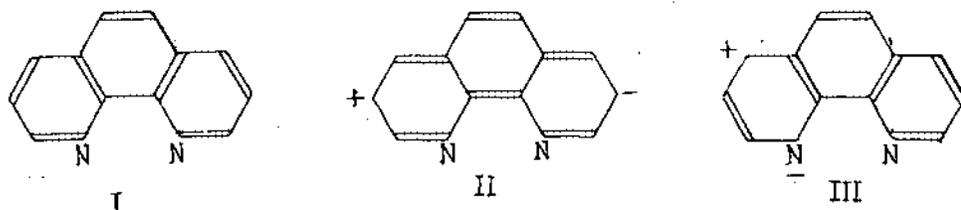
iii) The trans form of B has a dipole moment 0.91 D where cis- B has $\mu = 3.80$ D and Ph has $\mu = 4.11$ D^{36,37}.

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.



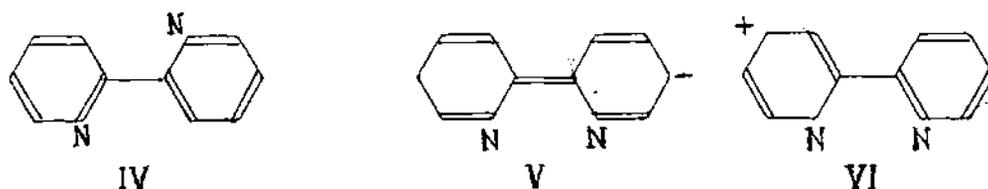


Fig. 4

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.

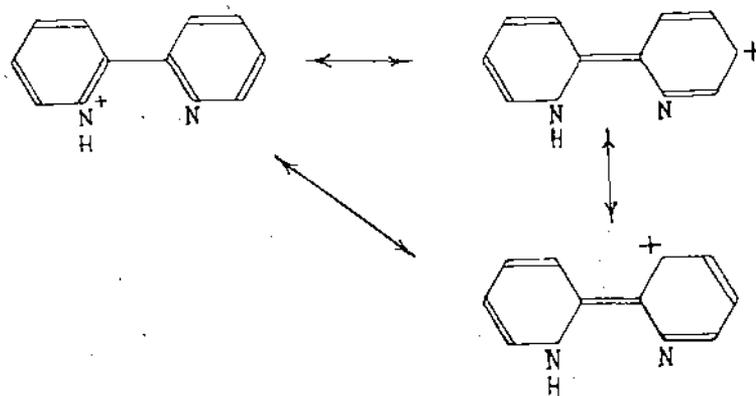


Fig. 6

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 2,2' - bipyridine		$\bar{\nu}_{\max}$ in cm^{-1} of 1, 10 - phenanthroline		$\bar{\nu}_{\max}$ in cm^{-1} of 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 ₂ O	-	36,630
dmf - H ₂ O	-	36,630
dmsO - H ₂ O	-	36,860
PC - H ₂ O	45,450	36,900

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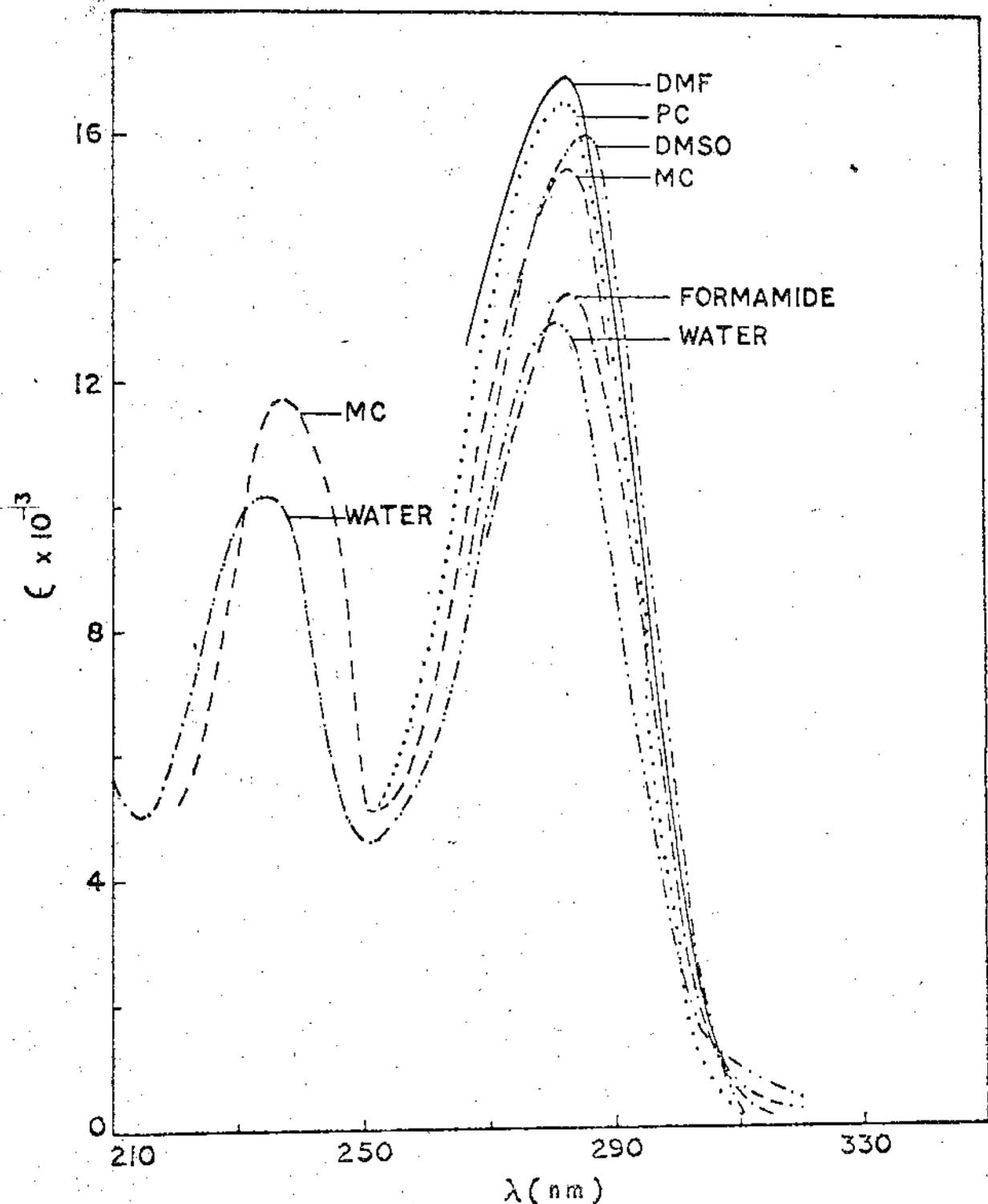


FIG. 1 THE SPECTRA OF 2, 2'-BIPYRIDINE IN VARIOUS SOLVENTS.

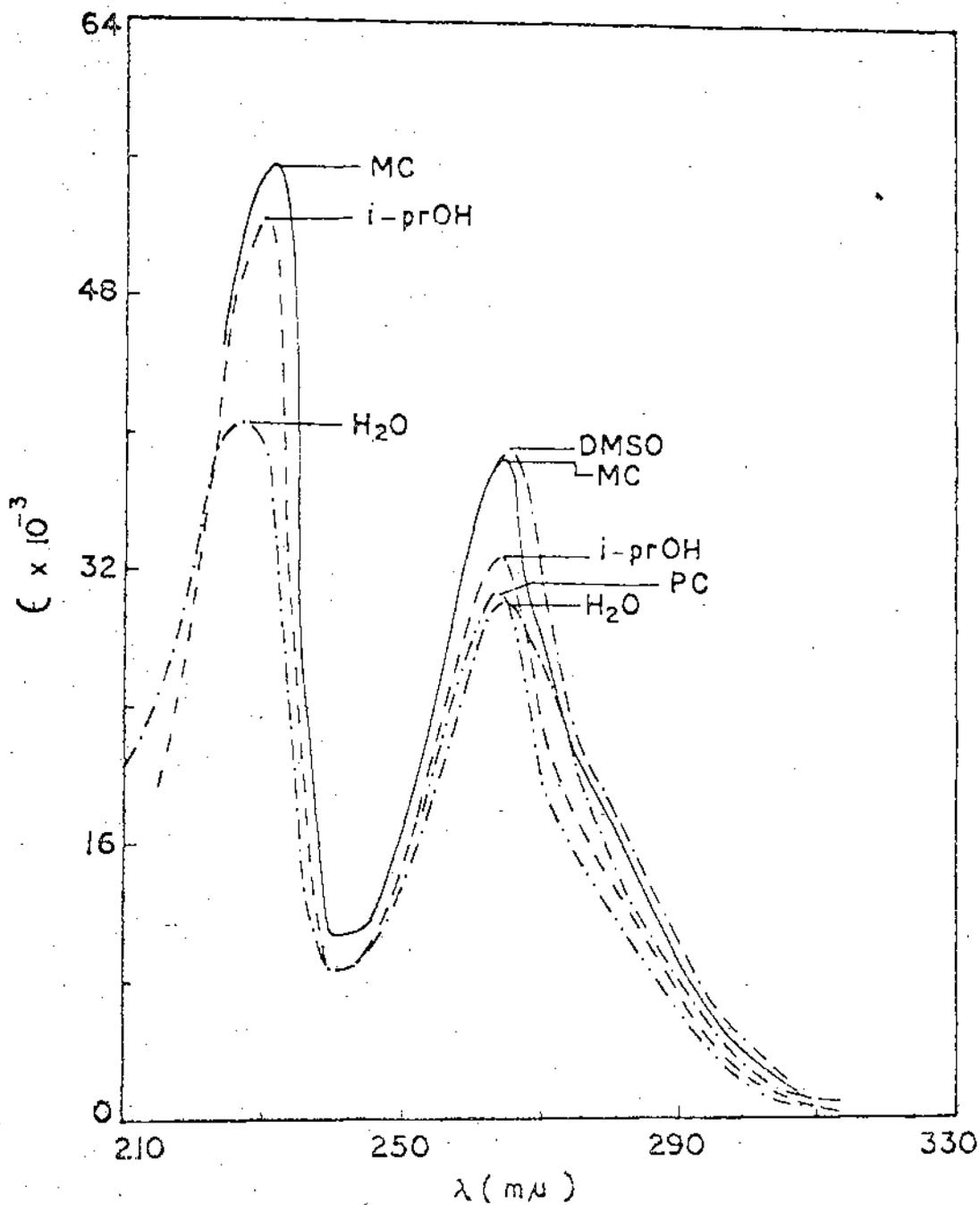
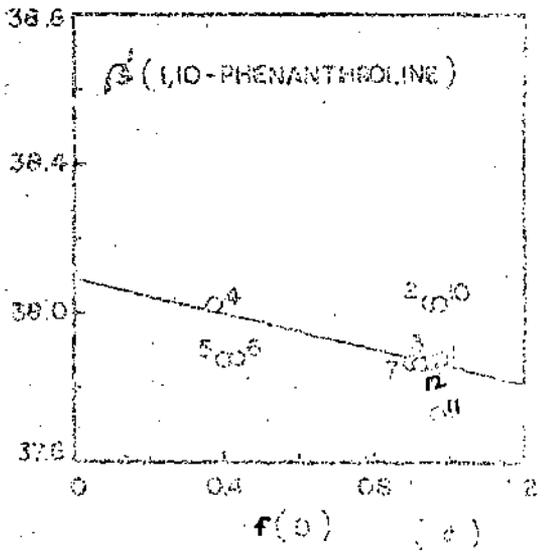
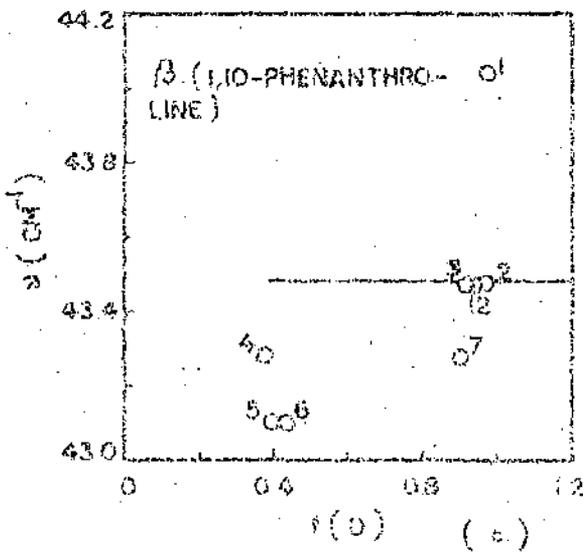
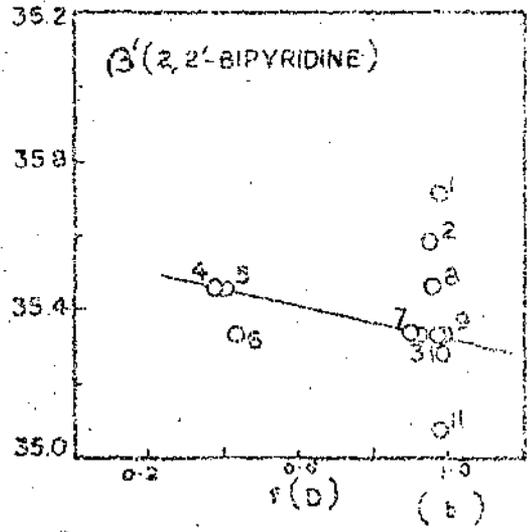
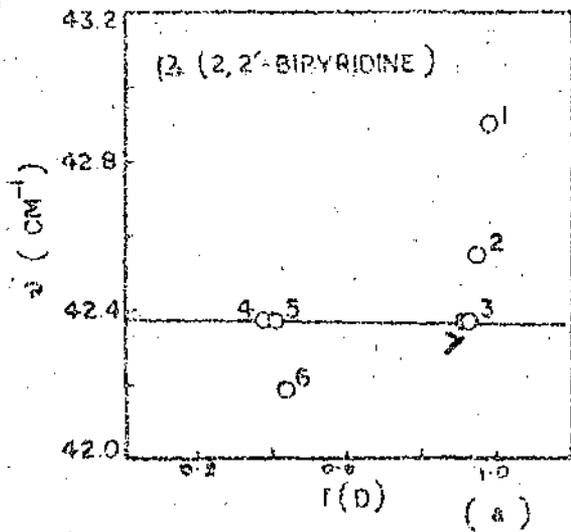


FIG. 2. THE SPECTRA OF 1,10-PHENANTHROLINE IN VARIOUS SOLVENTS.



1. WATER 2. METHANOL 3. ISOPROPANOL 4. n-HEPTANE
 5. CYCLOHEXANE 6. DIOXAN 7. METHYLCELLULOSE 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

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

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

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

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

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

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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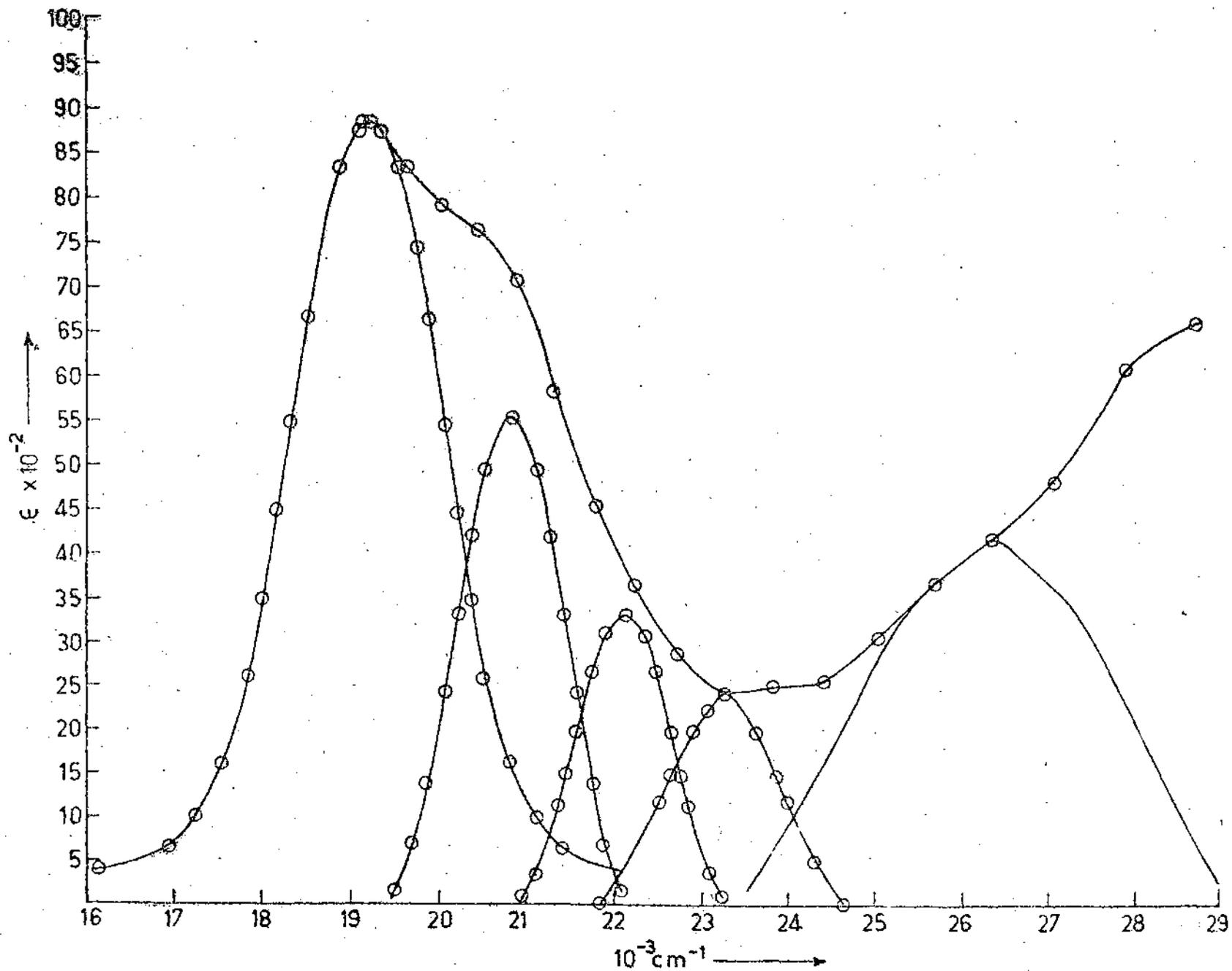


Fig. Absorption spectra of ferrodin in 90% v/v formamide-H₂O

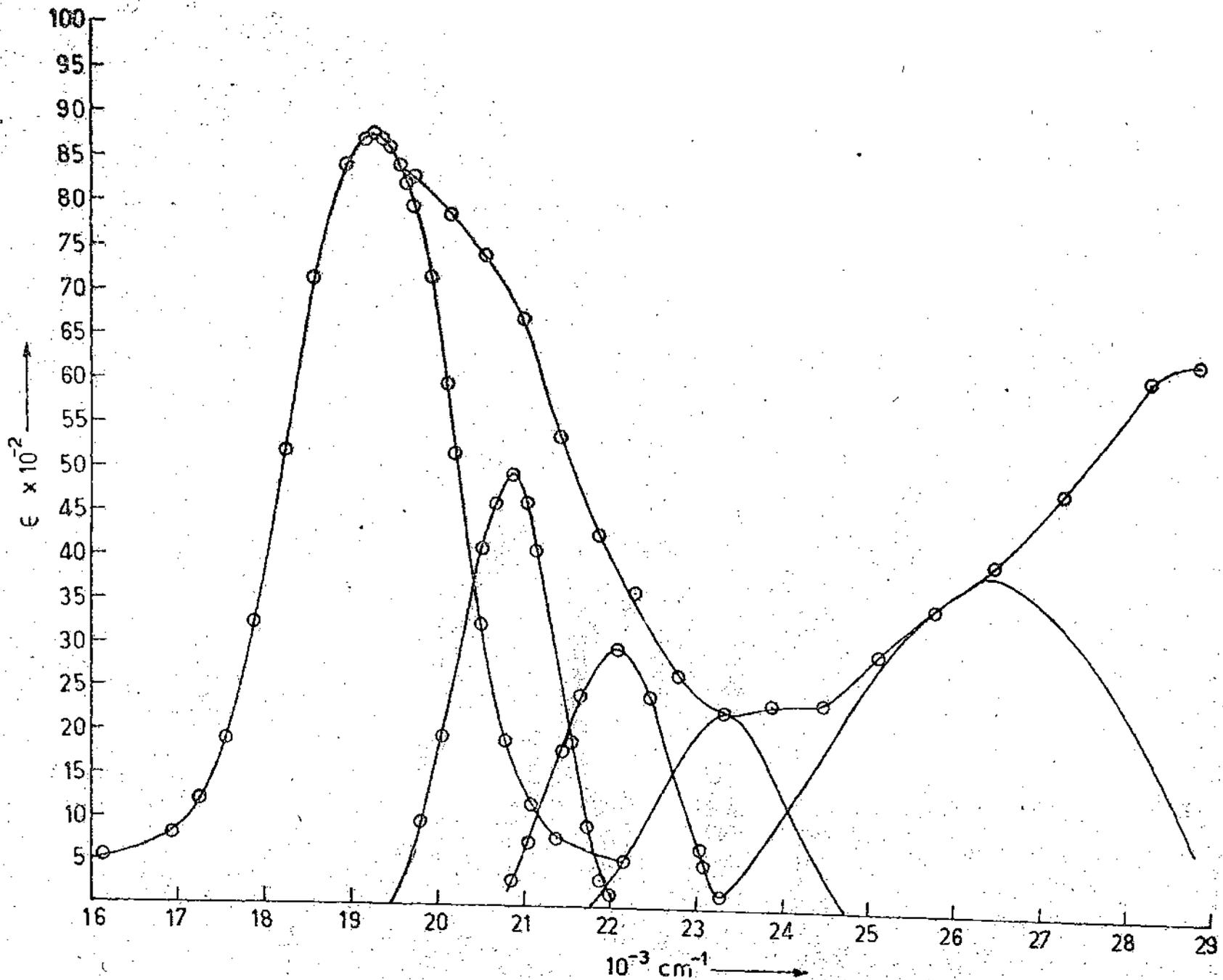


Fig. Absorption spectra of ferrodiin in 90% v/v dmsO-H₂O

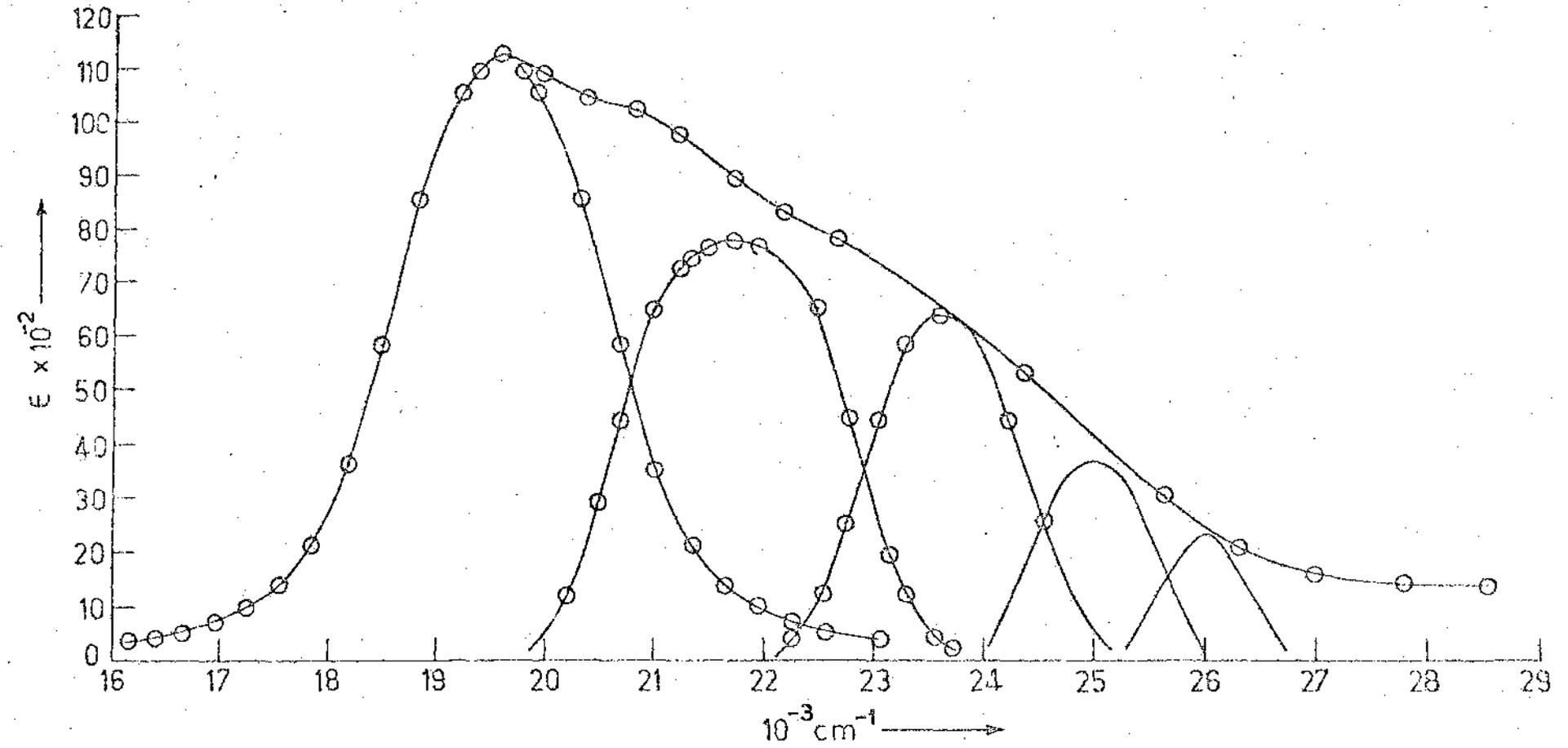


Fig. Absorption spectra of ferriin in 90% v/v formamide-H₂O.

Fig. 3

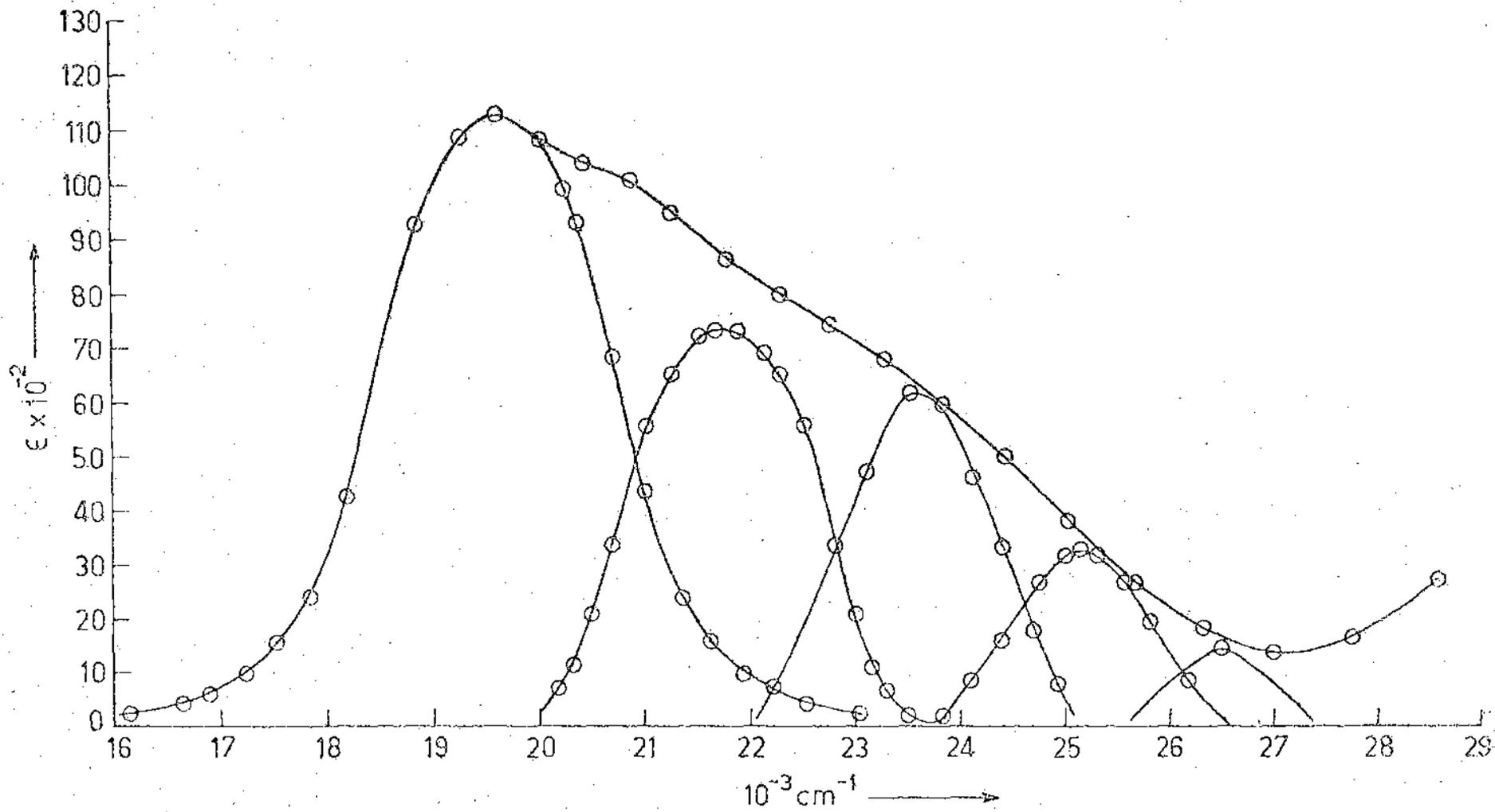


Fig. Absorption spectra of ferroiin in 90% v/v dmsO-H₂O.

Some concluding Remarks :-

With limited resources at our disposal, we have tried to explore the different aspects of solution chemistry and some useful conclusions have been derived.

Our studies on the dissociation constants of the ligands and their complexes only indicate that we are still in the dark regarding the proper elucidation of different types of interactions that occur in solution. Only it is possible for us to have a knowledge regarding the free-energies of transfer of ions from one solvent to the other. The limitations of the calculations of $\Delta G_t^\circ(\text{el})$ have been properly emphasized in the introduction. The $\Delta G_t^\circ(\text{neut})$ is not known in most cases. Still it is desirable to have a large number of data on the free-energy of transfer, particularly with ions of known radii and the $\Delta G_t^\circ(\text{neut})$ to understand the various aspects of solution chemistry. We have not used pure organic solvents as we are not properly equipped to carryout experiments in perfectly dry conditions.

One of the important aspects of solution chemistry is the determination of the thermodynamic dissociation constants in aqueous and mixed solvents.

The usual procedure to have the thermodynamic equilibrium or dissociation constants are :-

- (1) Determining the dissociation constants at infinitely dilute solutions where feasible¹
- (2) Determining the dissociation constants at different ionic strengths and using various extrapolations²⁻⁸.
- (3) Determining the dissociation constant at any particular ionic strength and making activity corrections using different theoretical as well as semiempirical equations which are valid at best up to 0.1 mol dm^{-3} ²⁻⁸.

But the exact thermodynamic dissociation constants are more or less elusive. Thus most of the workers⁴⁻⁸ prefer to use a constant "ionic medium" so that the formation constant at any particular ionic strength may be calculated. Unfortunately, the effect of different electrolytes (having same ionic strength) on the dissociation constants are different and the comparisons of the results difficult unless the determinations are carried out at the same ionic strength using the same electrolytes.

Furthermore, the increased knowledge of the ion-solvent interactions have pointed to a number of limitations particularly when the ionic strengths are high. These are :

- 1) In presence of electrolytes, the solvent molecules would be highly polarised and variations of dielectric from 1.78 near the ions to bulk dielectric constant 78.5 would occur^{9,10}.

A variation of static dielectric constant of the solvent e.g., $D = 71.0$ in presence of 0.5 mol dm^{-3} LiCl to $D = 51.0$ at 2.0 mol dm^{-3} LiCl at 25°C in presence of electrolytes is also observed.

(2) In presence of different electrolytes the activity coefficients of uncharged electrolyte are altered to different extents e.g., $\text{CH}_3\text{COOH} = 1.16$ in 1 m NaCl and 0.97 in $1 \text{ m CH}_3\text{COONa}$ ¹².

(3) The tetrahedral water structure breaks down in presence of ions and ions are solvated resulting in a decrease in the effective concentration of solvent molecule particularly when the electrolyte concentration is high¹³⁻¹⁴. Solvation of different ions are different¹⁵.

(4) Ion-association leads to the reduction of ionic strength and association between the ions of neutral electrolyte with reacting species also lead to a number of complications.

It is thus apparent that the relative magnitudes of the different types of interactions are difficult to estimate. These interactions may reinforce or cancel each other making the real understanding extremely difficult.

In view of the limitations described above, it is always desirable to use dilute solutions avoiding "inert electrolytes" as far as practicable. These enable us to determine the thermodynamic dissociation constants of the ligands and the 'medium effects' of H^+ ion as described in the Chapter - I.

interactions. Though the spectral solvent shifts in case of 2,2'-bipyridine and 1,10-phenanthroline and their Fe(II) complexes are very small, but it is clear that the nature of the solutes and the solvents are important to understand the solute-solvent interactions. It has been observed that for solutes with hydrogen-bonding capability, blue shift is observed in going from non-polar to polar solvent be it $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transitions.

However, it is quite clear that the nature of solute-solvent interactions are very complex and different physico-chemical properties like solubility, viscosity, conductance, transference numbers, solvation numbers from N.M.R. or ultrasonic experiments or other techniques are necessary to have some understanding regarding the ion-solvent interactions.

In view of lack of funds and proper instrumental facilities, we could not explore fully the properties of the mixed solvents.

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Absorption Spectra of 2, 2'-Bipyridyl, 1,10-Phenanthroline & 5-Nitro-1,10-phenanthroline in Different Solvents

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The absorption spectra of 2,2'-bipyridyl, 1,10-phenanthroline and 5-nitro-1,10-phenanthroline have been recorded at 25°C in solvents of diverging characteristics. The spectral behaviour of 2,2'-bipyridyl has been analysed and no evidence of band at 308 nm due to covalent-hydrate formation of 2,2'-bipyridyl as reported by Henry and Hoffman is observed [*J. phys. Chem.*, 83 (1979), 625]. The transitions involved are all $\pi \rightarrow \pi^*$ transitions. The solvent-induced shifts of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions have been discussed in terms of ground state and excited state solvation arising from solute-solvent interactions of varied nature. It is noted that for solutes with hydrogen-bonding capability, blue shift is observed in going from non-polar to polar solvents be it $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transitions.

THE effect of solvent-induced shifts on the absorption spectra of organics is not only useful for spectral assignments but also for understanding different factors influencing solute-solvent interactions¹⁻³. However, lack of proper knowledge of the different factors associated with solute-solvent interactions makes such a study complicated and a clear picture is yet to come. This is particularly true for $\pi \rightarrow \pi^*$ transitions which are characterized by small solvent-induced shifts. This prompted us to undertake the title investigation. We have also examined the anomalous spectral behaviour of 2,2'-bipyridyl reported recently by Henry and Hoffman⁴.

Materials and Methods

2,2'-Bipyridyl (Bipy), 1,10-phenanthroline (phen) and 5-nitro-1, 10-phenanthroline (5-NO₂-phen) were of extra pure quality (E. Merck or Sigma Chemicals). Methanol (GR, E. Merck) and isopropanol (AR, BDH) were distilled. Formamide (GR, E. Merck), dimethyl sulphoxide (Baker analyzed) and propylene carbonate (K. Light, puriss) were dried over freshly ignited quicklime for several hours and then distilled under reduced pressure. N,N'-Dimethylformamide, *n*-heptane, isooctane, cyclohexane (Uvasol grades) were used as such. Methyl cellosolve was treated with lithium hydride until the evolution of H₂ ceased and finally distilled. Dioxane (AR, BDH) was refluxed for 48 hr over NaOH pellets, distilled twice, kept over metallic sodium overnight and distilled again. Absolute ethanol was treated with a little excess of freshly ignited quicklime, kept overnight and distilled. It was refluxed with Zn-dust and caustic potash for

48 hr and finally distilled. In all the cases, the middle fractions were used within several hours.

HClO₄ (GR, E. Merck) was estimated in the usual way.

The spectra of Bipy at different acidities were noted in aqueous and DMF-water and in other mixed solvents. In order to have approximate idea regarding the basicity of the solvents, we noted the pH-meter readings (which in no way measured the H⁺ion activity in mixed or non-aqueous solvents) of the solvents and their acidic solutions.

The meter readings were taken using a digital pH-meter (Systronics). The spectra were recorded on a Beckman DU-2 spectrophotometer at 298K.

Results and Discussion

Spectra of ligands and anomalous behaviour of 2,2'-bipyridyl -- All the ligands exhibit two intense bands in the UV region (Table 1). The longer wavelength band is ascribed to β -band and the short wavelength band to α -band⁵⁻¹⁰. However, in the case of Bipy, in addition to 233 and 281 nm bands, Henry and Hoffman⁴ observed a band at 308 nm in neutral solutions. They attributed the band at 308 nm to covalent hydrate formation [$\text{Bipy} + \text{H}_2\text{O} \rightleftharpoons \text{Bipy} \cdot \text{H}_2\text{O}$], but found no evidence of Phen.H₂O though Phen is known to retain water tenaciously due to its fixed coplanarity and better feasibility of hydrate formation (see Fig. 1). In the present study Bipy did not show any band corresponding to α - or β -band of Phen (Table 2).

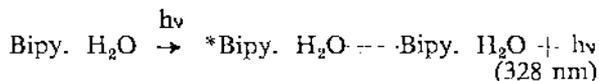
In the pH region (4.5-7.0)⁴, the spectra were characteristic of Bipy and protonated Bipy and the spectra of pure Bipy could only be obtained above

TABLE 1 — ABSORPTION MAXIMA OF 2,2'-BIPYRIDYL, 1,10-PHENANTHROLINE AND 5-NITRO-1,10-PHENANTHROLINE

Solvent	ν_{\max} (cm ⁻¹)					
	2,2'-Bipy		1,10-Phen		5-Nitro-1,10-phen	
<i>n</i> -Heptane	42,370	35,460	43,290	38,020	43,290	37,740
Isocetane	—	—	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
Dimethyl formamide	—	35,460	—	—	—	36,900
Dimethyl sulphoxide	—	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	—	—

pH 7 ($pK_{\text{BipyH}^+} = 4.48$)¹¹; $\epsilon_{\text{BipyH}^+}$ is high and ϵ_{Bipy} is almost zero in this region. The reason that "the disappearance of the 308 nm band on the addition of OH⁻ is not accompanied by any change in extinction coefficient of 281 nm band of Bipy. within the experimental precision (3%)" is due to the fact that the isobestic point of Bipy and BipyH⁺ is in the region 282 ± 1 nm and is not due to the reaction $\text{Bipy} \cdot \text{H}_2\text{O} + \text{OH}^- \rightleftharpoons \text{Bipy} \cdot \text{OH}^- + \text{H}_2\text{O}$ as conjectured by Henry and Hoffman⁴.

Similarly, the strong emission at 328 nm observed in the pH region 4–10 was shown⁴ to originate due to reaction



Due to change in acid-base behaviour in the excited state ($pK_{\text{BipyH}^+}^* = 9.5$)^{12,13}. Bipy should exist as ${}^*\text{BipyH}^+$ or a mixture of ${}^*\text{Bipy}$ and ${}^*\text{BipyH}^+$ and not as ${}^*\text{Bipy} \cdot \text{H}_2\text{O}$. Obviously, similar pH dependence of intensities of the band at 328 nm (emission) and 308 nm is due to the gradual conversion of BipyH⁺ to Bipy. DMF is highly basic and addition of water makes it comparatively acidic. This is the reason why the band at 308 nm of Bipy is observed in DMF + water but not in DMF alone. It is to be noted that the pK -values of the ligands undergo appreciable change in non-aqueous or mixed solvents due to change in electrostatic and non-electrostatic characters of the solvents. Much of the derived conclusions⁴ arose due to neglect of

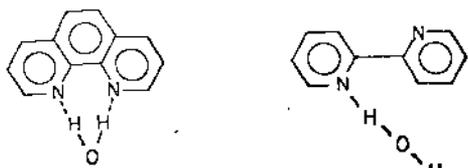


Fig. 1

TABLE 2 — ABSORPTION MAXIMA OF 2, 2'-BIPYRIDINIUM ION IN DIFFERENT SOLVENTS

Solvent*	ν_{\max} (cm ⁻¹)	
Water	41,490	33,220
MeOH-H ₂ O	41,490	33,110
Pr ^t OH-H ₂ O	41,580	33,060
Dioxane-H ₂ O	41,150	33,000
Formamide-H ₂ O	—	34,360
DMF-H ₂ O	—	34,900
DMSO-H ₂ O	—	32,790
Methyl cellosolve-H ₂ O	41,240	32,890

*90% (v/v) of organic solvent.

this fact. Moreover, the presence of high concentrations of H₂SO₄ (or other acids) changes the solvent structure and the acid-base properties of the media enormously. The emission spectra is known to be susceptible to the nature of the medium. Thus the conclusions of Henry and Hoffman⁴ are hardly justifiable.

We are not in a position to check the emission spectra. The anomalies are apparent in the reported values, e. g. $\lambda_{\max}^{\text{em}}$ values of Phen and PhenH⁺ are 360 nm ($\lambda_{\max}^{\text{ab}} = 264$ nm) and 410 nm ($\lambda_{\max}^{\text{ab}} = 272$ nm) respectively. The emission spectra of Bipy could not be detected whereas BipyH⁺ has $\lambda_{\max}^{\text{em}}$ at 335 nm ($\lambda_{\max}^{\text{ab}} = 301$ nm.) The abnormally large Stokes' shifts of Phen and PhenH⁺ compared to the Stokes' shift (3371.9 cm⁻¹) of BipyH⁺ require explanation and further study.

Kasha¹⁴ and McConnel¹⁵ have used the solvent-induced shifts as criteria for distinguishing $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The blue shifts of $n \rightarrow \pi^*$ transitions in the case of acetone, formaldehyde etc. are due to increasing hydrogen-bonding capabilities from non-polar to polar solvents³ and can be correlated to Z -values of solvent polarities¹⁶. How-

ever, the hydrogen-bonding capabilities of the solutes are also important.

It is known that $n \rightarrow \pi^*$ transitions usually involve less energy compared to $\pi \rightarrow \pi^*$ transitions. Due to the presence of lone-pair of electrons having high dipole-moments, the solutes are susceptible to marked solute-solvent interactions and H-bonding making solvent shifts appreciable. Solvent shift in case of $\pi \rightarrow \pi^*$ transitions involves a large change in energy and would be observable if $\pi \rightarrow \pi^*$ transitions are in the long wavelength region and energy changes due to solute-solvent interactions are high.

The 'solvation energies' of solutes in different solvents are obviously different arising from the differences in energy changes²⁷ due to (i) the creation of a cavity of appropriate size in the bulk solvent, (ii) the reorganization of solvent molecules around the cavity, (iii) solute-solvent interactions (e.g. dispersion interactions, dipole-dipole and dipole-induced dipole interactions and specific interactions like H-bonding, charge-transfer and intermolecular energy transfer etc.) of different magnitude and (iv) the energy changes due to change in the standard states from gas to solution. The step (iii) is most important and the step (iv), however, vanishes for comparison.

Thus, the proper interpretation of solvent-induced shifts involves the knowledge of ground state (as well as excited state) solvation energies. It is known that

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

In the absence of $\nu(\text{gas})$ data, we consider ν (heptane or hydrocarbons) roughly equal to $\nu(\text{gas})$, so that $\Delta \nu_{\text{ab}}$ can be a measure of solute-solvent interactions (exothermic in the case of blue shift and endothermic in the case of red shift) or an approximate measure of the differences in the ground state solvation energies of a solute assuming the energies of the Franck-Condon (F. C.) excited states to be the same in all the solvents. Similarly, $\Delta \nu_{\text{em}}$ is expected to give a rough estimate of the differences in the excited state solvation energies of the solute¹³.

The large blue-shifts observed in case of $n \rightarrow \pi^*$ transitions of ketones or azo compounds in going from hexane to ethanol have been ascribed by Haberfeld^{18,19} to increased ground state solvation (which is greatest in the case of H-bonding solvents) accompanied by diminished excited state solvation in going from polar to non-polar solvents.

Moreover, the observed blue shifts of nitroaromatics like 1-nitronaphthalene²⁰ etc., from DMF to MeOH cannot be correlated with the greater ground state solvation by H-bonding solvent or the greater Franck-Condon (F.C.) strain as would be apparent from the uniformly endothermic enthalpies of transfer of the F. C. excited states (or the relaxed excited states). It is clear that the blue shift does not necessarily implies $n \rightarrow \pi^*$ transitions or greater H-bonding capability. If the H-bonding capabilities of the solutes are weakened by $-\text{NO}_2$, $-\text{Cl}$ groups etc. red-shift may also be observed.

From a study of the spectral solvent-induced shifts of Bipy and Phen Badger and Walker and others²¹⁻²³

found no evidence of $n \rightarrow \pi^*$ transitions. The solvent shift (emission) of Bipy observed and attributed to $n \rightarrow \pi^*$ transitions by Harriman and coworkers^{24,25} was, however, contradicted by Henry and Hoffman⁴. It is to be noted that all solutes are to some extent modified by the solvents. Spectral solvent shift is, thus, always probable be it $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transitions. But the observed transitions of Bipy, Phen and 5- NO_2 -Phen are $\pi \rightarrow \pi^*$ transitions as (i) these bands are located at relatively short wavelength regions characterized by high intensities, (ii) the transitions are insensitive to heteroatom substitution, (iii) the bands show large redshifts due to protonation in acid solutions contrary to the large blue shifts or disappearance of bands in case of $n \rightarrow \pi^*$ transitions and (iv) the long-wavelength transition of Phen and 5- NO_2 -Phen show almost no or slight red shift in going from non-polar to polar solvents.

In spite of similar linkages, the differences in spectral behaviour of Bipy and Phen must be due to (i) fixed coplanarity and resonance stabilization of Phen compared to Bipy, (ii) capability of free-rotation of 2,2'-bipyridyl and preferred *trans*-configuration in the molecular form and slightly twisted *cis*-configuration in the ionic form (the geometry of the molecule may also be changed due to twisting of the molecule), and (iii) the dipole moments of the *trans*-Bipy, *cis*-Bipy and Phen are 0.91D, 3.80D and 4.11D^{23,27}.

Thus, due to greater dipole-dipole interactions, H-bonding and resonance stabilization, Phen is in the lower energy level in the ground state compared to Bipy requiring much more energy for solvent-induced shift. 5- NO_2 -Phen will be in the higher energy state as the resonance stabilization is disturbed and the capability of H-bond formation is weakened. These are well reflected in the spectra. However, small shifts indicate little solute-solvent interactions.

In spite of anomalies, both β' - and β -bands of Bipy and β -band of Phen show slight blue shifts in going from non-polar (having high intensities) to polar solvents (having low intensities), an indication generally ascribed to $n \rightarrow \pi^*$ transitions, though H-bonding solvents are also known to cause marked blue shifts of $\pi \rightarrow \pi^*$ transitions of chromophores^{23,28}. The blue shifts could also arise from the differences of the ground state and excited state solvation energies arising from the differences in dispersion forces, dipole-dipole, dipole-polarization forces, orientation-strain, etc.

The $pK^* > pK$ values of Bipy, Phen and 5- NO_2 -Phen suggest that the electron densities on the N-atom and dipole moments of the molecules increasing in the excited states and may be due to the canonical structures like II, III, V, VI, etc. (see Fig. 2) similar those of acridine, naphthylamine etc. suggested by Jackson and Porter²⁹. Coulson and Jacobs³⁰ from MO calculations predicted a migration of charge towards N-atom of pyridine. This is expected in the case of Bipy and Phen also. A considerable increase in the dipole moment of Phen is observed from the large Stokes' shift in aqueous solution (ν_{Phen} is calculated to be 3.70Å). The red shift is expected in the case of non-polar solvents but a

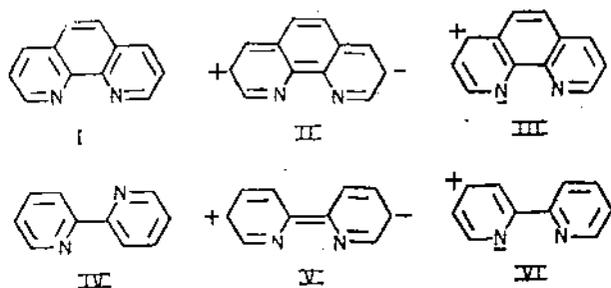


Fig. 2

resultant blue shift is expected in the case of H-bonding solvents due to greater ground state solvation and orientation strain. This is actually observed as seen from the data in Table 1. In the case of dipolar aprotic solvents wherein the polarization shift and the dipole-dipole interaction would be high in the excited state, a red shift is observed. The small blue shift or no shift, however, suggests similarity of solvation in the ground and excited states.

The introduction of nitro group (as in 5-NO₂-Phen) increases the dipole-dipole and dipole-induced dipole interactions but weakens the H-bonding ability. A resultant red shift is thus observed in going from isoctane to water to DMF (Table 1).

Though the solvent effects of UV transitions are poorly correlated by the dielectric constants or functions of the dielectric constants, the transition energies have been found to be a linear function² of

$$f(D) \text{ [where } f(D) = \frac{2(D-1)}{D+1} \text{ where } D \text{ is the}$$

dielectric constant of the medium] within limitations. Deviations from linearity indicates 'specific association' like 'band specific' H-bonding. The $\nu(\text{cm}^{-1})$ vs $f(D)$ plots of both Bipy and Phen show band-specificity indicating H-bonding.

However, greater anomalies are observed in solvents having lone pair of electrons (H₂O, dioxane, DMF, DMSO, etc.) even if there is no H-bonding.

The deviation in the case of dioxane has been ascribed³¹ to greater effective reaction field than indicated by the macroscopic property. In DMSO, introduction of CH₃-groups leads to strong solute-solvent interactions or complex formation; *d*-orbital of S may be involved in the case of DMSO which possesses polarized π -bonding.

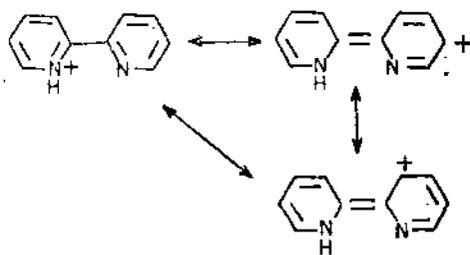


Fig. 3

The spectra of Bipy H⁺ show some interesting features (Table 2). In this case *cis*-form predominates (see Fig. 3) and the dipole moment in the excited state is likely to be increased due to resonance stabilization³² and a red shift is expected in mixed solvents (90% v/v of organic solvents) like MeOH, Pr'OH, dioxane, MC and DMSO.

The blue shift as observed in formamide + H₂O and DMF + H₂O mixtures are due to the presence of both Bipy and BipyH⁺ in these solvent mixtures.

It is thus apparent that for solute molecules with H-bonding ability, the spectral shift is dependent on the type of solvents and their degree of order determined by (i) H-bonding, (ii) dipole-dipole interactions and (iii) molecular shape³³. In H-bonding solvents, the blue shift is expected in $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transitions. If the H-bonding capability of solute is weakened, red shift may also be observed. In the case of polar or dipolar aprotic solvents, the solvent shift would depend mainly on the dipole-dipole, dipole-induced dipole interactions; the blue or red shift may be expected depending on the decrease or increase in the dipole moment of the solute in the excited states.

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