CHAPTER-II

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[1]. 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 solvent[2].

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 Amis[3], Amis and Hinton[1], Bosolo and Pearson[4,5], Parker[6,7] & others[8-12].

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 radii[12]. These differences are manifested in profound rate effects particularly in bimolecular reactions involving anionic nucleophiles.

The constrasting responce 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 transfer[12].

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

$$A + B \longrightarrow X^{*} \longrightarrow \text{Products}$$

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

$$k' = k'_{o} \frac{\gamma_A . \gamma_B}{\gamma^{*}}$$

The activity coefficient γ relates the behaviour of a solute species to its behaviour in ideal solutions and k'_{o} 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 rates[13].

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

$$\text{Thus} \quad k^{s} = k^{o} \frac{^{o}\gamma^{s}_{A} + {}^{o}\gamma^{s}_{B^-}}{^{o}\gamma^{s}_{x^*}}$$

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], Wilkins[16]. 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

$$[MS_m]^{2+} + L \overset{k}{\rightleftharpoons} [M(S)_m]^{2+}, L \xrightarrow{k_{ex}} [M(S)_{m-1} L]^{2+}, S \quad \ldots (1)$$

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

$$MS_6 + L \longrightarrow MS_5L + S \qquad \ldots \qquad (3)$$

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 :-

$$MS_6 + L\ (\text{or } S) \xrightarrow{k_L \text{ or } k_s} S + MS_5L\ (\text{ or } MS_6) \quad \ldots (4)$$

Dissociative Mechanism :-

$$\begin{tikzcd} & & MS_5L \quad (k_L') \\ MS_6 \arrow[r, "k_{MS}"] & MS_5 \arrow[ur, "L"] \arrow[dr, "S"'] & \\ & & MS_6 \quad (k_s') \end{tikzcd} \quad \ldots (5)$$

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 - compoent 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.

References:

1. E.S. Amis and J.F. Hinton,
Solvent Effects on Chemical Phenomena, Vol - I
Academic Press, New York, N.Y., 1973.

2. A. McAuley and J. Hill,
Quart. Rev., 23, 18, 1969.

3. E.S. Amis,
Solvent effects on Reaction Rates and Mechanism,
Academic Press, New York, 1967.

4. F. Bosolo and R.G. Pearson,
"Mechanisms of Inorganic Reactions",
2nd Edn., Wiley, New York, 1967.

5. F. Basolo and R.G. Pearson,
Progr. Inorg. Chem., 4, 381, 1962.

6. A.J. Parker
in Recent Advance in Physical Organic Chemistry
(Ed. V. Gols), Academic Press, 5, 8, 173, 1967.

7. A.J. Parker,
Chem. Rev., 69, 1, 1969.

8. D.R. Stranks,
Modern Co-ordination Chemistry, Ed,
J. Lewis and R.G. Wilkins , Interscience, New York, 1960.

9. J.O. Edwards,
Inorganic Reaction Mechanisms, Benjamin, New York, 1963.

10. M. Eigen and R.G. Wilkins
Mechanisms of Inorganic Reactions, Amer. Chem. Soc.,
Advances in Chemistry Series, NO-49, 1965.

11. C.H. Langford and H.B. Gray,
Ligand Substitution Processes, Benjamin, New York, 1966.

12. D.W. Watts
in Physical Chemistry of Organic Solvent Systems,
Ed. A.K. Covington and T. Dickinson, Plenum Press,
London and New York, Chapter - 6 (1973).

13. K.J. Laidler,
Chemical Kinetics, 2nd Edn., Mc Graw Hill Book Co. Inc.
New York, N.Y., 1965.

14. H.P. Bennetto and E.P. Caldin
J. Chem. Soc., 2191, 2198, 2207, 2211, 1971

15. E.F. Caldin and R.C. Greenwood,
J. Chem. Soc., Faraday Trans. I, 77, 773, 1981.

16. R.G. Wilkins,
The Study of Kinetics and Mechanisms of Reactions of

Transition Metal Complexes (Albyn and Bacon, Boston,1974).

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, $Febipy_3^{2+}$ 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 solutions[4]. Furthermore, studies on equilibrium and kinetics in mixed solvents may be of great assistance in interpreting the role of solvents in inorganic reactions[5].

The rates of formation and dissociation of the red complex, $Febipy_3^{2+}$ in water have been extensively studied by Baxendale and George[6] and Krumholtz[7]. 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 $Fe(bipy)_3^{2+}$ takes place at pH $\approx$ 4.0 having λ_{max} at 524 nm. The maximum changes to 522 nm is mixed solvents[8]. 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 ferrodiin[8] [$Febipy_3^{2+}$] and their thermodynamics in dmf + water mixtures (0 - 100%).

Experimental:

The dark-red coloured complex tris (2,2'-bipyridine) iron(II) perchlorate $[Fe(bipy)_3][ClO_4]_2$ was prepared following Dwyer and McKanzie[9] 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 literature[10] in the usual way using the law of mixtures and comparing the dielectric constant values given in the literature[11].

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 $HClO_4$ = 0.22 $moldm^{-3}$ 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_α) 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 ± 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 ferrodiin in water were extensively studied by Baxendale and George[6]. Though we are particularly interested in the study of the rates of formation of ferrodiin in dmf + H_2O 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 Fe^{2+} 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 :-

$$Fe^{2+} + bipy \longrightarrow Fe\ bipy^{2+} \qquad \ldots (1)$$

$$Fe\ bipy^{2+} + bipy \longrightarrow Fe\ bipy_2^{2+} \qquad \ldots (2)$$

$$Fe\ bipy_2^{2+} + bipy \longrightarrow Fe\ bipy_3^{2+} \qquad \ldots (3)$$

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

$$\text{i.e.;}\ Fe^{2+} + 3\ bipy \longrightarrow Febipy_3^{2+} \qquad \ldots (4)$$

Thus when the concentration of bipy is very high, the rate is dependent only on Fe^{2+} 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

$$\text{bipy} + H^{+} \rightleftharpoons \text{bipyH}^{+} \qquad \ldots (5)$$

$$(\text{bipy } H^{+} + H^{+} \rightleftharpoons \text{bipyH}_2^{+} \text{(in high concentrations of acid)} \qquad \ldots (6)$$

and $$\text{Febipy}_3^{2+} + 3H^{+} \rightleftharpoons Fe^{2+} + 3\ \text{bipyH}^{+} \qquad \ldots (7)$$

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 George[6] consider the step (3) to be rate determining. But the works of Irving and co-workers[12] 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 :

i) The rate of formation of ferrodiin 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 dmf[13] 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 $\frac{A_\alpha - A_0}{A_\alpha - A_t}$ vs time (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 interms of free-base as done by Baxendale and George[6] is given below :

$$\text{Rate} = k_f[\text{bipy}]^3[\text{Fe}^{2+}] = k_f[\text{bipy}]_T^3\,[\text{Fe}^{2+}]\,.\ k_a^3/(ka + [H^+])^3$$

$$= \text{kobs}[\text{bipy}]^3[\text{Fe}^{2+}] \qquad \ldots \quad (8)$$

$$\text{or kobs} = k_f\ ka^3/(ka + [H^+])^3 \qquad \ldots \quad (9)$$

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 Ka-values determined in this laboratory[13]. The values of $^{ka^3}/_{(ka + [H^+])^3}$ 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 ferrodiin 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 George[6] in aqueous solutions is not possible due to changed experimental conditions. However, the energies of activation for the formation of ferrodiin 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 ferrodiin 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 moldm^{-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 H_2^+[8] (at high acidities).

Following the same arguments as before the rate determining step for the dissociation of Febipy_3^{2+} can be represented as

$$\mathrm{Febipy}_3^{2+} \rightleftharpoons \mathrm{Febipy}_2^{2+} + \mathrm{bipy} \qquad \ldots \quad (8)$$

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 George[6], more than 95% of bipy is in the form of bipy 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

$$\mathrm{Febipy_3H^{+++}} \rightleftharpoons \mathrm{Febipy_3^{2+}} + \mathrm{H^+} \qquad (9)$$

seems to have no significance as the equation(9) does not hold good over the whole range of H^+ ion which the authors[6] 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 $-\frac{d[\mathrm{Fe\ bipy_3^{2+}}]}{dt} = kd.\,[\mathrm{Fe\ bipy_3^{2+}}]$. But the values of kd are lower in presence of acid.

The values of kd 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 ferrodiin 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 kd vs $\frac{1}{D}$ (fig-9) show linearity in the region 70 - 100% dmf.

The increase in kd 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 kd in dmf + water media.

A plot of kd against volume percentage of dmf in acidic solution (Fig. 10) shows that kd 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 $Febipy_3^{2+}$ is highly stable compared to weak $Fe(dmf)_6^{2+}$, the exchange reaction

$$\mathrm{Febipy}_3^{2+} + 6\ \mathrm{dmf} \longrightarrow \mathrm{Fe(dmf)}_6^{2+} + 3\ \mathrm{bipy}$$

is possible only under favourable conditions.

But the reverse reaction

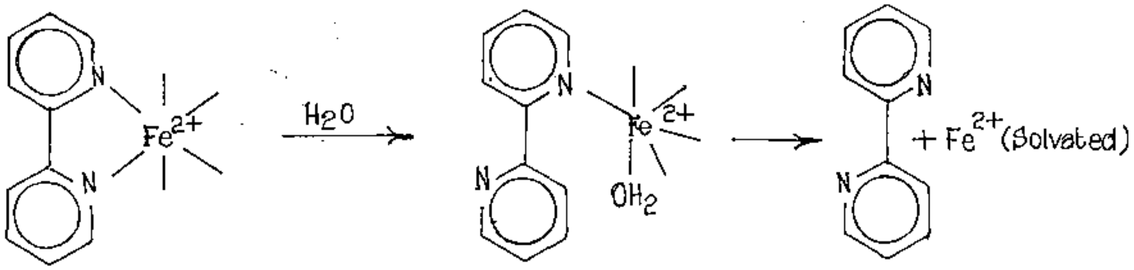
$$\mathrm{Fe(dmf)}_6^{2+} + 3\ \mathrm{bipy} \longrightarrow \mathrm{Febipy}_3^{2+} + 6\ \mathrm{dmf}$$

should be easier to follow.

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

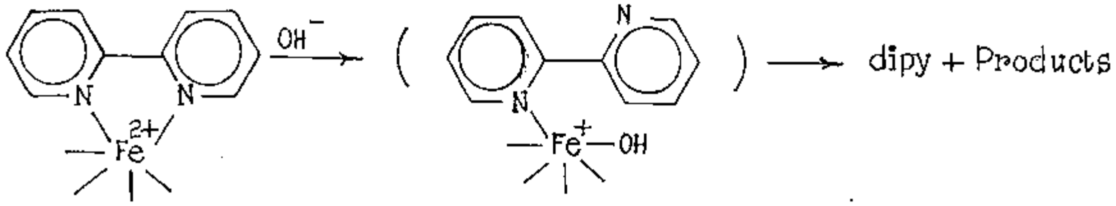
The observed dissociation or exchange kinetics follow either a dissociative or interchange mechanism. The mechanism of dissociation under various conditions can be given as follows[14] :

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 - $bipyH^+$ would take place.

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



c) In dmf - medium

$$\begin{tikzcd}
{[\mathrm{Fe(bipy)_3}]^{2+}} \arrow[r, "1"] & {[\mathrm{Fe(bipy)_2(bipy)}]^{2+}} \arrow[d, "\mathrm{dmf}"] \\
& {[\mathrm{Fe(bipy)_2(bipy)\ (dmf)}]^{2+}} \arrow[d, "\mathrm{dmf}"] \\
& {[\mathrm{Fe(bipy)_2(dmf)_2}]^{2+} + \mathrm{bipy}}
\end{tikzcd}$$

Total reactions :

$$[\mathrm{Fe(bipy)_3}]^{2+} + 6\ \mathrm{dmf} \rightleftharpoons [\mathrm{Fe(dmf)_6}]^{2+} + 3\ \mathrm{bipy}.$$

It is apparent that in all the cases the bond-repture is the major process in the formation of transition state[15].

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 ligands[16]. 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 $\Delta H^{\neq}$ values of the rates of decomposition are highly endothermic implying that the rupture of the metal-ligand bond is difficult. The observed variation of kd, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ 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 $\Delta H^{\neq}$ vs $\Delta S^{\neq}$(fig 11) indicating that the structural factors associated with $\Delta H^{\neq}$ and $\Delta S^{\neq}$ 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 ferrodiin 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 takesplace 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 concomittant formation of dmf-water structure. This may lead to slight decrease in entropy values which would be totally reflected in $\Delta H^{\neq}$ 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 ferrodiin 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_α = 1.38 Temperature = 293K

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

Temperature = 300.5K

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

Temperature = 308K

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

Table - 2

Dissociation of ferrodiin

a. Solvent = 90%(v/v) dmf + water. Complex Conc = 4×10^{-5} moldm^{-3}

$[H^+]$ = 0 moldm^{-3} Temp = 291 K

A_α (Absorbance of at infinite time) $\approx$ 0.00

Time (min)	O.D	$-\log (A_t - A_\alpha)$	kobs X 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	$-\log (A_t - A_\alpha)$	kobs X 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.

$[Fe^{2+}] = 4 X 10^{-5}$ mol dm^{-3}, Bipy. Concn. = $1 X 10^{-3}$ mol dm^{-3}

Temp=298K.

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

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

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

[Bipy] 10^4 mol^{-1} dm^3	kobs X 10^4 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

$[Fe^{2+}] = 4 X 10^{-5}$ mol dm^{-3}; Bipy. Concn. = $1 X 10^{-3}$ moldm^{-3}

$[H^+] = 0.206$ moldm^{-3}

$[NaClO_4]$ mol^{-1}dm^3	kobs X 10^4 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 ferrodiin.

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

Temp = 300.5K

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

b. $[Fe^{2+}] = 1.5 \times 10^{-4}$moldm^{-5}$[bipy] = 7.5 \times 10^{-3}$ moldm^{-3}

Temp = 298 K

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

Table - 5

Pseudo-first order rate constants kobs of formation of ferrodiin complex in dmf+water media.

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

$[\mathrm{H}^{+}] = 0.9$ moldm^{-3}

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

Table - 6

Calculation of k_f from kobs. at various percentage of dmf + water media.

% (v/v) of dmf	k_{a}(at 298K)	$\left(\frac{k_a}{k_a + [H^+]} \right)^3$	kobs X 10^5 (at 300.5 K)	k_f X 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 Ferrodiin Complex in dmf + water media.

Complex Conc = 4 X 10^{-5} moldm^{-3} Temp = 291 K

% v/v of dmf	[HClO$_4$] moldm^3	kobs X 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.

CONTD FROM PAGE - 36.

% v/v dmf	$[HClO_4]$ moldm^{3}	kobs 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 ferrodiin complex in dmf + water media

[Complex] = 8×10^{-5} moldm^{-3}; [$HClO_4$] = 0.22 mol dm^{-3}

% (v/v) of dmf	Temp (Kelvin)	kobs X 10^{-4} Sec	$\log A_{10}$	$\Delta H^{\neq}$ (kJK^{-1} mol^{-1})	$\Delta S^{\neq}$ (JK^{-1} mol^{-1})
90	293	3.17	14.19	99.27	26.92
	298	5.91			
	303	12.08			
80	293	2.71	14.66	102.27	35.82
	298	4.56			
	303	9.20			
70	293	1.84	14.87	104.38	40.13
	298	3.91			
	303	7.85			
60	293	1.39	14.45	108.36	51.00
	298	3.05			
	303	6.25			

References

1. H.P. Bennetto and E.P. Caldin,
J. Chem. Soc., (A), 2207, 1971.

2. S.T. Danny Lo, M.S. Sisley and T.W. Swaddle,
Cand. J. Chem., 56, 2609, 1978.

3. M. Galvas,
J.C.S. Dalton., 10, 1446, 1977.

4. T.W. Swaddle,
Coord. Chem. Rev., 14, 217, 1974.

5. S.T.D. Lo, E.M. Oudeman, J.C. Hansen and T.W. Swaddle,
Cand. J. Chem., 54, 3685, 1976.

6. J.H. Baxendale and P. George,
Trans. Farad. Soc., 40, 736, 1950.

7. P. Krumholtz,
J. Am. Chem. Soc., 71, 3654, 1949.

8. D.K. Hazra and S.C. Lahiri
Analytica. Chim. Acta., 79, 335, 1975
Z. Physik Chem. (Leipzig); 257, 497, 1976.

9. F.P. Dwyer and H.A. McKanzie,
Proc. Roy. Soc. N.S.W.; 81, 93, 1947.

10. A.K. Covington and T. Dickinson
in Physical Chemistry of Organic Solvent system.
Ed. A.K. Covington and T. Dickinson
Plenum Press, London and New York,
1973, Chapter - 1.

11. K.K. Mui, W.A.F. Mc Boyd and E. Nieboer,
Cand. J. Chem., 52, 1821, 1974.

12. C.C. Deb, D.K. Hazra and S.C. Lahiri
unpublished work.

13. R.D. Gillard, D.W. Knight and P.A. Williams
Transition. Met. Chem., 5, 321, 1980.

14. D.L. Pisaniallo and S.F. Lincoln
Aust. J. Chem., 32, 715, 1979.

15. A.C. Adams and E.M. Largen
Inorg. Chem., 5, 814, 1966.

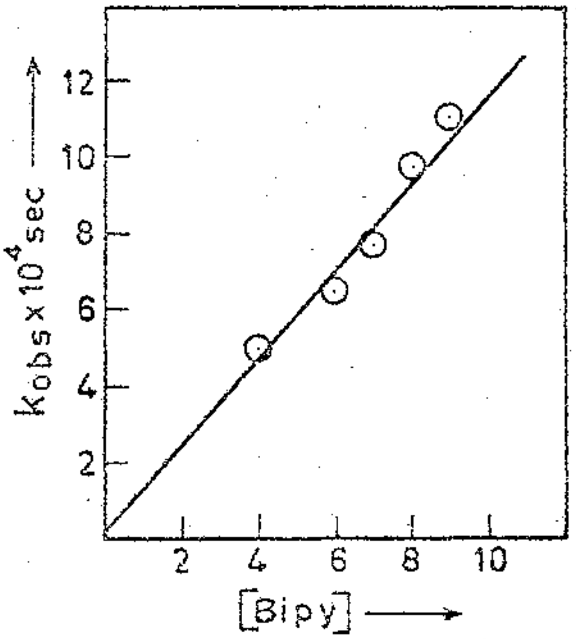


Fig.1 Plot of k_{obs} vs [Bipy]

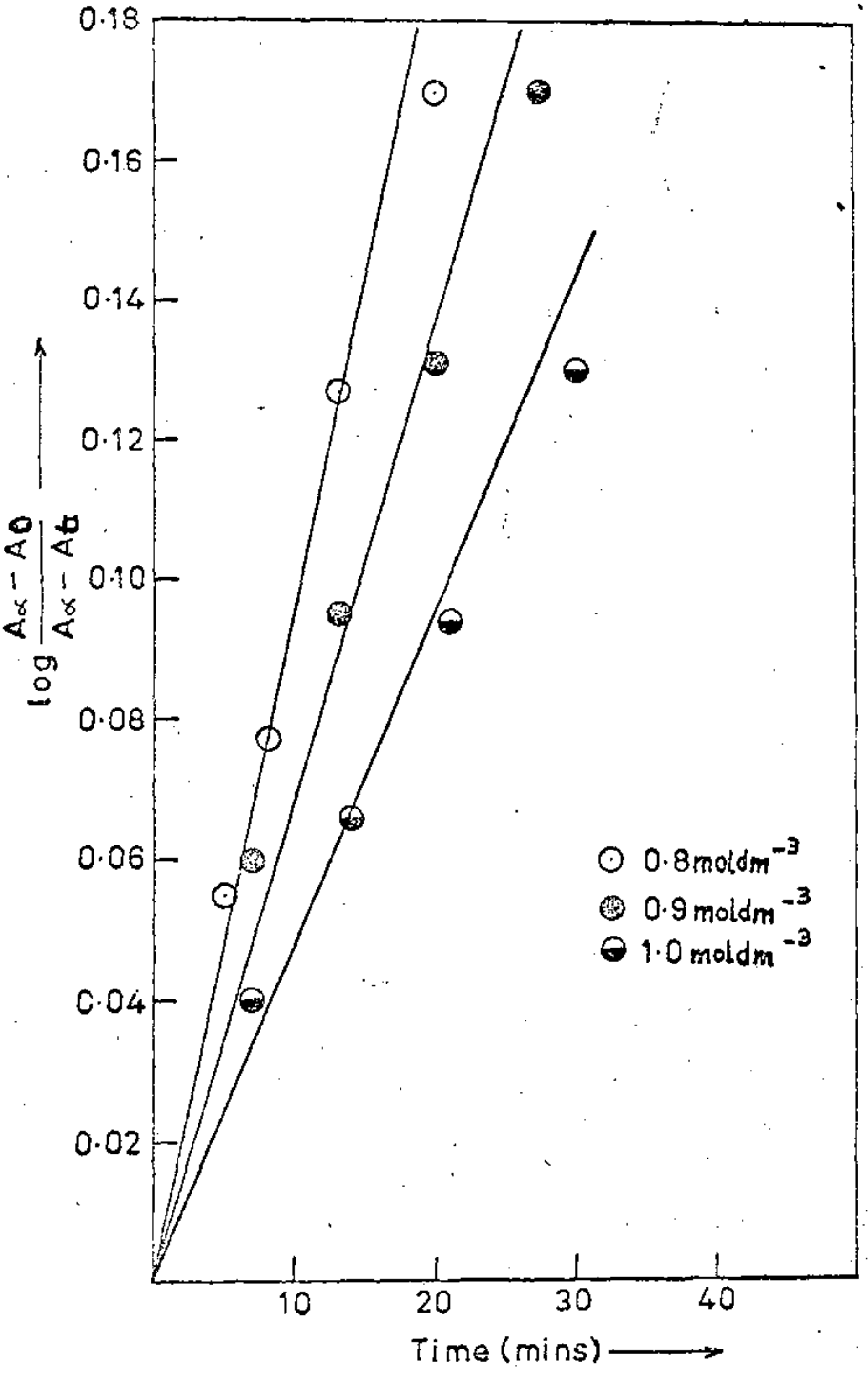


Fig. 2 Effect of [H$^+$] on reaction rate at 300.5K. Solvent: 80 % (v/v) dmf-water.

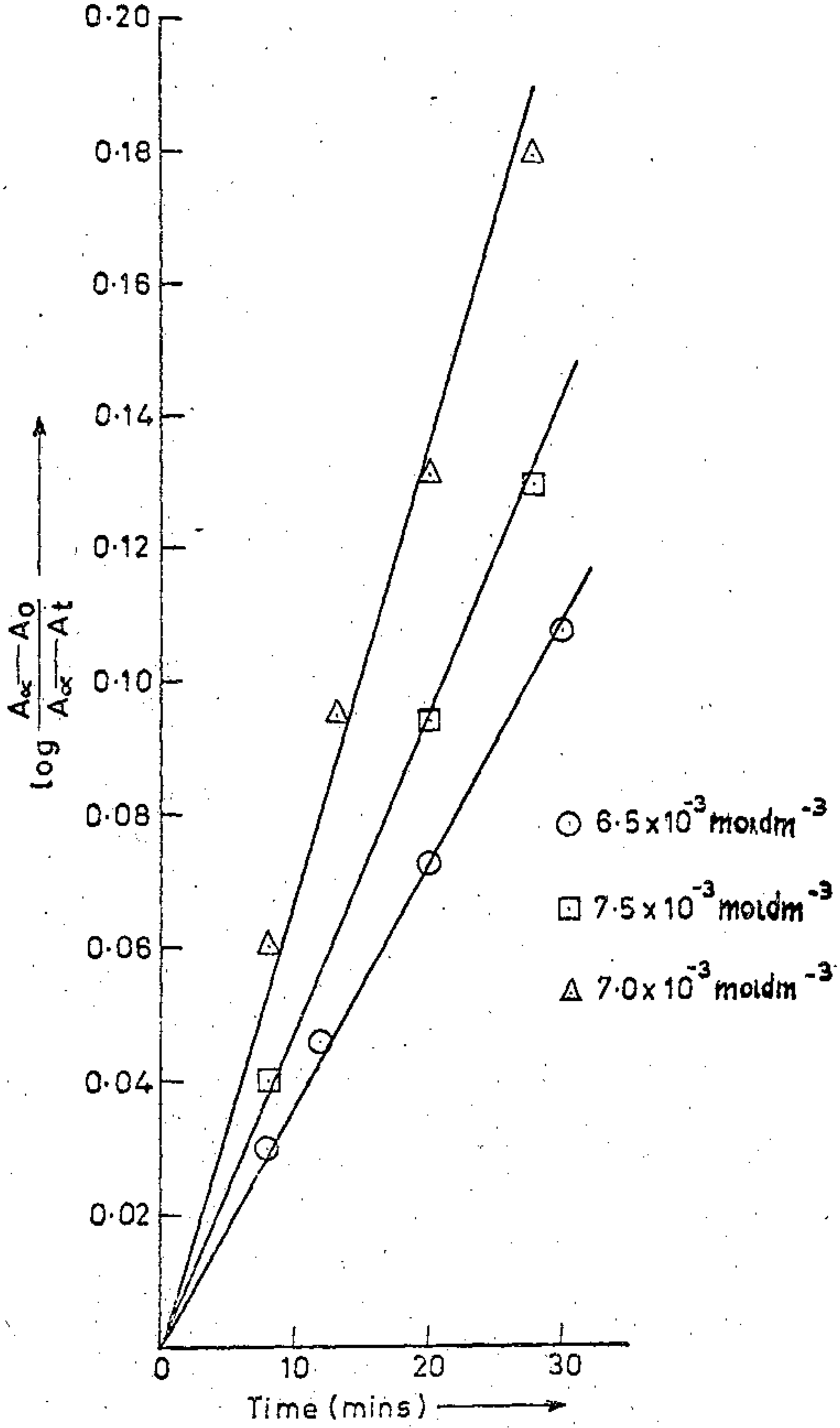


Fig. 3 Effect of [BIPY] on reaction rate at 300.5K
Solvent : 80% (v/v) dmf-water.

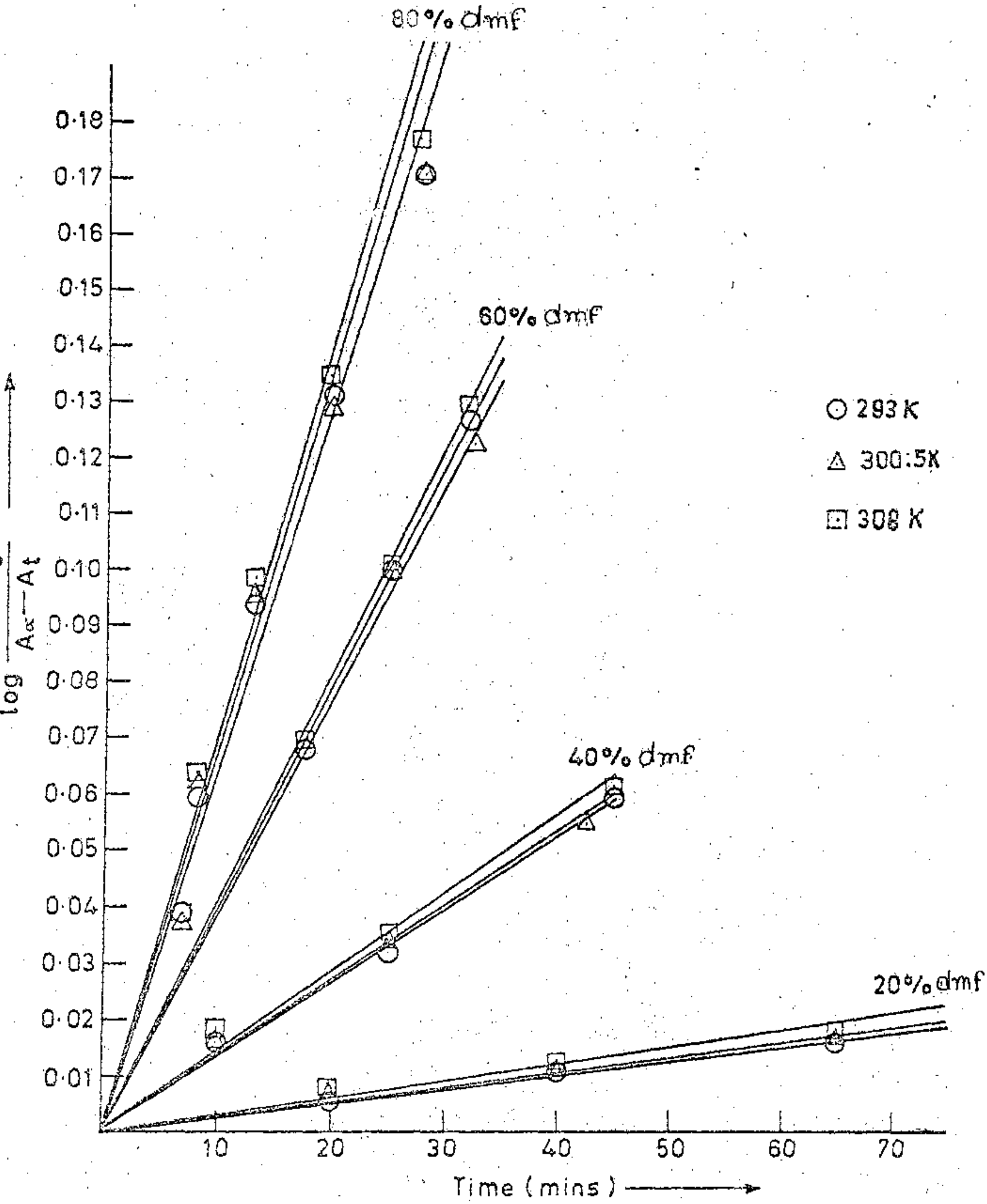


Fig. 4 Effect of temperature on the reaction rate at different percentage of mixed solvents.

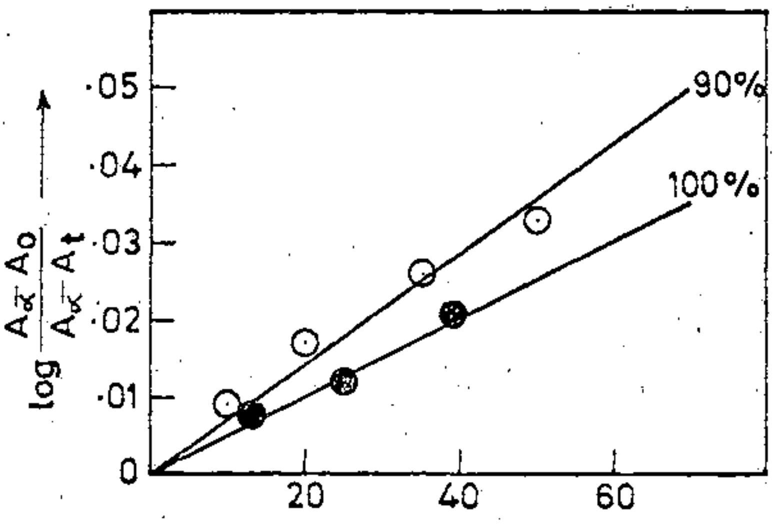

·05
·04
·03
·02
·01
0
20
40
60
90%
100%
$\log \frac{A_\alpha - A_0}{A_\alpha - A_t}$
Time in mins

Fig. 5

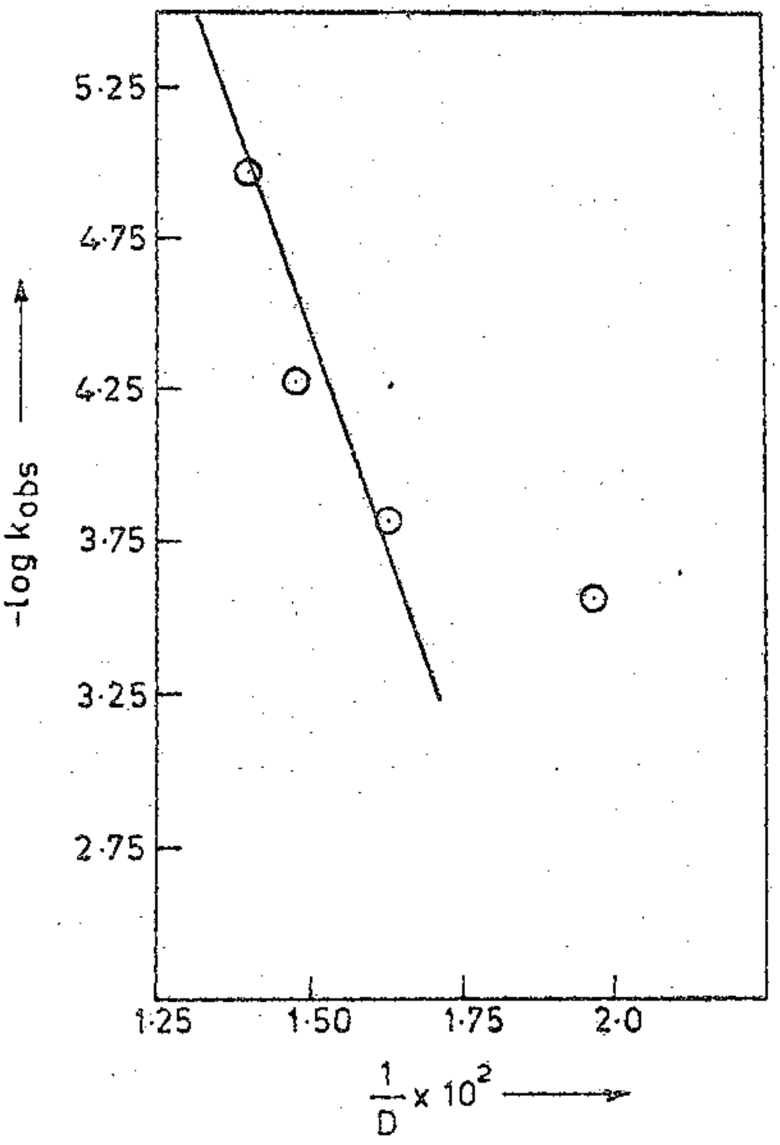


Fig.6 Effect of dielectric constant on the reaction rate of formation of Ferrodiin.

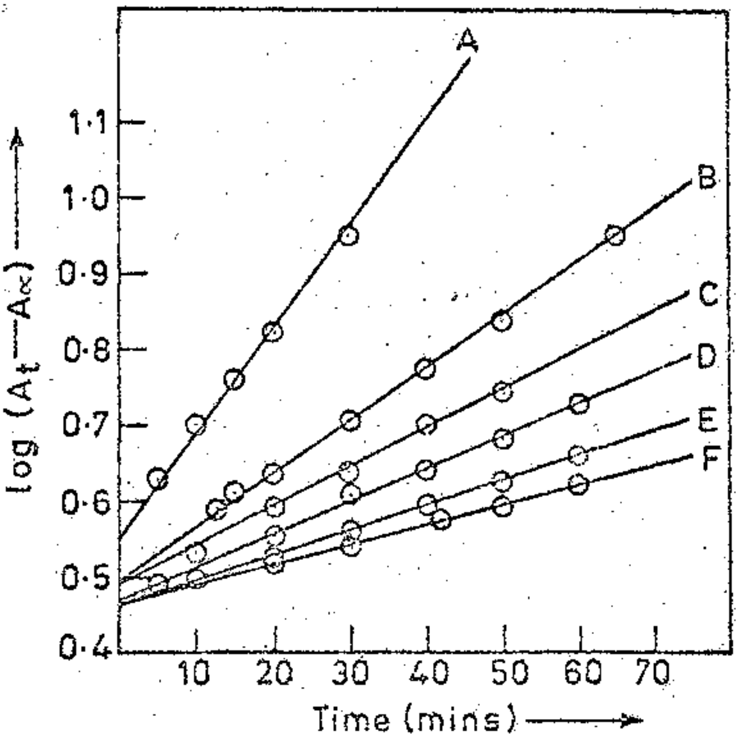


Fig.7 Plot of $[-\log(A_t - A_\alpha)]$ vs time for the dissociation of ferrodiin complex at different percentage of mixed solvents.

Complex concentration = $4{\cdot}0 \times 10^{-5}$ moldm^{-3}
Added acid concentration = 0·22 moldm^{-3}
A 100%; B 90%; C 80%; D 70%;
E 60%; F 50% v/v dmf + water mixtures.

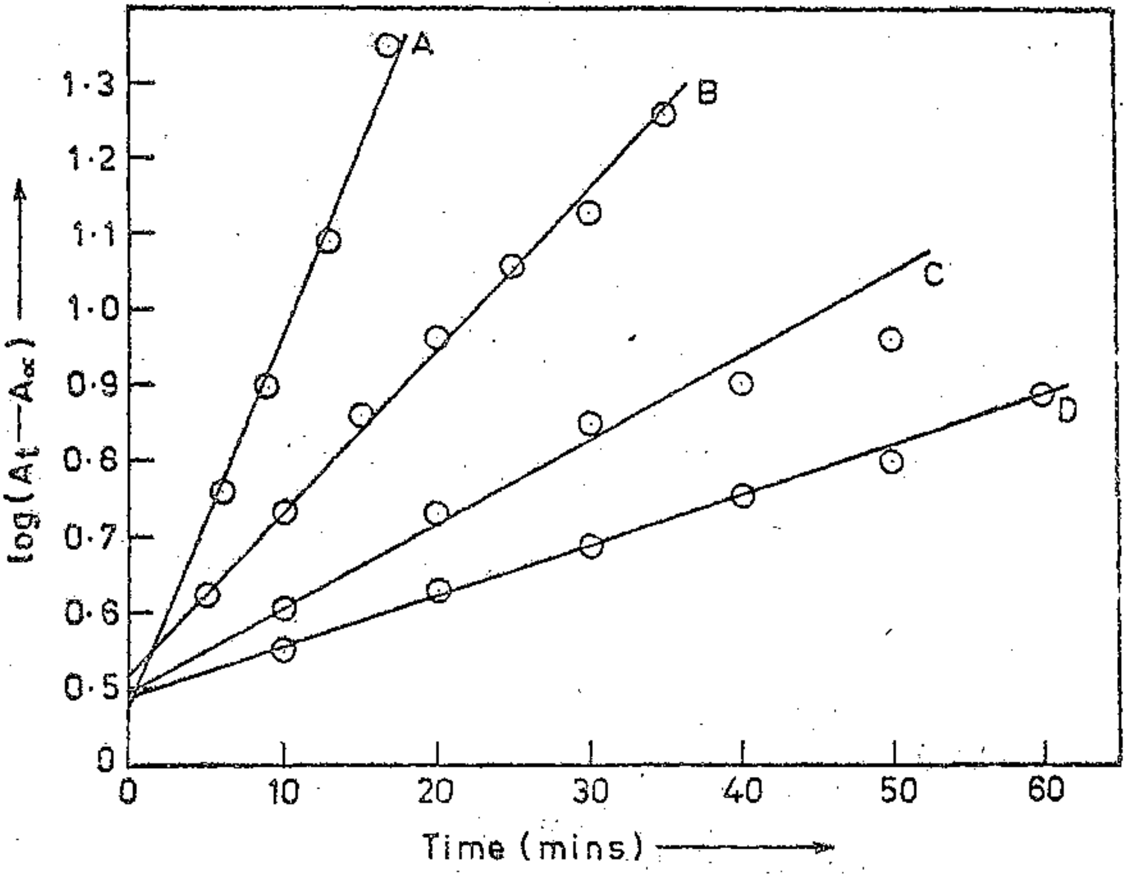


Fig. 8 Plots of [log (A_t — A_α)] vs time for the dissociation of Ferrodiin complex at different percentage of mixed solvents without any added acid and at 291K.

(Initial concencentration of ferrodiin complex = $4{\cdot}0 \times 10^{-5}$ moldm^{-3} [A 10 %, B 90 %; C 80 %; D 70 % v/v dmf + water mixtures])

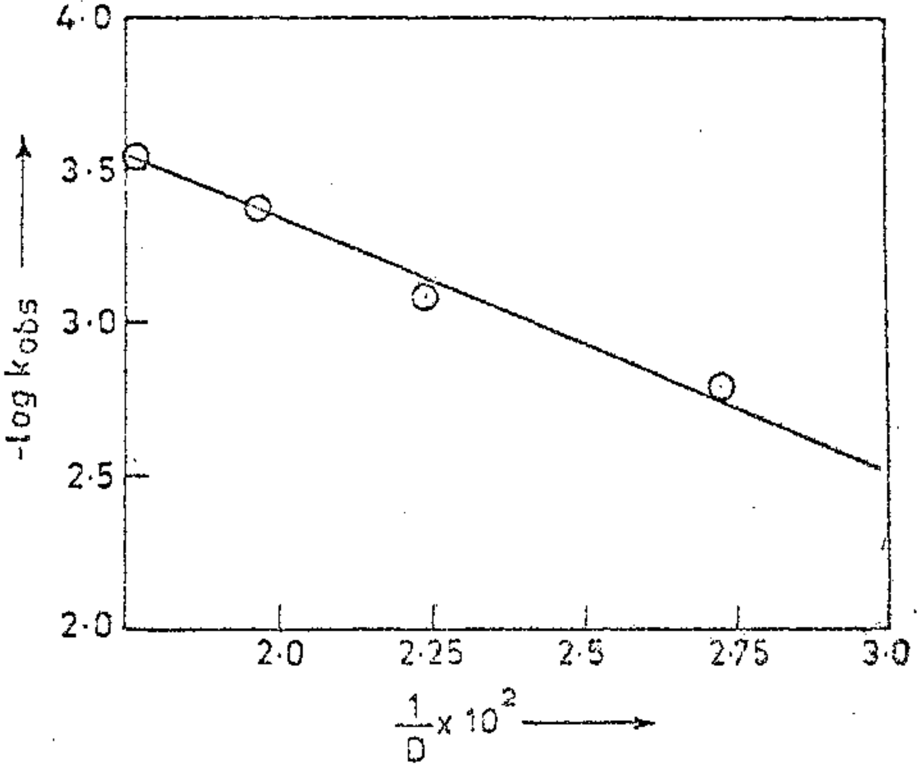


Fig.9 Variation of rate constants with the dielectric constant of the medium.

Fig. 10

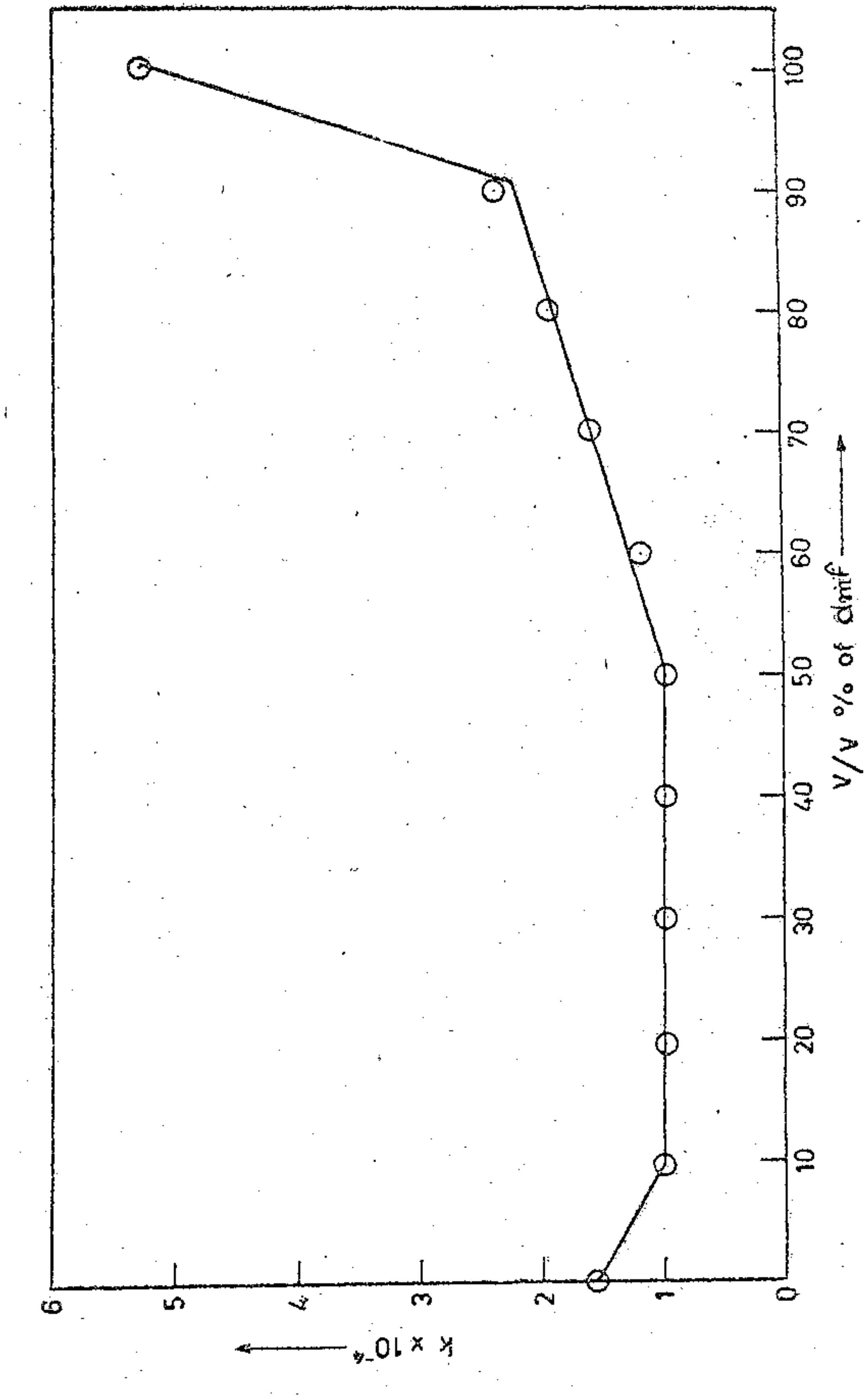


Fig.

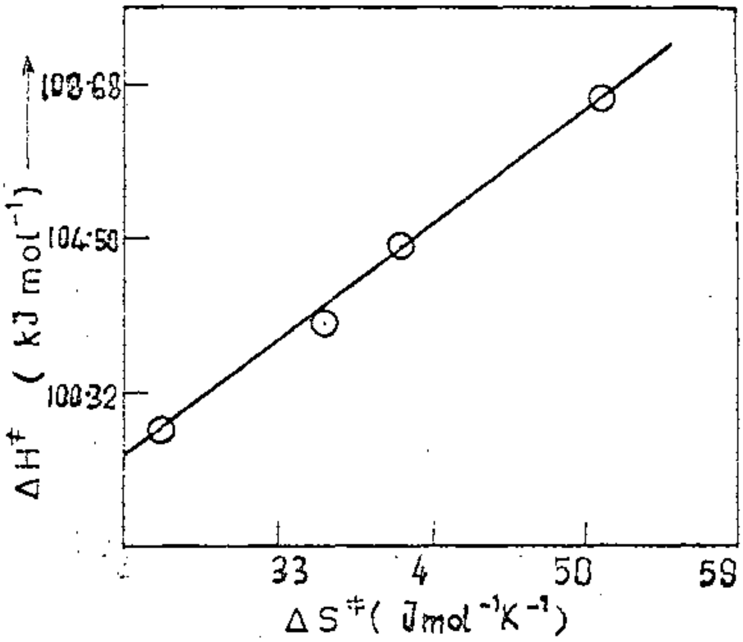


Fig. 11 Plot of $\Delta H^{\ddagger}$ vs $\Delta S^{\ddagger}$ for the dissociation of Ferrodiin

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 George[1], Kolthoff et.al.[2], Krumholtz[3], Bosolo et.al.[4,5], Twigg[6] and Raman[7]. 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 Neumann[8], 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 McKanzie[9] 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. 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 literature[10].

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_α) 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 comparision of reaction rates in different solvent compositions, the concentrations of Fe^{2+} (1.5×10^{-4} mol dm^{-3}) and 1,10-phenanthroline (7.5×10^{-3} 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_α -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 ± 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 $\log \frac{A_\alpha - A_0}{A_\alpha - A_t}$ 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

$$Fe^{2+} + Phen \xrightarrow{rapid} FePhen^{2+} \quad (1)$$
$$FePhen^{2+} + Phen \xrightarrow{rapid} FePhen_2^{2+} \quad (2)$$
$$FePhen_2^{2+} + Phen \xrightarrow{slow} FePhen_3^{2+} \quad (3)$$

so that the overall reaction

$$Fe^{2+} + 3\, Phen \longrightarrow FePhen_3^{2+} \quad (4)$$

seemed to be one of the fourth order similar to the formulation given by George and Baxendale[1] in case of Fe $bipy_3^{2+}$.

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

$$Phen + H^+ \rightleftharpoons PhenH^+ \quad (5)$$

and $$FePhen_3^{2+} + 3H^+ \rightleftharpoons Fe^{2+} + 3PhenH^+ \quad (6)$$

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 ⟶ low spin occurs but we consider the step (1) to be rate determining due to the following reasons :

1) In the dissociation of $Febipy_3^{2+}$ or $FePhen_3^{2+}$ the step low spin state ⟶ high spin state
($Febipy_3^{2+} \longrightarrow Febipy_2^{2+} + bipy$)
is rate determining. The reverse should be true in case of forward process.

2) The rate law

$$\frac{d\,[Fe\ bipy_3^{2+}]}{dt} = k_f \cdot [Fe^{2+}]\,[bipy]^3$$

With zero activation enthalpy (as reported)[1] is unacceptable in view of the fact that the apparent activation enthalpy is composite containing three $\Delta H^{\neq}$ values for successive equilibria as well as $\Delta H^{\neq}$ for the rate determining addition of the third bipy. molecule. This should be true in case of Ferroin complex also.

3) The change in electron configuration (high spin state → low spin state) should be fast compared to the rate process we measure. The works of Irving and co-workers[11] 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 $Nibipy^{2+}$ 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 $Fe\ Phen_2^{2+}$, the addition of third molecule of Phen and consequent removal of two molecules of water shoud 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 /¯Phen_7 as is apparent from the plots of log $\frac{A_\alpha - A_o}{A_\alpha - A_t}$ against time /¯Figures 1(a) and 1(b)_7.

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 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

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

where K_a (the dissociation constant in mixed solvents for the reaction $PhenH^+ \rightleftharpoons Phen + H^+$)[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 ferroin decreases rapidly with increase in dmf concentration (Table 5) inspite of the fact that the apparent rate constant increases with solvent composition.

The changes in log k_{obs} are well-correlated with the change in 1/D values upto 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).

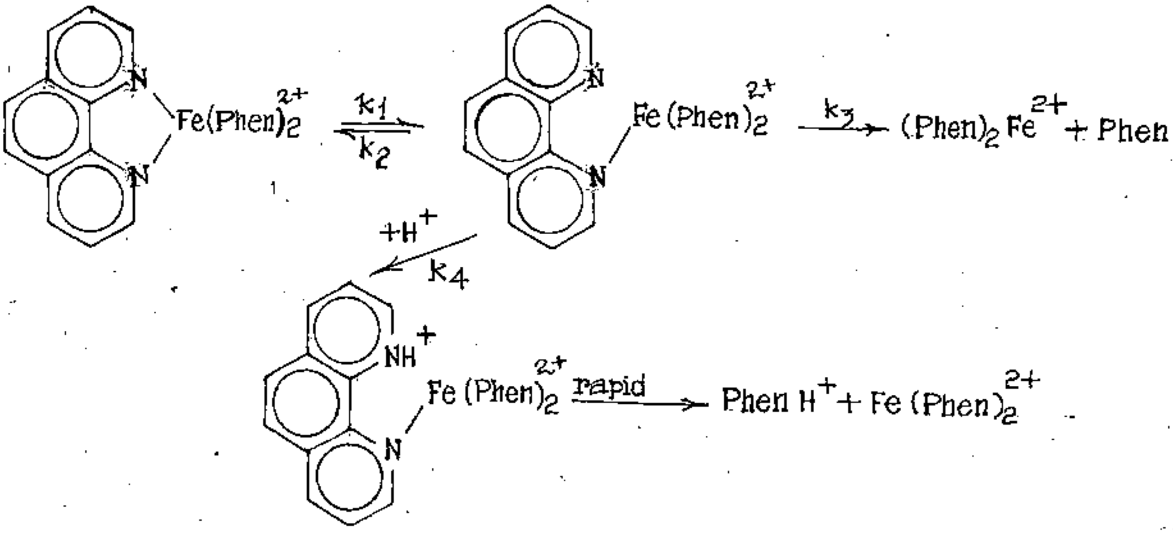
It is not possible to compare our results with those of Kolthoff[2] in view of different experimental conditions and the formulations suggested by them are defective.

Experimental activation energies could not be compared due to lack of data. However, the $\Delta H^{\neq}$ values are considerable (about 42.03 $kJK^{-1}mol^{-1}$) 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 $Febipy_3^{2+}$ involves the conversion of trans bipy to cis bipy (an exothermic process)[13] whereas the formation of $FePhen_3^{2+}$ 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 sheath[14]. This is probably reflected in the enthalpy values at 20% and the k_{obs} values above 80% v/v.

It is to be noted that the dissociation of ferroin or ferrodiin follow almost the same path as suggested by Bosolo[4,5,15]. Twigg and others[16].



(The scheme is more appropriate for bipy due to its flexibility) However, Kolthoff et.al.[2] observed acid independence of the rate of dissociation in the range 0.005 to 0.5 mol dm^{-3} H_2SO_4. The acid dependence has been explained assuming the reaction

$$\underset{\text{I}}{Fe(Phen)_3^{2+}} + H^+ \rightleftharpoons \underset{\text{II}}{Fe(Phen)_3\,H^{3+}}$$

where the rate of decomposition of II is much faster than I and at high acid concentrations only II is present. However, there is no evidence of protonated species as manifested in the change of λ_{max} or optical density. Bosolo[4,5,15] et.al. concluded that no acid dependence is involved in the kinetics in such a way that at no time is there ever a very large concentration of $FePhen_3^{2+}H^+$.

The rate reaction has been formulated to be

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

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 $(A_t - A_\alpha)$ against time (Fig 4).

The specific rate constant has been found to be dependent on $[H^+]$ ion concentrations (in addition to ferroin) which is also corroborated from the extensive studies of Bosolo et.al.[4,5,15] (and Raman[7] 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

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

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

$$FePhen_3^{2+} + 6dmf \longrightarrow Fe(dmf)_6^{2+} + 3\ Phen$$

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 4.5×10^{-3} min^{-1} or 7.5×10^{-5} 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 7.0×10^{-5} sec^{-1} in 1 mol dm^{-3} HCl at 298 K which compares very well with our value, 1.79×10^{-4} 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 ± 2.1 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 Neumann[8] using 1.5×10^{-4} mol dm^{-3} $Fe(Phen)_3^{2+}$ in 1.5×10^{-2} mol dm^{-3} Ni^{2+} (as perchlorate) ion. Though the k_d value 7.7×10^{-5} 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 $>$co-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 $\Delta H^{\neq}$ 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, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ 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 complexe 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 $\Delta H^{\neq}$ and $\Delta S^{\neq}$ 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 ferroin

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

$[H^+]$ = 0.22 mol dm^{-3} Temp = 293 K

A_α (O.d at infinite time) $\simeq$ 1.25

Time (mins)	O.d	$\log \frac{A_\alpha - A_0}{A_\alpha - A_t}$	kobs x 10^4 sec
9	0.300	0.119	3.85
16	0.450	0.194	
24	0.620	0.298	
30	0.710	0.365	

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

$[H^+]$ = 0.22 mol dm^{-3} Temp = 300.5 K

A_α = 1.25

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

Table - 2

Dissociation of ferroin

a. Solvent = 100% dmf. Complex concentration = 6×10^{-5} mol dm^{-3}

$[H^+]$ = 0.00mol dm^{-3} Temp = 303 K

A_α (O.d at infinite time)= 0.00

Time (mins)	O.d	$-\log (A_t - A_\alpha)$	$k_{obs} \times 10^4$ 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 = 6×10^{-5} mol dm^{-3}

$[H^+]$ = 0.00 mol dm^{-3} Temp = 308 K

$A_\alpha = 0.00$

Time(mins)	O.d	$-\log (A_t - A_\alpha)$	$k_{obs} \times 10^4$ 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. $[Fe^{2+}]=1.5 \times 10^{-4}$ mol dm^{-3}, $[H^+]= 0.9$ mol dm^{-3}; Temp = 300.5 K

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

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

Temp = 300.5 K

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

c. $[Fe^{2+}]=1.5 \times 10^{-4}$ mol dm^{-3}; $[Phen]=7.5 \times 10^{-3}$ mol dm^{-3};
$[H^+]=0.9$ mol dm^{-3} Temp = 300.5 K

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

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

% V/V of dmf	Temp(K)	$k_{obs} \times 10^{4}$ sec	$\log_{10}A$	$\Delta H^{\neq}$ ($kJK^{-1} mol^{-1}$)	$\Delta S^{\neq}$ ($JK^{-1} mol^{-1}$) at 300.5 K
0	293 300.5 308	0.294 0.460 0.690	3.11	42.93	-185.60
20	293 300·5 308	1.10 1.72 2.55	3.41	30.00	-178.90
40	293 300.5 308	3.85 6.00 8.92	4.52	43.72	-159.90
60	293 300.5 308	11.51 16.88 25.71	5.21	45.98	-145.30
80	293 300.5 308	23.03 34.54 57.57	5.79	47.53	-134.30
90	293	6.23	-	-	-
100	293	4.51	-	-	-

Table - 5

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

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

Table - 6

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

Complex Conc^{n} = 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 Conc^n = 6×10^{-5} mol dm^{-3}; $[HClO_4]$ = 0.0 mol dm^{-3}

%(v/v) of dmf	Temp(K)	$k_{obs} \times 10^4$ sec	$\log_{10}A$	$\Delta H^{\neq}$ (kJK^{-1}mol^{-1})	$\Delta S^{\neq}$ (JK^{-1}mol^{-1}) at 309 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			

References

1. J.H. Baxendale and P. George,
   Trans. Farad. Soc., 40, 736, 1950.

2. T.S. Lee, I.M. Kolthoff and D.L. Leussing,
   J. Am. Chem. Soc., 70, 3596, 1948.

3. P. Krumboltz, Nature 163, 724, 1949.

4. F. Bosolo, J.C. Hayes and H.M. Neumann,
   J.Am.Chem.Soc., 76, 3807, 1954.

5. J.E. Dickens, F. Bosolo and H.M. Neumann,
   J. Am. Chem. Soc., 79, 1286, 1957.

6. M.V. Twigg, Inorg. Chim. Acta, 10, 17, 1974.

7. S. Raman, Inorg. Nucl. Chem., 37, 1747, 1975.

8. F.M. Van Meter and H.M. Neumann
   J. Am. Chem. Soc. 98, 1388, 1976.

9. F.P. Dwyer and H.A. McKanzie, Proc. Roy. Soc.
   N.S.W., 81, 93, 1947.

10. K.K. Mui, M.A.F. McBoyd and E. Nieboer
    Canad. J. Chem. 52, 1821, 1974.

11. H. Irving and D.H. Mellor, J. Chem. Soc., 1962, 5222.

12. C.C. Deb, D.K. Hazra and S.C. Lahiri, Unpublished data.

13. D.K. Hazra and S.C. Lahiri, Z. Physik. Chem., 257, 497, 1976.

14. E.S. Amis and J.F. Hinton,
Solvent Effects on Chemical Phenomena
Academic Press, New York and London 1973, p. 186.

15. F. Bosolo and R.G. Pearson,
Mechanism of Inorganic Reactions, Wiley, New York. 1967.
2nd Edn., p-218-

16. R. Davies, M. Green and A.G. Sykes,
J.C.S. Dalton, 1171, 1972.

17. N.F. Ashford, M.J. Blandamer, J. Burgess, D. Laycock,
M. Waters, P. Wellings, R. Woodhead and F.M. Mekhail,
J. Chem. Soc., Dalton Trans. 869, 1979.

18. M. Tubino and E.J.S. Vichi, J.C.S. Dalton 1064, 1981.

19. R.D. Gillard, D.M. Knight and P.A. Williams,
Transition Met. Chem. 5, 321, 32 1980.

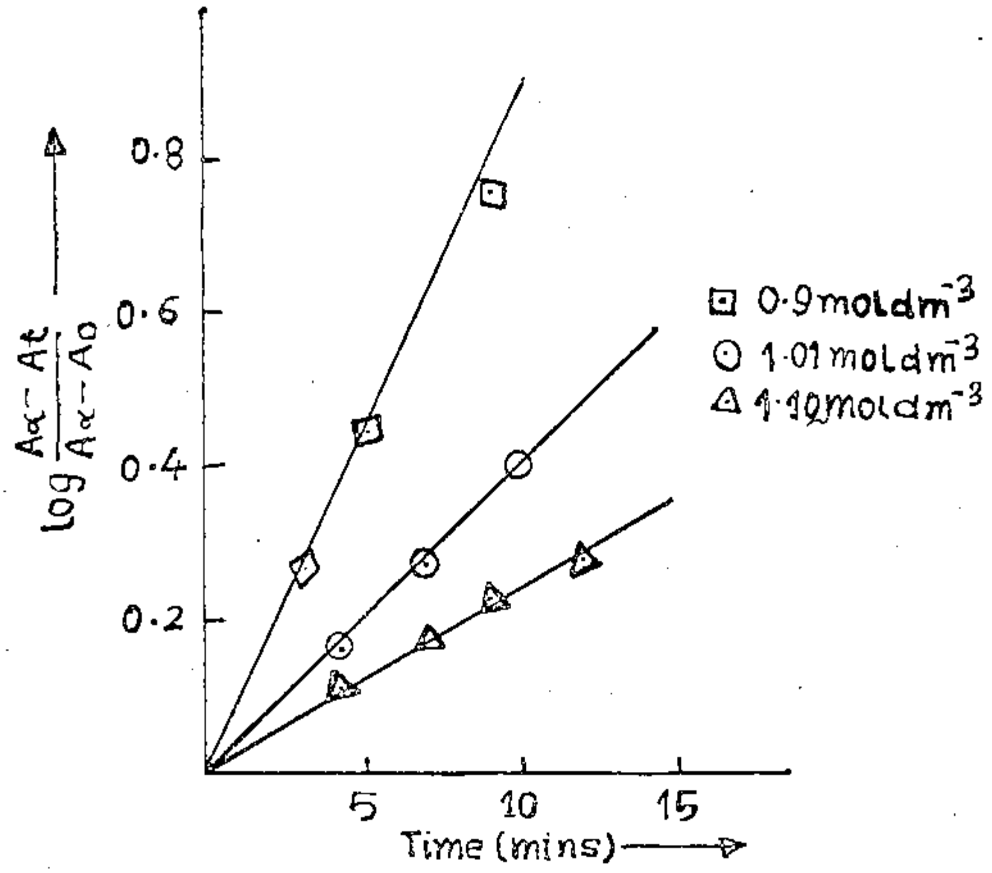


Fig. 1(a) Effect of $[H^+]$ on reaction rate at 300·5K
Solvent: 80% (V/v) dmf-water.

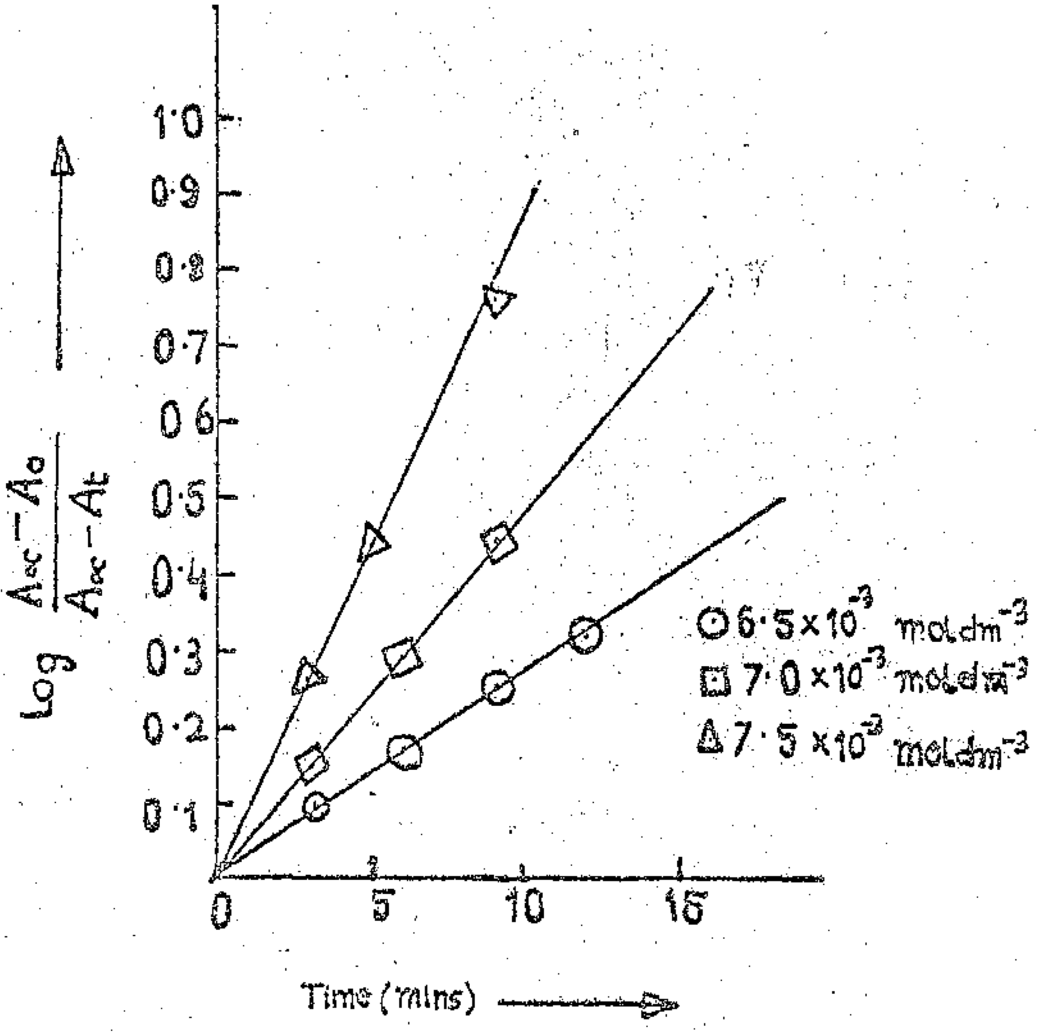


Fig.1(b) Effect of [Phen] on reaction rate at 300·5K
Solvent : 80%(v/v) dmf-water

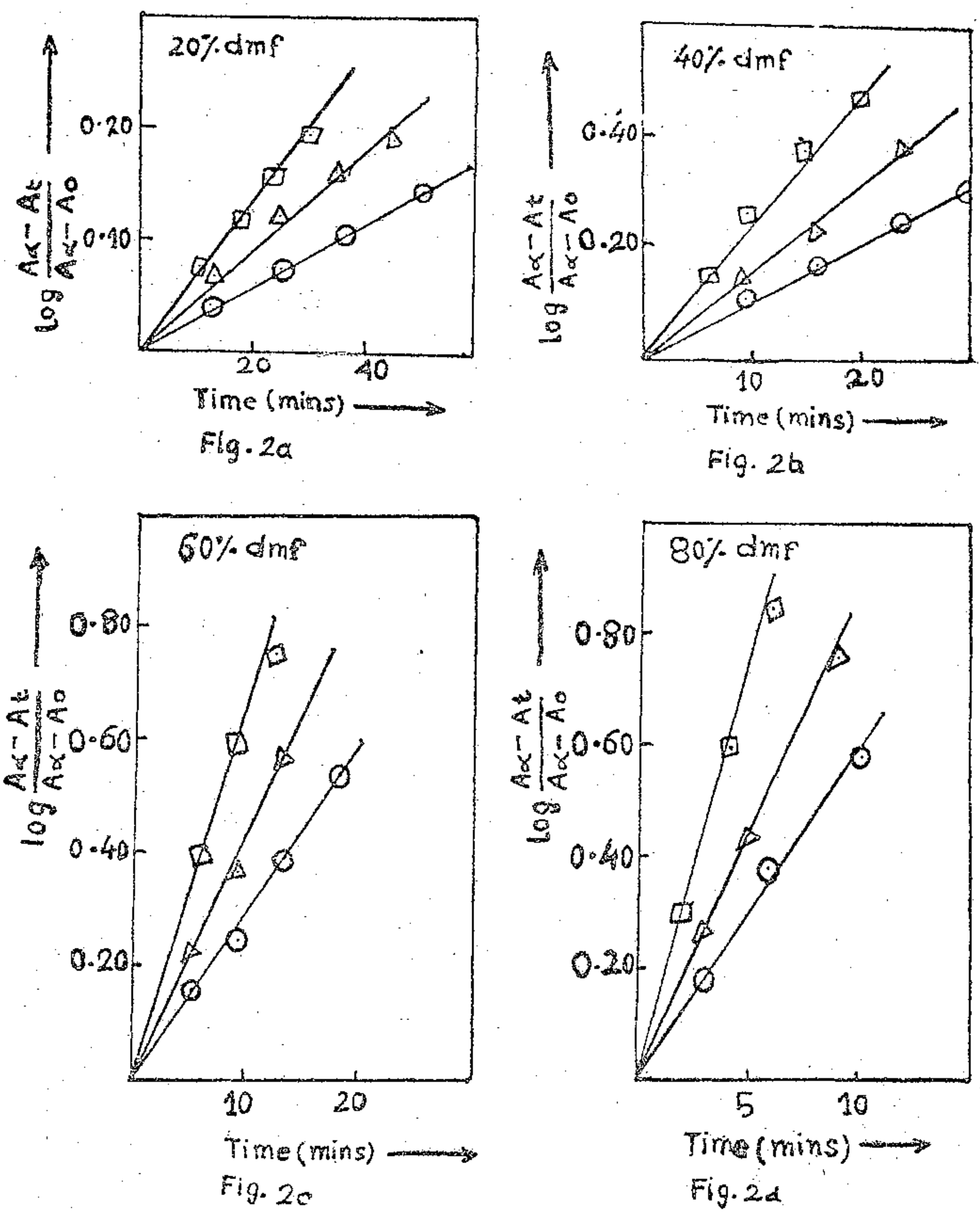


Fig. 2a

Fig. 2b

Fig. 2c

Fig. 2d

⊙ 293K ; △ 300·5K ; ⊡ 308K

Rate of Formation of Ferroin

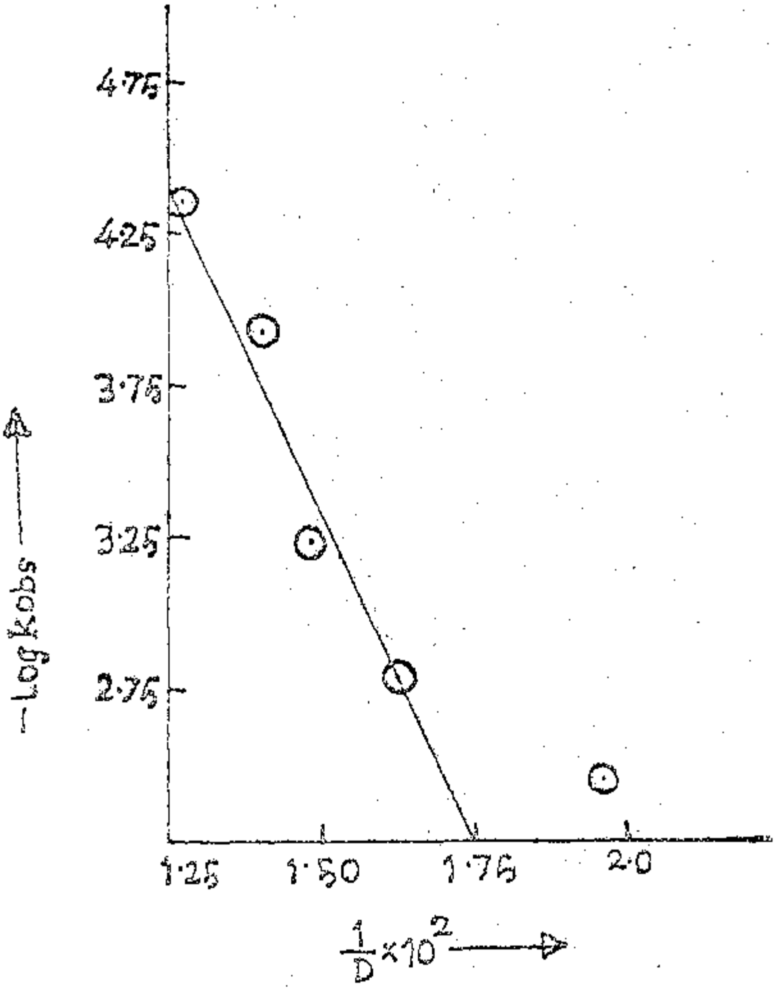


Fig. 3 Effect of dielectric constant on the reaction rate of formation of Ferroin.

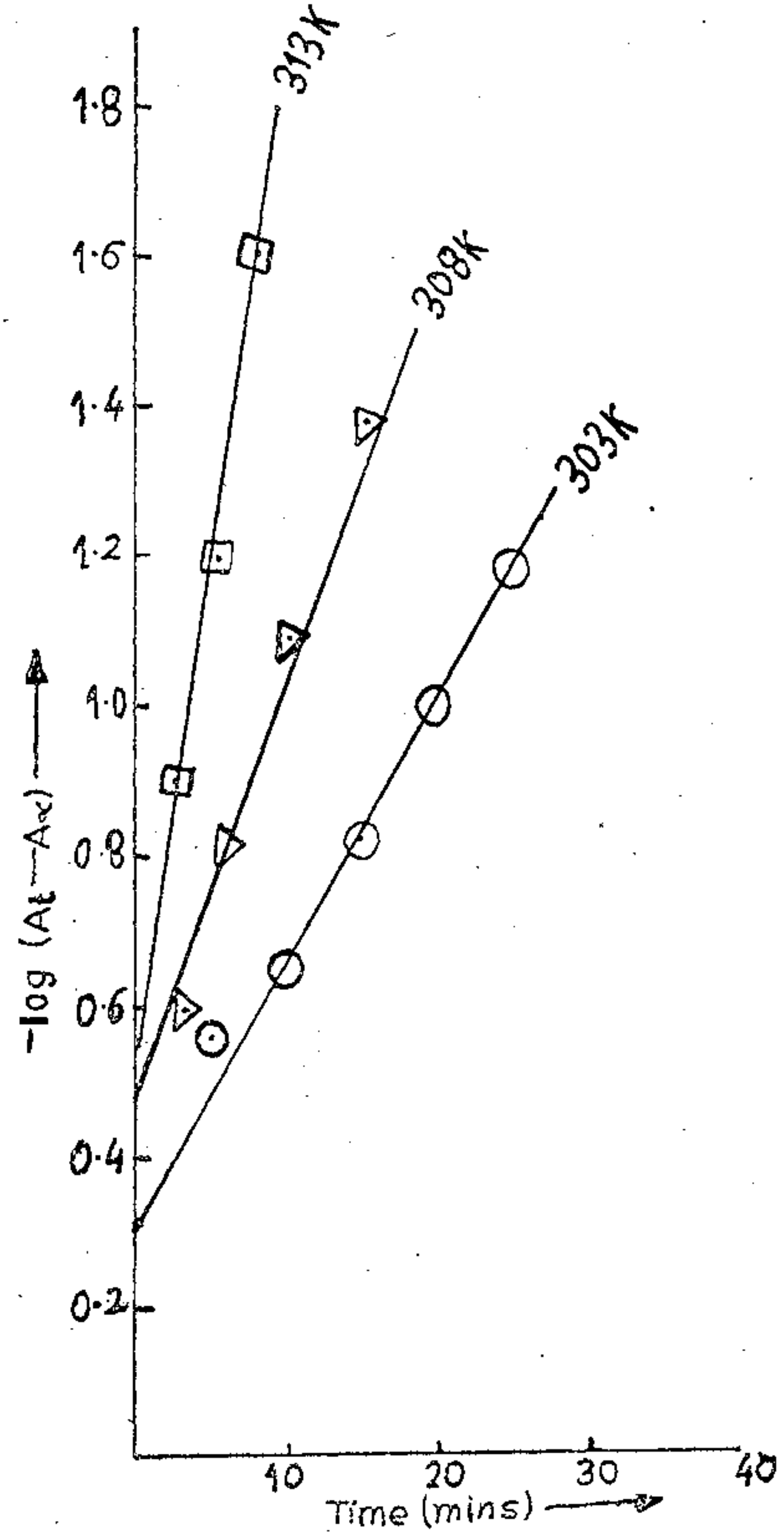
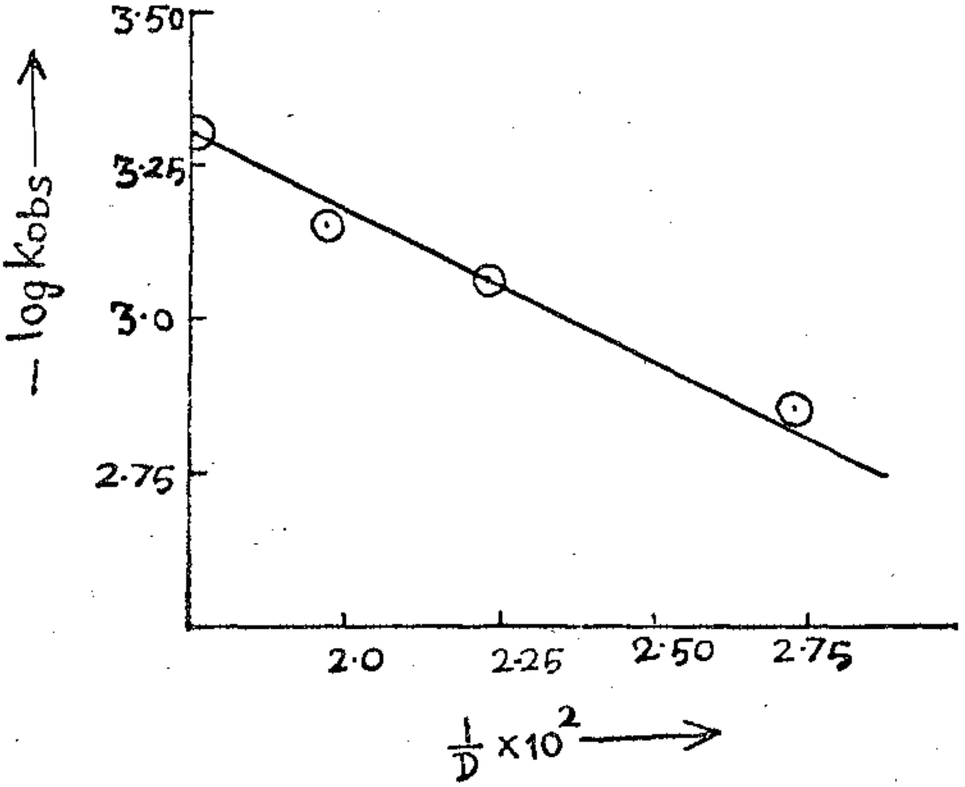


Fig 4 dissociation of ferroin in 100% dmf



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